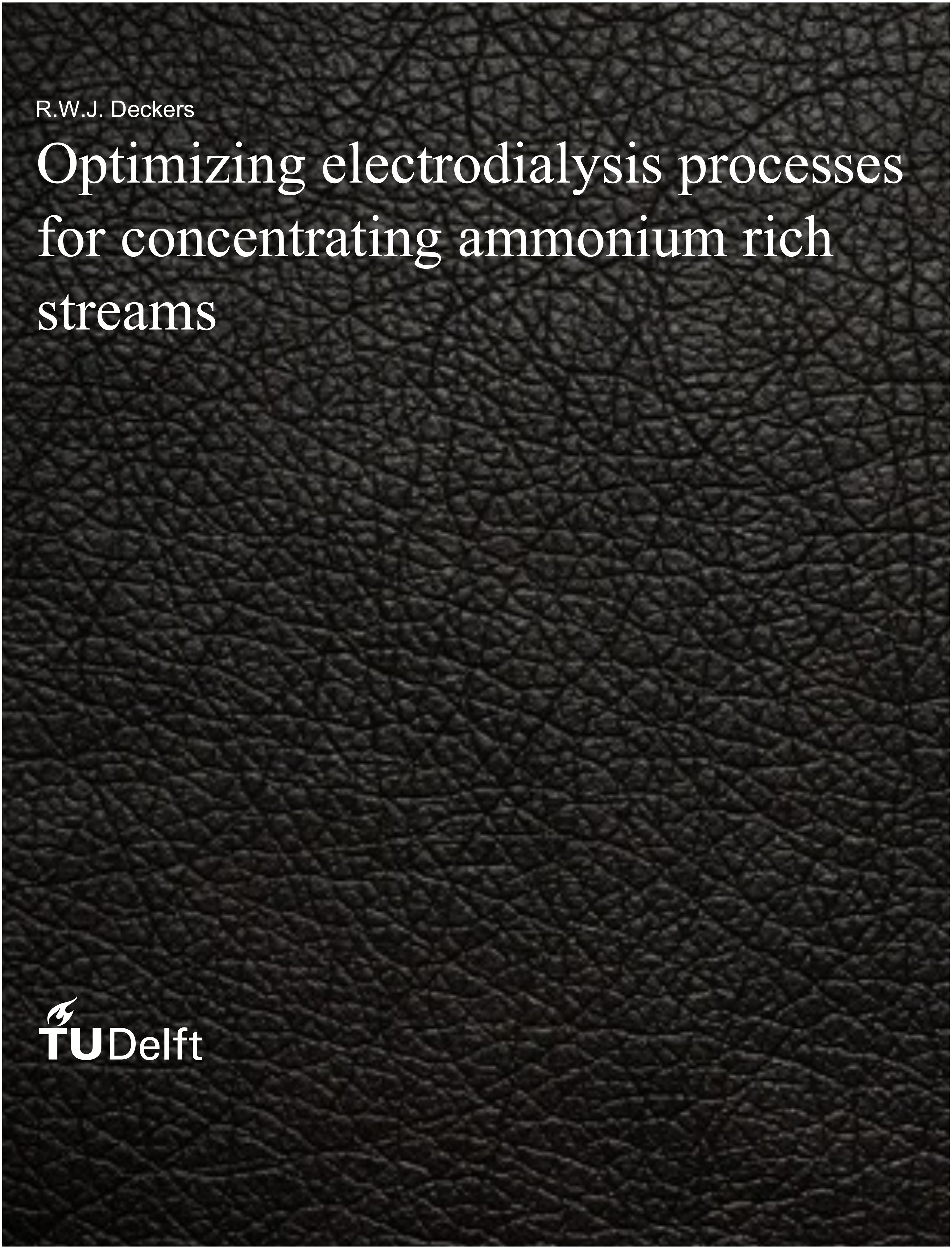

R.W.J. Deckers

# Optimizing electrodialysis processes for concentrating ammonium rich streams

TU Delft

# Optimizing electrodialysis processes for concentrating ammonium rich streams

By

R.W.J. Deckers

in partial fulfilment of the requirements for the degree of

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*This thesis is confidential and cannot be made public until November 7, 2018.*

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The first one and a half year of the master consisted mainly of following courses, with a very instructive period in Bandung, Indonesia. The only remaining criteria for achieving my master title was the graduation. An experimental study on an innovative project, with the opportunity to change the way we treat water at this moment, attracted me most.

Over the course of the last year I had the chance to extend my knowledge on the electrochemical process of electrodialysis, within the boundaries of the "from pollutant to power" project. Niels and Henri, I am very thankful for giving me the opportunity to work in this project group, the support you gave me to get through the graduation procedure on a day to day basis and for the knowledge and insights you elucidated many challenges encountered during this thesis.

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Rob Deckers,
November 2017

# Abstract

The reuse of residual water is highly beneficial for the environment and also has a financial benefit. The “from Pollutant to Power” project focusses on the recovery of ammonia from residual streams, in order to produce electrical and thermal energy when electrochemically combusted in a SOFC. In this context, ammonium from digested sludge reject water will be concentrated with electrodialysis, in order to minimalize chemical or thermal additions.

Electrodialysis is often researched as desalination technique, neglecting the concentrated waste stream. Moreover, limited amount of data can be found on the utilization of energy, as current efficiencies is an often used parameter in the operation efficiency of electrochemical processes. Therefore, no clear overview is available for the energy requirement for the concentration of ammonium with electrodialysis.

*“How can the maximum ammonium concentration from residual stream be optimized, utilizing energy as efficient as possible for the concentration of ammonium in an electrodialysis setup?”* will be researched in this thesis.

Within the electrodialysis process four main processes occur, namely, migration of salts, back diffusion of salts, osmosis and electro-osmosis. As only the migration of salt is desirable, all other processes should be minimized in order to reach an effective utilization of energy for concentrating ammonium rich streams. During regular electrodialysis operations, a maximum ammonium concentration of 7.3 g/L is achieved. The energy used to reach this concentration is equal to 32.10 Wh. During this experiment it was noticed ammonium ions accumulate in the electrode rinse solution.

Two optimization steps have been experimentally researched in order to minimize the energy consumption. As these undesirable processes are driven by the ion concentration gradient between concentrate and diluate stream, a staged experiment was performed. For achieving the same maximum ammonium concentration as during regular operation, only 4.43 Wh is needed. However, it should be mentioned the obtained volumes are less compared to the regular operation of electrodialysis. The other optimization step focuses on the time to perform an experiment, as this influences the total transported volume (due to osmosis). Volume ratios between concentrate and diluate are applied to achieve higher concentrations in the concentrate more quickly. Experiments with 2.0 L diluate and 0.1 L concentrate needed 0.46 Wh to reach an ammonium concentration of 7.3 g/L.

Lastly, all experiments discussed above are performed in an idealistic situation were only ammonium bicarbonate ions are present in the feed water. However, real anaerobic digested reject water also contains other ions. Monovalent salts influence the concentration of ammonium negatively, while no clear relation can be found between the energy efficiency and multivalent salts. It can also be concluded all beneficial effects expected from the addition of bivalent salts are made undone by the non-selectivity of the cation exchange end membranes.

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# 1 Introduction

This chapter will serve as introduction to this master thesis and will give information about the necessity of this research.

## 1.1 Background information

### 1.1.1 Nitrogen in the environment

Nitrogen is the fifth most abundant element in our solar system and is essential for the synthesis of acids and proteins (Canfield et al., 2010). It is essential for all living organisms and is also present in food, fertilizer, poison, explosives and many more. However, nitrogen gas by itself can often not be used for human or plant consumption due to its strong triple bonds. The Haber-Bosch process converts nitrogen, present in the air, together with hydrogen, under high temperature and pressure to ammonia ($NH_3$). Human activity resulted in a doubling of the total amount nitrogen fixated compared to the primary use by plants (Galloway, 1998). After organic protein degradation ammonia will end up in waste streams and will be considered as pollutant.

Ammonia in aqueous environments leads to eutrophication and toxicity of the receiving water body (Metcalf & Eddy, 2003). In order to prevent environmental pollution, ammonia needs to be removed from residual water streams, before the water can be discharged to the aqueous environment (Song et al., 2012). Waste water treatment plants (WWTPs) reduce the ammonia-nitrogen concentration by applying biological treatment technologies. However, the oxidation of ammonia by bacteria requires high amounts of oxygen and consequently has a high energy consumption. The nitrification and denitrification of wastewater requires 15.83 kWh per kg-N (Magrí et al., 2013). Moreover, the reject water from the digested sludge contains high amounts of nitrogen, which is fed back to the biological treatment, and can contribute 15-20% of the nitrogen load (Fux et al., 2002).

### 1.1.2 Alternative removal technologies

Many studies have been performed on the optimization of existing treatment steps, in order to reduce the ammonia concentration in the effluent. This resulted in different removal techniques, including Anammox (anaerobic ammonium oxidation), which requires less, 5.3 kWh per kg-N, energy compared to the standard nitrification-denitrification process (Magrí et al., 2013). Moreover, approaches to recover ammonia from residual streams are conducted with chemical precipitation, either struvite or ammonium sulfate production, or by gas stripping (Luther et al., 2015). These alternatives often need addition of chemicals, while the return on investment is low due to their low market value. Therefore, alternative strategies should be considered.

### 1.1.3 The N2kWh project

The potential of ammonia as an energy carrier in residual water streams is the main focus of the N2kWh project. This master thesis is part of this project, executed by the TU Delft and KU Leuven, and focusses on the recovery of ammonia from residual streams and subsequent processing of $NH_3$ fuel in a solid oxide fuel cell (SOFC). More information about the N2kWh project and the SOFC can be found in chapter 7.1.

## 1.2 Concentrating of ammonium-nitrogen

### 1.2.1 Concentrating ions from residual streams

Concentrating ions automatically results in the decrease of ions in another flow. Often, this flow is subject of research. However, the reuse of waste waters, for example reverse osmosis brine, is highly beneficial for the environment. Reduction of waste streams, with as optimum a zero-liquid-discharge, also has a financial benefit. In this case, dissolved solids will leave the treatment facility as dry salts.

Within the boundaries of the N2kWh project, the goal is to extract ammonium from residual streams as ammonia gas. The extraction of this gas is highly influenced by the pH, temperature and ammonium concentration in the fluid. Besides the benefit of higher initial ammonium concentrations, also relative less chemicals or thermal energy need to be added.

### 1.2.2 Feed water composition

The conclusions of this thesis should serve a broad scope for different applications. However, some initial assumptions have to be made in order to conduct experiments. As this thesis is part of the N2kWh project, a water composition of digested sludge reject water is chosen. As this composition is not similar for all treatment plants, a range is shown below in Table 1.

| Parameters | Units | Range |
|---|---|---|
| Ammonium | mg $NH_4 \cdot L^{-1}$ | 1000 - 1500 |
| Calcium | mg $Ca \cdot L^{-1}$ | 32 - 89 |
| Magnesium | mg $Mg \cdot L^{-1}$ | 12 – 18 |
| Phosphates | mg $PO_4 \cdot L^{-1}$ | 126 - 324 |
| Potassium | mg $K \cdot L^{-1}$ | 152 - 290 |
| Sodium | mg $Na \cdot L^{-1}$ | 140 - 170 |
| COD | mg $O_2 \cdot L^{-1}$ | 280 – 350 |
| | | |
| Temperature | °C | 20 - 27 |
| pH | pH | 7.49 – 7.84 |

*Table 1 – Digested sludge reject water characteristics ((STOWA, 2016); (Suschka & Popławski, 2003))*

### 1.2.3 Available techniques

Within the boundaries of this project, three possible concentration techniques are distinguished, namely reverse osmosis, ion exchange and electrodialysis. These techniques are briefly explained in appendix 7.2, showing not only the potential but also the limiting factors in order to achieve the concentration of ammonium. Electrodialysis is, due to its decreasing energy usage for increasing salts concentrations, most promising and will therefore be investigated in this report.

## 1.3 Scope of this project

### 1.3.1 Knowledge gap

Electrodialysis is already commercially available since 1950, and can therefore not be considered as a new technology. However, due to the fast improvement of the ion exchange membranes, better constructing material and advances in technology, this technology is still very promising (Valero et al., 2011).

Available literature on electrodialysis mainly concerns its internal processes and the comparison of this technology with the widely used reverse osmosis. Moreover, also many researches focus on creating a clean diluate stream, and omit data on the concentrate stream.

From this perspective electrodialysis is an alternative desalination technology, which is only preferred when initial and final salt concentrations are within certain limitations (Walha et al., 2007). This thesis focusses on concentrating the salt streams, where the diluted stream is submissive to the main goal. However, only little research is conducted on electrodialysis for concentrating ions. Mondor et al. (2008) focusses on concentrating ammonium from swine manure. This research shows a maximum achievable ammonium concentration of 13 g/L with an initial concentration of 4 g/L. The share of volatized ammonia amounts another 3 g/L and can, if trapped in the solution, contribute to a maximum achievable ammonium concentration of 16 g/L. This hindrance of water transports limits the operation of electrodialysis, however, no solutions for this problem are proposed.

Moreover, no clear overview can be made from the available knowledge as different salts appear to have different effects on the efficiency of electrodialysis. Lastly, no literature can be found on the energy usage of an ED setup.

### 1.3.2 Research goal

The objective of this research is to qualitatively and quantitatively describe the effect of the processes within electrodialysis, and how these processes influence the energy consumption for concentrating ammonium. It should be considered that as electrodialysis is used for concentrating ammonium streams, a maximum concentration is favorable. This is attempted by performing a literature study, supplemented with experimental tests in order to answer the research question. The research question of this thesis can be described as:

*How can the maximum ammonium concentration from residual stream be optimized, utilizing energy as efficient as possible for the concentration of ammonium in an electrodialysis setup?*

### 1.3.3 Sub-questions

The following sub questions are considered:

1. Is there a conceptual difference between current- and energy efficiency?
2. What is the maximum achievable ammonium concentration, using digested sludge reject water with an ammonium influent concentration of 1.5 g/l?
3. To which extent is the energy efficiency influenced by back diffusion of ions?
4. To which extent is the energy efficiency influenced by (electro-) osmosis?
5. Do residual streams with mono- and bivalent salts have a positive or negative influence on the energy efficiency?
6. Can the performance of electrodialysis be increased by staging or applying different volume ratios?

### 1.3.4 Approach

In order to answer the sub-questions and research goal of this thesis, first a literature study has been performed. Knowledge from this study can be found in chapter 2. Hypotheses drawn from this literature study are validated by experiments. The experimental goal, setup, used materials and methods of all experiments can be found in chapter 3. The results of these experiments are elaborated in chapter 4, giving essential information about the sub-questions. Lastly, chapter 5 and 6 will be used to discuss found results and processes, while also advantageous adaptions to the set-up will be proposed. Additional information and data can be found back in the appendices.

# 2 Theoretical background

## 2.1 Electrodialysis

### 2.1.1 Technology review

Electrodialysis is a membrane separation technique utilizing an electrical potential difference between both ends of the cell to move charged ions through ion exchange membranes. These membranes obtained their name from the ion exchange resin they are made from, while no ions on the membrane surface are exchanged with ions in solutions, as is the case in ion exchange (Strathmann, 2010). In an electrodialysis cell altering anion (AEM) and cation (CEM) exchange membranes are placed, divided by flow spacers, between two electrodes. These membranes only allow respectively negatively or positively charged ions to pass through the membrane. Due to the positioning of the membranes, ions are transferred from one solution to the other, leading to a concentration of one stream and the dilution of another. This principle is shown in Figure 1.

Besides membranes who allow all anions and cations (AEM and CEM) to pass through, also monovalent selective membranes can be applied. Due to the functional group on these membranes, only monovalent charged ions are allowed to pass through these membranes (MVM).

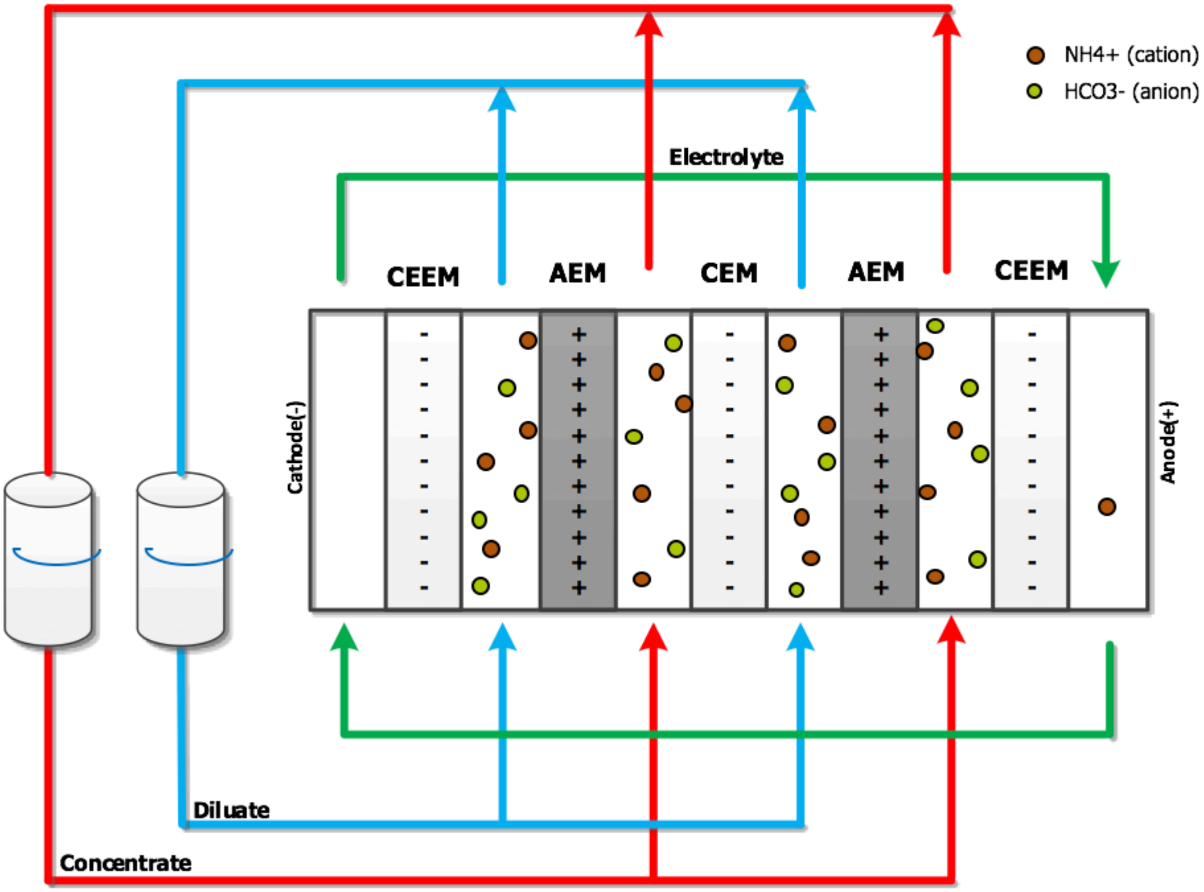


*Figure 1- Electrodialysis layout*

At both electrodes a concentrated electrode rinse solution allows the transfer of electrical potential through the cell. This solution is separated from the other cell pairs, consisting of one diluate and one concentrate stream, by cation end membranes (CEEM). By recirculating the electrode rinse solution, ions that are transferred through the CEEM into this electrolyte will be transferred back into a concentrate cell after recirculation.

Electrodialysis is already widely used for desalination of brackish water, treatment of industrial process waters and the recovering of reverse osmosis reject (Korngold et al., 2009; Reahl, 1990). Treatment of brackish water, in order to produce fresh water streams, reverse osmosis is often preferred as this offers a more cost-effective approach and also forms a barrier against biological contamination (F. Valero, et al. 2011). However, this thesis focuses on the production of a highly concentrated ammonium volume, rather than producing clean water. Compared to the treatment of reverse osmosis reject, electrodialysis yields the best hydraulic recovery and is the most cost-effective membrane technique (Xu & Huang, 2008).

In most membranes techniques, an external force is used to force water through the membranes, while in electrodialysis only ions are transferred through the ion exchange membranes. The resistance in such a setup will be determined by the stream that has the lowest electrical conductivity, the diluate stream. Higher concentrations therefore lead to lower resistance and a better utilization of the energy. However, electrodialysis is limited by the properties of the ion exchange membranes and the high costs of electrodes and ion exchange membranes (Xu & Huang, 2008).

### 2.1.2 Electrochemical potential difference

Solutions, separated by semi-permeable membranes, tend to have a concentration equilibrium on both sides of the membrane. Electrodialysis uses energy, as induced electrical potential difference, to create a disbalance between concentrate and diluate stream, and thereby creates a potential energy source. Each chemical species has its own electrochemical potential in space, which will be constant in the solutions when an equilibrium is reached. The dissimilarity created in electrodialysis is reversible by not applying an external electrical potential. In this matter, ions will flow from high concentration to low concentration. The transport of ions, and therefore electrons, across the membrane yields an electrical current that can be translated to electrical energy. This phenomenon is described in the addapted Nernst equation, shown below.

$$\Delta\phi = \frac{RT}{\mathrm{F}} \cdot \ln\left(\frac{X_c/MW}{X_d/MW}\right)$$

Where:

$\Delta\phi$: electrochemical potential difference [V]
F: Faraday constant [96485 C · mol$^{-1}$]
$X_c$: salt concentration concentrate stream [g · L$^{-1}$]
MW: molecular weight of the used salt [g · mol$^{-1}$]

R: universal gas constant [8.3144 J · mol$^{-1}$ · K$^{-1}$]
T: water temperature [K]
$X_d$: salt concentration diluate stream [g ·L$^{-1}$]

This theoretical potential difference is temporal and changes when ion concentration differences between concentrate and diluate flow change. The time it takes for the solutions to reach an equilibrium state, combined with the electrochemical potential and the current it generates, can be translated to the amount of energy moved. However, the energy demand can only be determined by experimental studies.

## 2.2 Operation parameters

### 2.2.1 Current efficiency (CE)

The current efficiency is one of the key parameters determining the operation efficiency of an electrochemical process. The definition of current efficiency, also known as the Faraday efficiency, is the ratio between actual mass transferred by the passage of current from an electrolyte to the theoretical mass transferred according to Faraday's law. Simplified, it determines the percentage of current that is used for the transfer of ions through the charged membranes. Monitoring the CE gives insight on undesirable phenomena like the non-perfect perm-selectivity, or impurities in the membranes (Sadrzadeh & Mohammadi, 2009). It can be calculated using the following equation:

$$CE = \frac{z \cdot F \cdot Q_f \cdot (C_i - C_0)/MW}{N \cdot I}$$

Where:
CE: current efficiency [%]
F: Faraday constant [96.485 A s · mol$^{-1}$]
$C_i$: feed concentration [g · L$^{-1}$]
N: the number of cell pairs [-]
MW: molecular weight of the used salt [g · mol$^{-1}$]
z: charge of the ion [-]
$Q_f$: diluate flow rate [L$^{1}$ · s$^{-1}$]
$C_0$: diluate concentration [g · L$^{-1}$]
I: applied current [A]

Current efficiencies between 61.3 and 67 percent can be reached for respectively synthetic and natural urine, containing a mixture of ions, with main components as ammonium carbonate, sodium chloride, potassium chloride and sodium sulfate (Luther et al., 2015). The composition of the feed solution has a big influence on the current efficiency as intertwined in the factor z. Understanding the basic mechanisms in essential for optimizing the electrodialysis process. Therefore, only the transport of ammonium bicarbonate through the charged ion exchange membranes is considered before synthetic ammonium streams are tested.

### 2.2.2 Limiting current density (LCD)

The driving force for ion transfer over charged membranes, as in electrodialysis, is known to be the electrical potential difference between the anode and cathode. An important parameter in its operation is determined to be the current density. This parameter, equal to the electrical current over the membrane area, has a strong relation with the resistance and the utilization of the current, and thus the current efficiency (Sadrzadeh & Mohammadi, 2009). These parameters are, as basic physics show us, related as shown below.

$$E = I \cdot R$$

Where:
E: Electrical potential [V]
R: resistance [Omh]
I: current [A]

A minimum resistance can be obtained by operating electrodialysis on limiting current density (LCD). The LCD is the current density where the ion concentration of the depleted solution, the diluate stream, at the ion exchange membranes surface becomes zero (Ho & Sirkar, 2012). Operating electrodialysis cells above the LCD does not only result in a lower current efficiency, introducing an additional cost element, but also leads to the dissociation of water and permanent damage to the membranes. Moreover, pH changes, consequential to the dissociation of water in hydrogen and hydroxyl can be harmful for the membranes. Permanent damage of the membranes, charging the membrane its surface, will occur when operational settings are far above the LCD (Cowan & Brown, 1959).

The influence of several parameters on the LCD, in an electrodialysis set-up, has intensively been studied on experimental scale. Design parameters, such as the flow velocity, stack design, feed concentration, membrane properties and hydrodynamic conditions are tested to have a correlation with the LCD (Lee et al., 2002). Empirical determination of the limiting current density has led to an equation, which is accepted widely and shown below.

$$i_{lim,emp} = a \cdot \frac{C \ \cdot \mathrm{z}}{MW} \cdot u^{b}$$

$$\ln\left(\frac{i_{lim,emp}}{C}\right) = \ln(a) + b ln(u)$$

Where:
$i_{\mathrm{lim,emp}}$ : empirical limiting current density [A]
u : linear flow velocity [m · $s^{-1}$]
MW: molecular weight of the used salt [g · $mol^{-1}$]
C : concentration of solute [keq · $l^{-1}$]
z : equivalent weight [eq · $mol^{-1}$]

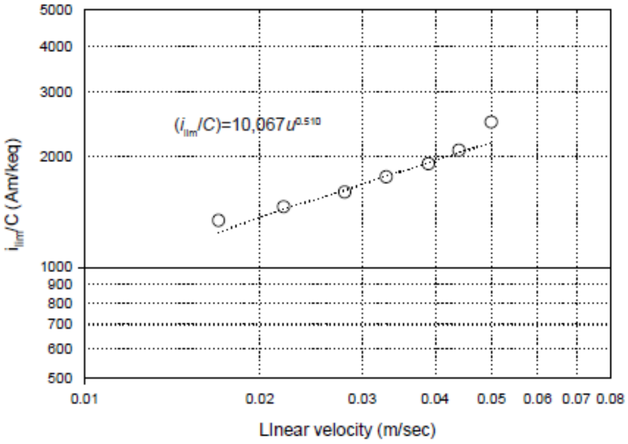


*Figure 2 - Determination of constants a* and *b for determining the LCD* on double logarithmic paper scale

It can be concluded that the LCD is proportional to the ion concentration in the diluate stream and quadratic to the linear velocity along the membrane. Moreover, constants *b* and *a* are respectively related to the hydrodynamic conditions in the ED cell and the concentration in the solution, cell configuration and properties of the ion exchange membranes. These constants can be calculated by plotting equation 1 on double logarithmic paper, as shown in Figure 2.

As different chemical elements have different quantitative influences on the limiting current density, the empirical formula can only be applied on stable solutions. Therefore, in this thesis the LCD is determined by plotting the reciprocal current against the resistance (Cowan & Brown, 1959). This method is shown in Figure 3, where also the pH is shown. The example shown in this figure has a LCD value of 3.85 A, or a reciprocal current of 0.26. Operating electrodialysis above this value leads to water dissociation and therefore pH changes.

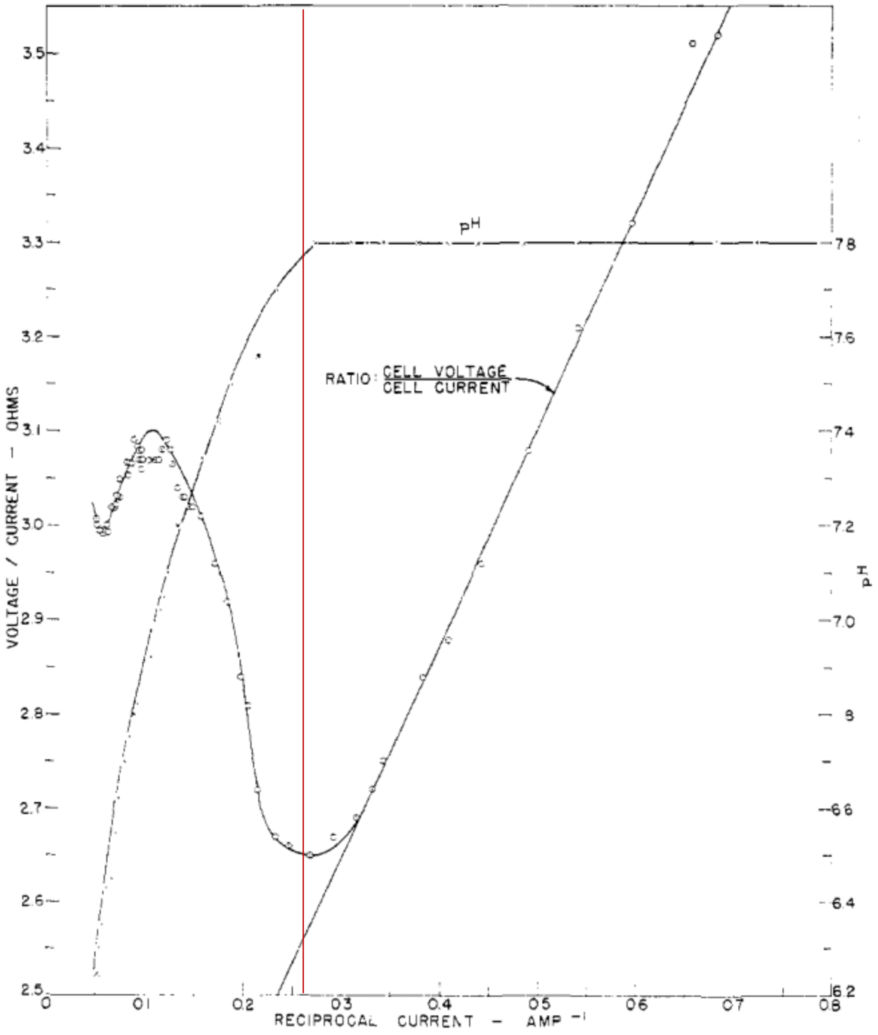


*Figure 3 – Relation between (reciprocal) current and resistance/pH for a sodium sulfate solution (Cowan & Brown, 1959)*

### 2.2.3 Energy efficiency (EE)

As mentioned above, current efficiency is one of the most important parameters to measure the efficiency of electrochemical processes. However, current efficiency neglects the electrical potential required for the electrodialysis process. Within the focus of this thesis, not only the utilization of current is important, but also the usage of the available electrical energy. No information can be found in the acquired literature about the relation between the current efficiency and the energy efficiency. Moreover, energy efficiency is a term usually used in the combustion of energy carriers and can best be described as the percentage of energy input which is consumed usefully (Patterson, 1996).

As it is not possible to determine the amount of energy which is consumed usefully, and the electrodialysis process does not generate energy from an electrical potential source, it is not possible to determine the energy efficiency is this way. Concentrating ions is the main objective of electrodialysis and could therefore be compared to the used amount of energy. Within this thesis, the following definition of energy efficiency will be used.

$$EE = \frac{CF}{E} = \frac{C_{ct} \; / \; C_{C0}}{E}$$

Where:

CF: concentration factor [ - ]
$C_{ct}$: salt concentration concentrate cell at time t [$g \cdot m^{-3}$]
$C_{co}$: initial salt concentration concentrate cell [$g \cdot m^{-3}$]
EE: energy efficiency [$Wh^{-1}$]
E: consumed energy [Wh]

## 2.3 Processes in electrodialysis

### 2.3.1 Migration of salts

The migration of salt from one stream to another is the main objective of electrodialysis and is strongly influenced by the applied potential difference at both electrodes. The relation between the transfer of sodium chloride over time for different applied currents is displayed in Figure 4. No information is provided on the initial concentrations and membrane properties (Han et al., 2015).

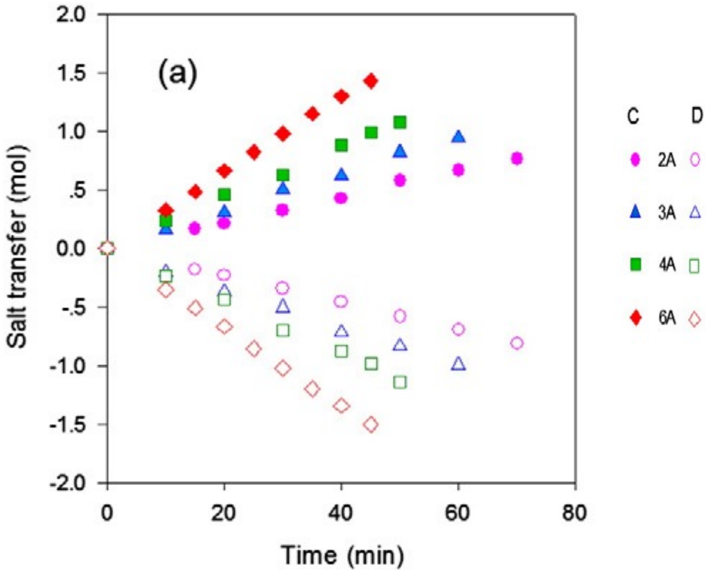


Figure 4 – Transfer of NaCl over time for different electrical currents (Han et al., 2015)

Two ion fluxes can be distinguished, of which one is coupled to the electrical current induced by the potential difference in electrodialysis, and is called the migration flux ($J^{mig}$). The other flux is coupled with the chemical potential gradient induced by the different ion concentrations in the solutes on both sides of the ion exchange membrane, and is called diffusion flux ($J^{diff}$). The sum of these two fluxes yield the total transfer of salt across the membrane. As both fluxes work in opposite directions, the sign of these fluxes will also be opposite.

According to Han et al. (2015), the diffusion flux is negligible compared to the migration of ions flux. Moreover, plotting salt flux transfer rates against the applied currents, found in Figure 4, a linear trend can be found. Therefore, the following relation between salt transfer and current can be expressed with the following equation.

$$J^{mig} = \alpha \cdot I$$

Where:

$J^{mig}$: migration salt flux [mol·m$^{-2}$·s$^{-1}$]

C: current [A]

$\alpha$: current coefficient [mol·m$^{-2}$·s$^{-1}$·A$^{-1}$]

The current coefficient ($\alpha$) considers the utilization of current for the transfer of salt, comparable to the current efficiency. The current coefficient will strongly decrease if electrodialysis is operated above limiting current density, as in this scenario energy is also used for the dissociation of water. Moreover, resistances induced by current transfer and ion exchange membranes also influence this coefficient.

### 2.3.2 Back diffusion of ions

In the latter paragraph the influence of the diffusion flux is neglected. However, its relative influence and the relation to the concentration difference between two adjacent cells are not described. Moreover, the ion transport number is often completely assigned to the migration flux, while its determination shows a combination of migration and diffusion flux (Barragán & Ruız-Bauzá, 1999).

However, the transport of salt across membranes, when on both sides two electrolyte solutions are placed with a different concentration, can be observed. This phenomenon is found in literature as back-diffusion of ions, back-migration of ions and electrolyte permeation, and is widely studied by membrane researchers (Izquierdo-Gil et al., 2012; Rottiers et al., 2014). In electrodialysis operations, back diffusion of ions is always present and hinders the purpose of its application. Literature shows the diffusion rate of ions is proportional to the concentration gradient. However, these diffusion constants show different values for different ions and different used membranes. Determining the diffusion constant for the transport of ammonium bicarbonate for the used membranes in this thesis, can be determined by conducting experiments.

### 2.3.3 (Electro-) Osmosis

The cation and anion exchange membranes are especially designed as ion exchange membranes, rejecting all non-charged molecules like water. However, multiple papers recall not only solute transport, but also the transport of its solvent during the operation of the ED-cell (Gain et al., 2002; Han et al., 2015; Lee et al., 2002; Ling et al., 2002). This flow can be divided into the common transfer of water, together with the salt ions, and the transfer of water due to osmotic pressure difference in adjacent concentrate and diluate cells.

**Salt-Water bonds**

Salts are bound by electrostatic forces, which are neutralized when making contact with water molecules. The polar covalent function of these water molecules, together with strong ionic bonds of certain salts, make it very easy to ionize these salts in water. The two compounds, a cation and an anion, for this thesis ammonium bicarbonate ($NH_4HCO_3$) salt is considered, has covalent bonds. This indicates the molecules share electrons and therefore the negative side of water molecules is attracted to the positive charged ammonium ions, and the positive side of the water molecules is attracted to the negatively charged bicarbonate ions. Schematically this is shown in Figure 5.

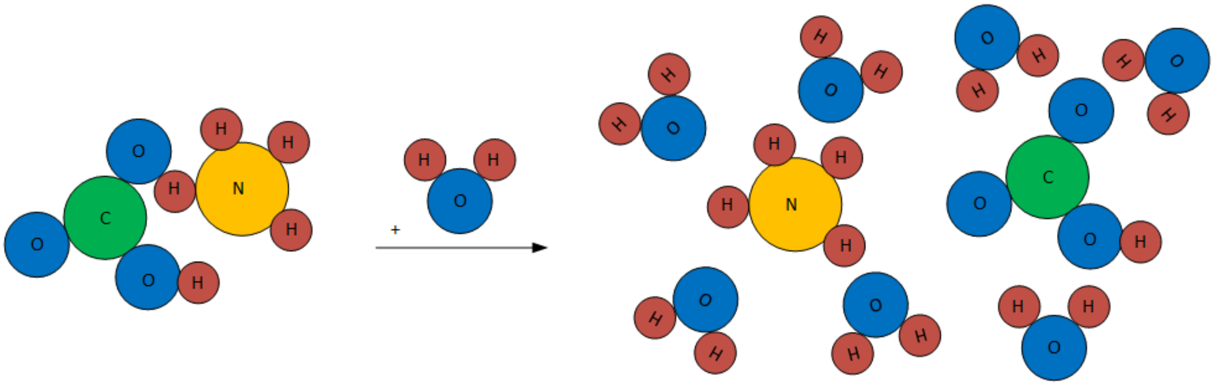


*Figure 5 – Dissolving of ammonium bicarbonate in water, including the arrangement of water molecules*

Applying electrical current induces the transport of ions through the membrane and, besides, also transfers water molecules bonded to this ion. According to Lee et al. (2002) the variation of water removed from the diluate stream responds to a ratio of 2-10 mole of water per mole of sodium chloride. However, no division is made between the share of water transport due to osmosis and electro-osmosis. Moreover, as the water transport due to osmosis and electro-osmosis only consists of 1% of the total produced volume, these processes are neglected in this paper. Electrodialysis is used in this particular case for the desalination of brackish/sea water, and therefore transports sodium chloride through the membranes. The amount of water molecules co-migrating with salt ions will be different for each salt, as hydration numbers of salts are different.

During experiments conducted with ammonium nitrate a volume transfer, equal to 13 moles water per mole of charge was be observed. In this case, one mole of charge is equal to one mole of ammonium, as its charge is equal to one (Ling et al., 2002). Again, no division is made between osmotic and electro-osmotic fluxes. It should be noticed osmosis and electro-osmosis transfer solvent in the opposite direction, when current is applied during regular operations.

Literature shows electro-osmosis and osmosis are two different processes, influencing the solvent flux from diluate to concentrate stream. However, (Han et al., 2015) links all the solvent flux to electro-osmosis, neglecting the transfer of solvent due to ion concentration gradients between concentrate and diluate cells.

Therefore, proving the existence of osmosis and electro-osmosis should be demonstrated, while also the relation between solvent fluxes and its driving forces should be investigated.

The driving force for electro-osmosis is known to be electrical current, as this transfers ions through ion exchange membranes. Han et al. (2015) describes the transfer of salt, as shown in Figure 4, and the corresponding transfer of solvent, which is shown in Figure 6. A clear relation between current density and water transport rates can be observed. However, this relation is proportional to the ratio of NaCl transfer over time, for different electrical currents. Therefore, (Han et al., 2015) states the transfer of solvent is only influenced by the transfer of ions, and therefore electro-osmosis.

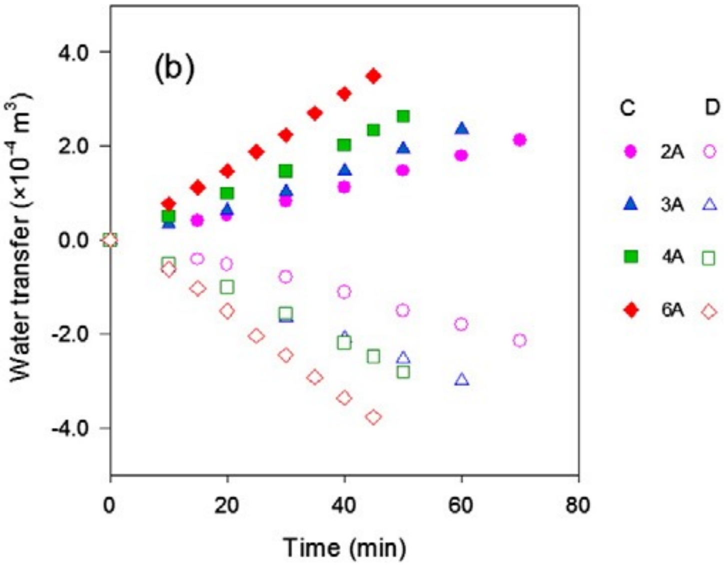


*Figure 6 – Water transfer for the dilution of NaCl over time for different electrical currents (Han et al., 2015)*

This same relation between current density and water transport rates can be seen in Figure 7 (Ling et al., 2002). Within the boundaries of this experiment, 1500 ml concentrate and diluate batches with ammonium nitrate are treated from an initial molarity of 0.11, until a concentration of 0.01 M is reached. This point is defined as the point where the concentration in the concentrate is not increasing further due to the transportation of water molecules. Three experiments, done in triplets, with corresponding current densities of 216, 345 and 432 A · m$^{-2}$ yield a linear relation with the variation in water transport in the concentrate cell.

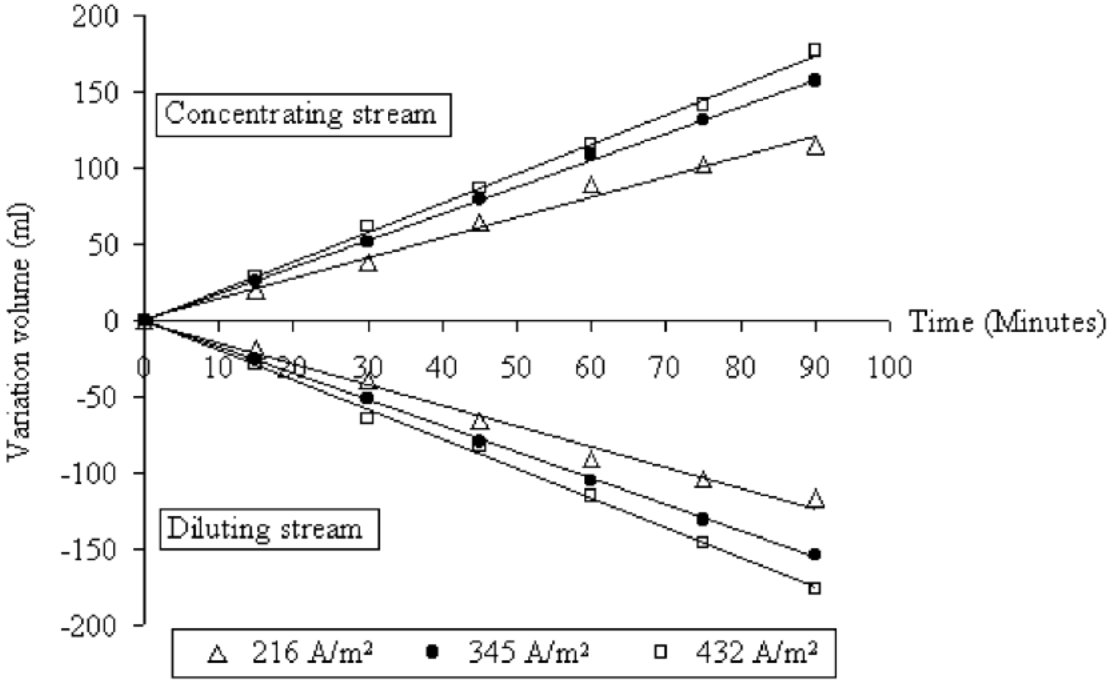


*Figure 7 - Water transport profile for different current densities as a function of time (Ling et al., 2002)*

Different water transfer rates can be distinguished from Figure 7 for the various current densities. It can be concluded from this graph that lower current densities lead to smaller water transport values. Values between 80.4 ml · $h^{-1}$ and 109.8 ml · $h^{-1}$ for respectively 216 and 432 A · $m^{-2}$ are obtained. However, higher current densities also lead to a quicker transfer of salts through the membranes, and therefore more transport of water. As more water is transferred out of the diluate cell, more salt mass can be transferred before reaching the final molarity of 0.01.

Calculations show that for this dataset a constant value is achieved in the concentrate cell for the transfer of salts over the transfer of water, regardless of the current density. Conclusively, in both tests from (Han et al., 2015; Ling et al., 2002), solvent transfer is proportional to salt transfer, and therefore electro-osmosis.

However, if only temporal variations are considered on the volume transfer for different current densities a clear relation can be found (see

Figure 8). From this graph it can be concluded that when no current is applied, still water is transferred from low to high solute concentration, and is defined as osmosis.

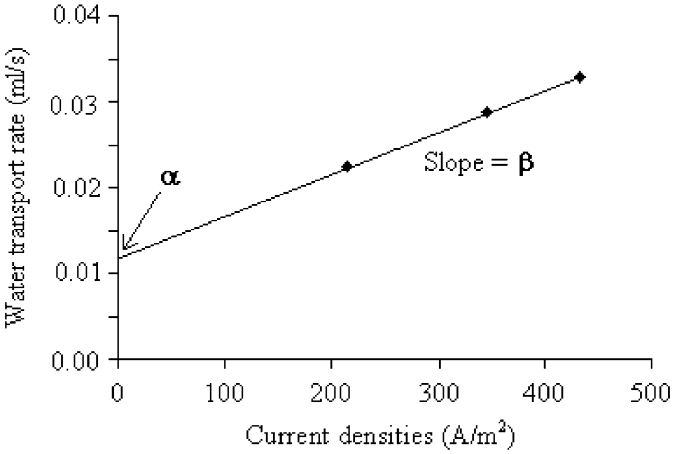


*Figure 8- Relation between water transport and current densities (L.-P. Ling, et al.)*

Osmosis is a natural occurring process and is driven by the ion concentration gradient between two adjacent concentrate and diluate cells. No literature is found defining the share of osmosis to the total solvent flux. However, reverse osmosis theory shows the relation between water flux and externally applied pressure (TMP). In electrodialysis this pressure is not present and will therefore be equal to zero, leading to a natural flow of solvent from low to high ion concentration streams.

$$J = \frac{1}{\mu \cdot R} \cdot (TMP - \Delta\pi)$$

Where:

J : volumetric flux [$m \cdot s^{-1}$]

$\mu$ : dynamic viscosity of water [$pa \cdot s^{-1}$]

R : membrane resistance [$m^{-1}$]

TMP : transmembrane pressure [pa]

$\Delta\pi$: Osmotic pressure difference [pa]

### 2.3.4 Influence of other salts

No direct literature is found on the influence of other salts on the energy efficiency for the concentration of one “goal” salt. However, with the knowledge gathered from literature it can be stated the transfer of ions is linear to the applied electrical current. The presence of other salts will have a negative influence on the concentration of ammonium bicarbonate, as these ions will also transfer from diluate to concentrate flux, and use electrical current for this process. On the other hand, the presence of other ions in solution will lead to higher electric conductivities and therefore lower resistances. As one process has a positive influence on the current usage, while the other process has a negative influence, it cannot be stated if the presence of other salts has a beneficial effect on the energy efficiency.

In the case of multiple-valent ions, retaining them in the diluate stream by applying monovalent selective membranes, will only to an increase in conductivity and therefore yields a positive effect.

### 2.3.5 Overview

Four main processes can be defined when taking electrodialysis into account, namely the transfer of ions, back diffusion of ions and the solvent of flux. This flux can be subdivided in **electro-osmosis** and **osmosis**. In Figure 9 below, these processes are shown. It should be noted that the transport of ions is always accompanied by the transport of solvent.

🟩 Migration of ions

🟥 Back diffusion of ions

🟦 Osmosis

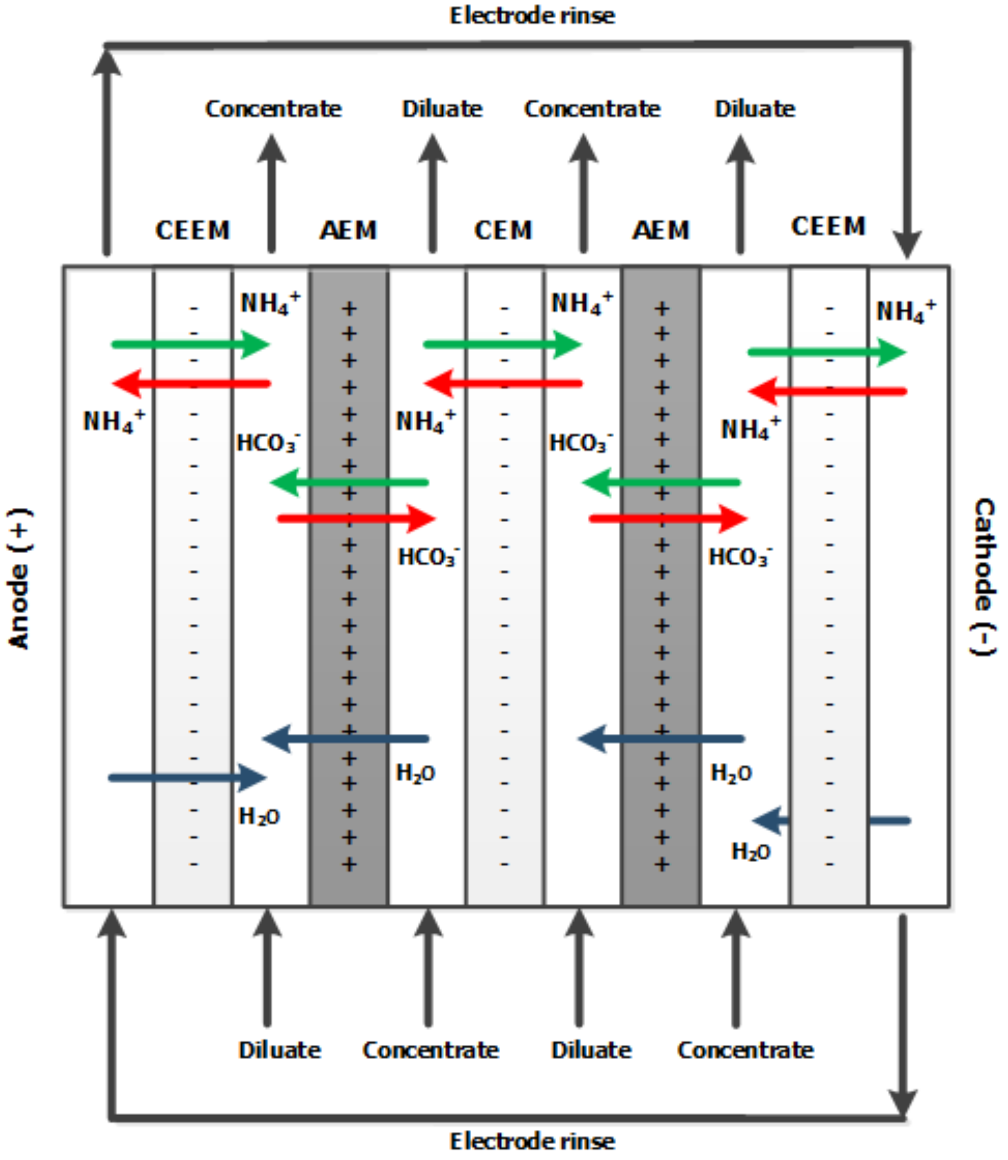


*Figure 9 – Processes in electrodialysis*

## 2.4 Optimization

The two obstacles determined in the latter paragraph are mainly driven by the ion concentration gradient between concentrate and diluate streams. Electro-osmosis cannot be prevented and therefore will give a minimal volume flux. Therefore, minimizing osmotic fluxes and back diffusion of ions can be prevented by limiting concentration differences.

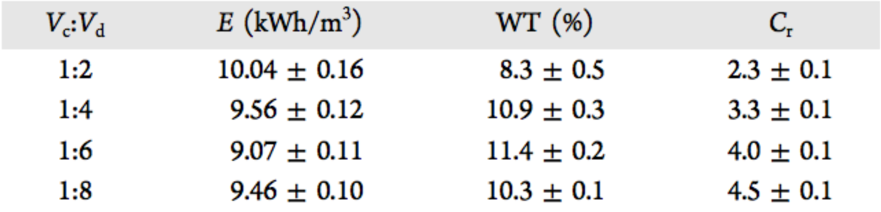
Moreover, ion transfer is linear related to the applied electrical current, as shown in paragraph 2.3.1. The main goal of this research is achieving a maximum ammonium concentration, utilizing energy as efficient as possible. The accumulation of ammonium in the concentrate cell leads to increased concentrations when concentrate volumes are decreased. Literature on these two optimization possibilities are gathered below.

### 2.4.1 Volume ratio

Optimizing electrodialysis for an energy efficient transfer of ammonium through the membranes is often accommodated by changing input parameters as applied voltage, flow speed and initial concentrations. However, the effect of volume is often neglected, while its natural occurrence in osmosis and electro-osmosis is always present.

The effect of changing several operation parameters in electrodialysis in order to produce coarse salt and fresh water from a concentrated reverse osmosis brine is investigated by  Jiang et al. (2014). This research considers the effect of a volumetric increase in the concentrate stream. Experiments show for a higher concentrate to diluate ratio (1:3), a quicker transport of salts from the diluate to the concentrate. Considering the processes mentioned above, higher ratios lead to lower ion concentration gradients between concentrate and diluate stream. Therefore, less back migration of ions will occur. No volumetric, current or electrical potential data is given for this ratio increase.

Moreover, (Yan et al., 2016) investigated the concentration of ionic liquids with electrodialysis. The results of volumetric changes are shown in Figure 10. The conclusion of these tests, an increase in diluate volume compared to the concentrate volume leads to a lower energy consumption, are similar to the ones found by (Jiang et al., 2014). The water transport increases from 33 ml to 165 ml per experiment for respectively volume ratios of 1:2 to 1:8. The concentration ratio (Cr), which is important in determining the energy efficiency in this thesis, increases significantly from 2.3 tot 4.5. In this paper an experiment is defined by applying a constant electrical potential difference of 10 Volts for 100 minutes long. However, a constant concentrate volume of 200 ml is used for all experiments, while the influence of total concentrate volume is not considered.



| $V_c$:$V_d$ | $E$ (kWh/m$^3$) | WT (%) | $C_r$ |
|---|---|---|---|
| 1:2 | 10.04 ± 0.16 | 8.3 ± 0.5 | 2.3 ± 0.1 |
| 1:4 | 9.56 ± 0.12 | 10.9 ± 0.3 | 3.3 ± 0.1 |
| 1:6 | 9.07 ± 0.11 | 11.4 ± 0.2 | 4.0 ± 0.1 |
| 1:8 | 9.46 ± 0.10 | 10.3 ± 0.1 | 4.5 ± 0.1 |

*Figure 10 – Effects of changing the volume ratio (VR)  on energy consumption (E), water transport ( WT) and concentration ratio (Cr) (Yan et al., 2016))*

It can therefore be concluded that larger diluate volumes, compared to concentrate volumes, lead to several desirable effects. Within the researched volume ratios an increasing energy efficiency can be noticed, with values respectively equal to 0.23, 0.35, 0.44 and 0.48 $Wh^{-1}$. It can be assumed that smaller volume ratios yield an even higher energy efficiency.

# 3 Materials and methods

## 3.1 Experimental setup

### 3.1.1 Objective

In order to validate hypotheses drawn from literature study, and in order to answer the sub questions and subsequent the research question of this thesis, experiments are conducted. The objective of the experimental unit is to study the influence of operational parameters on the ammonium ($NH_4^+$ (aq)) concentration performance of electrodialysis. In this study, the cross-flow rate, current density, volume ratios and concentration ratios were researched. Additionally, multiple types of membranes were subject of research (standard and monovalent selective), in order to determine selectivity performance of concentration in mixtures.

### 3.1.2 Experimental set-up

The experimental set-up consists of two PCCell units, respectively 64002 and 64004, as the casing for the ED stack. The main difference between these two PCCell ED units is the amount of streams they allow to enter the ED stack, which is respectively three and five streams. As only concentrate, diluate and electrode rinse streams were used during the experiments performed in this thesis, also two PCCell 64002 ED cell units could be used. The set-up consists of an ED stack enclosed by an anode (made of Pt/Ir- coated Titanium) and a cathode (made of V4A Steel) (PCCell, 2016). For the ED experiments, a standard membrane stack (STM) and a monovalent membrane stack (MVM) were used, which were both supplied by PCCell. Each stack consists of the following elements:

| | | | |
|---|---|---|---|
| - | n-1 | Cation exchange membranes | (CEM) |
| - | 2 | Cation exchange end membranes | (CEEM) |
| - | n | Anion exchange membranes | (AEM) |
| - | 2n | Associating spacers | |

| | Standard CEM | Standard AEM | Monovalent CEM | Monovalent AEM | Standard CEEM |
|---|---|---|---|---|---|
| **Functional group and ionic form** | Sulphonic acid –Na+ | Ammonium – Cl- | Sulphonic acid –Na+ | Ammonium – Cl- | Sulphonic acid –Na+ |
| **Membrane dim. [m]** Length x Height | 0.11 x 0.11 | 0.11 x 0.11 | 0.11 x 0.11 | 0.11 x 0.11 | 0.11 x 0.11 |
| **Eff. Mem. dim. [m]** Length x Height | 0.08 x 0.08 | 0.08 x 0.08 | 0.08 x 0.08 | 0.08 x 0.08 | 0.08 x 0.08 |
| **Thickness [m]** | $160 \cdot 10^{-6} - 200 \cdot 10^{-6}$ | $180 \cdot 10^{-6} - 220 \cdot 10^{-6}$ | $100 \cdot 10^{-6}$ | $110 \cdot 10^{-6}$ | $400 \cdot 10^{-6}$ |
| **Resistance [Ω/m2]** | $\sim 2.5 \cdot 10^{4}$ | $\sim 1.8 \cdot 10^{4}$ | | $\sim 20 \cdot 10^{4}$ | $\sim 9 \cdot 10^{4}$ |

*Table 2 – Membrane characteristics (PCCell, 2016)*

The cation exchange membranes, and its associated spacers, are situated next to the electrodes. Between these two CEEM, alternating cation and anion exchange membranes are situated, as shown in Figure 11. Membrane characteristics for the used membranes are shown in Table 2. The membrane stacks used in this research consists of ten cell pairs (n = 10), consisting of a cation-exchange membrane, a concentrate containing cell, an anion-exchange membrane and a diluate containing cell. The total effective membrane area of ten cell pairs is equal to 0.128 $m^2$. The spacer gaskets, allowing the water to flow between CEM and AEM membranes have a thickness of $0.5 \cdot 10^{-3}$ m.

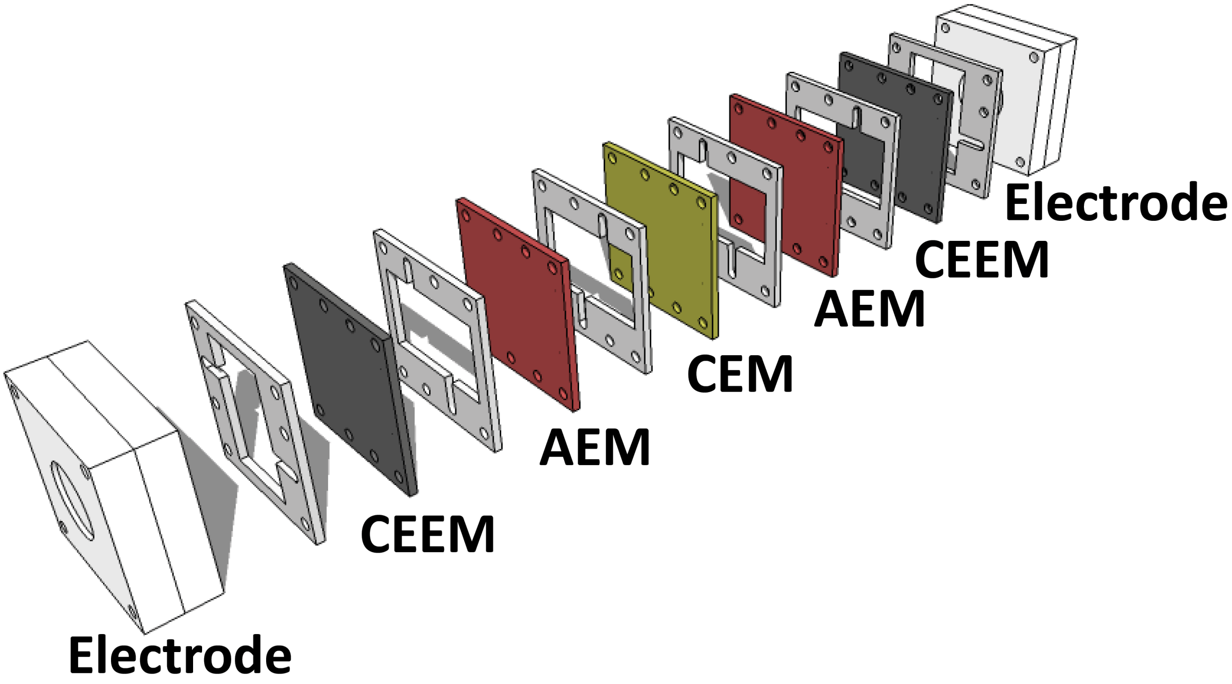


*Figure 11 – Lay-out of an electrodialysis membrane stack*

### 3.1.3 Schematic presentation

In Figure 12 a schematic representation of the experimental ED set-up is shown, including all streams and components.

A mixing table and magnetic stirrers are used for the constant mixing of the concentrate-, diluate- and electrolyte volumes to ensure the uniform distribution of ions in solution. From these volumes the electrolytes are pumped, through Watson Malow Marprene tubes with a bore of 6.4 mm and a wall thickness of 1.6 mm, to the ED stack by a Watson Marlow 520S pump and three 323 pump heads. The current and electrical potential is provided to the electrodialysis cell by a TENMA 72-2535 direct current power supply, with a current range of 0.0 – 3.0 A and an electrical potential range of 0.0 – 30.0 V.

The initial diluate and concentrate streams both consist of one liter demineralized water with an addition of a 6.58 g/L ammonium bicarbonate solution ($NH_4HCO_3$), which is equivalent to 1.5 g/L ammonium. Hence, this results in equal TDS concentrations and therefore an equal electrical conductivity in both streams. Due to high electrical potential differences at the electrodes, forming hydrogen and hydroxyl at respectively the anode and cathode, electrochemical reactions will occur in the electrolyte solution close to the electrodes. A highly concentrated electrode rinse solution limits the resistance of transferring electrical potential from the electrodes to the fluid, consisting of 1 molar (85 g/L) sodium nitrate ($NaNO_3$).

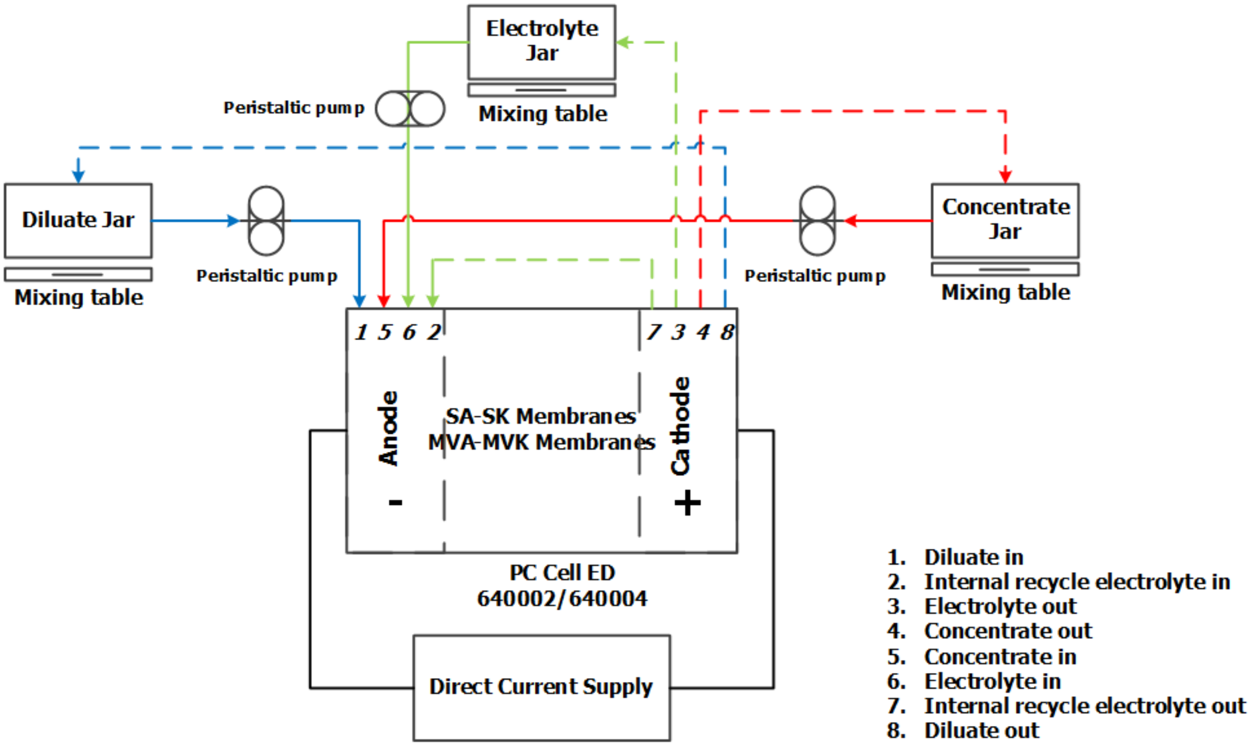


*Figure 12 – Schematic representation experimental ED set-up*

During standard experiments, electrical conductivity sensors are placed in the diluate and concentrate streams for continuous measurements every minute. When considering the influence of the electrode rinse solution in the ED performance, also the EC of this stream will be measured. Electrical conductivity, or pH, is measured with a WTW Multi 3630 IDS multi-meter. In addition, ammonium samples were taken with Machery-Nagel NANOCOLOR Ammonium 200 (for the range of 0.04 – 0.2 g/L $NH_4^+$) and 2000 (for the range of 0.4 – 2.0 g/L $NH_4^+$) test tubes.

The current and electrical potential are automatically logged every second by the direct current supply on a laptop.

The amount of energy needed to circulate the streams is determined by using a FESTO Span pressure sensor, with a range of 0 to 2 bars and an interval of 0.01 bar.

## 3.2 Experimental procedure

### 3.2.1 LCD procedure

Operating the ED cell above the limiting current density results in multiple disadvantages, as mentioned in paragraph 2.2.2. The LCD was determined by the empirical method of (Cowan & Brown, 1959).

Ten volumes with an ammonium concentration ratio of 1.0, 0.9, 0.8, 0.75, 0.6, 0.5, 0.25, 0.10, 0.05 and 0.01, compared to the initial ammonium concentration, are prepared for the determination of the LCD. In order to investigate the effect of concentration on the LCD, the concentration during one run needs to be kept constant. This is facilitated by recirculating the concentrate and diluate stream from the same volume, which will be constantly mixed on a mixing table. To ensure concentration differences were not occurring, the electrical conductivity of the salt solution is measured. The current is gradually increased every five second with a 0.01 A.

The used cell consists of ten cell pairs, with respectively twenty membranes, while the electrochemical splitting of water occurs around 1.23 V. Therefore, the test will be stopped when a current of 25 volts is exceeded, as to high currents can cause severe damage to the ion exchange membranes.

This test will be conducted for constant cross-flow speeds of 11.6 mm/s and 3.9 mm/s.

### 3.2.2 Experimental ED procedure

Different experiments were executed within this thesis, and are discussed below.

**Single diluate experiments**

All experiments will start with the concentration conditions as discussed in paragraph 3.1.3, and will be ended when the electrical conductivity of the diluate will reach approximately 1 mS/cm. The single run experiments are executed in order to determine the best condition for cross-flow speed and applied current density. Experiments are performed with 15.63 A/m$^2$, half LCD and full LCD for constant cross-flow speeds of 11.6 mm/s and 3.9 mm/s. The ammonium concentrations of the concentrate and diluate will be measured at the start and end of the run.

**Multiple diluate experiments**

Data concerning hindering factors and osmosis will be gathered by performing multiple diluate experiments in a feed and bleed system. In essence these experiments are the same as the single diluate experiment. When the diluate volume its ions are depleted (~ 1 mS/cm), the peristaltic pump and power supply will be turned off. The volume and ammonium concentration of the concentrate, diluate and electrode rinse volumes will be measured. The volume in the ED stack and tubing system will be brought back to the corresponding volume before measuring. A new diluate volume will be prepared and exchanged for the depleted diluate volume, as this is not containing enough salts for an effective process. This process will be repeated for twenty diluate volumes.

**Osmosis experiments**

As addition to the multiple diluate experiment two osmosis tests were performed to gather information about water transfer through the ion exchange membranes. An initial dissimilarity in concentration is created between the diluate and concentrate volume by adding respectively 13 and 0.2 grams of ammonium bicarbonate to half a liter of demineralized water. The test will be done for cross-flow speeds of 11.6 mm/s and 3.9 mm/s and will end after 18 hours.

The same experiment is repeated with different salt solutions, 1 gram of sodium chloride and 9 grams of ammonium bicarbonate in half a liter of water for respectively the concentrate and diluate is prepared. This experiment will only be conducted for a cross-flow speed of 11.6 mm/s and will end after 18 hours.

**Variable volume experiments**

The effect of volume on the performance of the electrodialysis process is tested by using different volume ratios and different total diluate volumes. The used volumes and membranes (STM, standard exchange membranes and MVM, monovalent selective membranes) are shown below in Table 3.

| Volume ratio | Total diluate volume | Membranes |
|---|---|---|
| [-] | [L] | STM/MVM |
| 1.0 | 1, 2, 2 | STM, STM, MVM |
| 0.65 | 1 | STM |
| 0.5 | 1, 2, 2 | STM, STM, MVM |
| 0.33 | 2 | STM |
| 0.25 | 1,2 | STM, MVM |
| 0.20 | 1 | STM |
| 0.10 | 2 | STM |
| 0.05 | 2 | MVM |

*Table 3 - Variable volume experiments input parameters*

**Monovalent selective membrane experiments**

These experiments are conducted in order to determine the influence of other mono- and multivalent ions, besides ammonium bicarbonate, in solution on the energy efficiency of the ED cell.

In order to investigate the influence of monovalent ions, a solution of one liter demineralized water with ammonium bicarbonate and sodium bicarbonate is prepared. To research the influence on the energy consumption of the monovalent salt quantity, a low and high concentration sodium bicarbonate (0.5 – 2.0 g/L is added in the different experiments.

Concerning bivalent ions, the water matrix of reject water shows calcium and phosphates ions have the highest concentrations of the multivalent cat- and anions. However, addition of tri-calcium phosphate ($Ca_3(PO_4)_2$) is not possible, as its solubility product is equal to 0.02 g/L. Moreover, the addition of almost all bivalent cations in combination with the standard solution containing ammonium bicarbonate forms precipitates directly after dosing (calcium- or magnesium carbonate). Determining the effect of multivalent salts on the energy consumption of concentration ammonium is therefore only possible when not ammonium bicarbonate ($NH_4HCO_3$) but another ammonium salt is used. Hence, ammonium chloride ($NH_4Cl$), is a good dissolvable in water and does not conflict with bivalent salts. Moreover, the solubility product of magnesium and sulfates is higher than calcium and phosphates. Therefore, the effect of a range between 0.3 – 0.5 g/L magnesium sulfate ($MgSO_4$) is tested on the concentration of ammonium chloride ($NH_4Cl$).

The experiments conducted with the bivalent ions are also used to determine the selectivity performance of the monovalent selective ion exchange membranes.

### 3.2.3 Cleaning procedure ED

After the experiments, both the STM and MVM membranes were cleaned by recirculation of both a 0.1 mol/L HCl and a 0.1 mol/L NaOH solution for 1.0 h, in order to remove potential inorganic (scaling products) and organic fouling, respectively.

# 4 Results and discussion

## 4.1 Efficiencies

The utilization of current and energy is determined in respectively the current and energy efficiency coefficients. As there is no theoretical background on determining energy efficiencies for operating electrochemical processes, only parameters influencing the current density are examined. In this matter, cross-flow speed and current density are considered. Boundaries for applying current are set between 15.63 A/m$^2$ and LCD. The determination of the LCD can be found in 7.3.3.

### 4.1.1 Current- and energy efficiency

With the formulas shown in paragraphs 2.2.1 and 2.2.3 both current and energy efficiency can be determined for different input parameters. Six tests are performed in order to calculate the trend in these efficiencies, namely with cross-flow speeds of 11.6 mm/s (High Cross-flow) and 3.9 mm/s (Low Cross-flow) and for 15.63 A/m$^2$ (Low Current), half the LCD (Intermediate current) and on LCD (High current). For single runs, the results are shown below in Figure 13.

It should be noted that the tests with intermediate- and high currents are always operated below respectively half LCD or LCD. This means that for a certain diluate electrical conductivity value, the current density is decreased, in order to prevent undesirable effects.

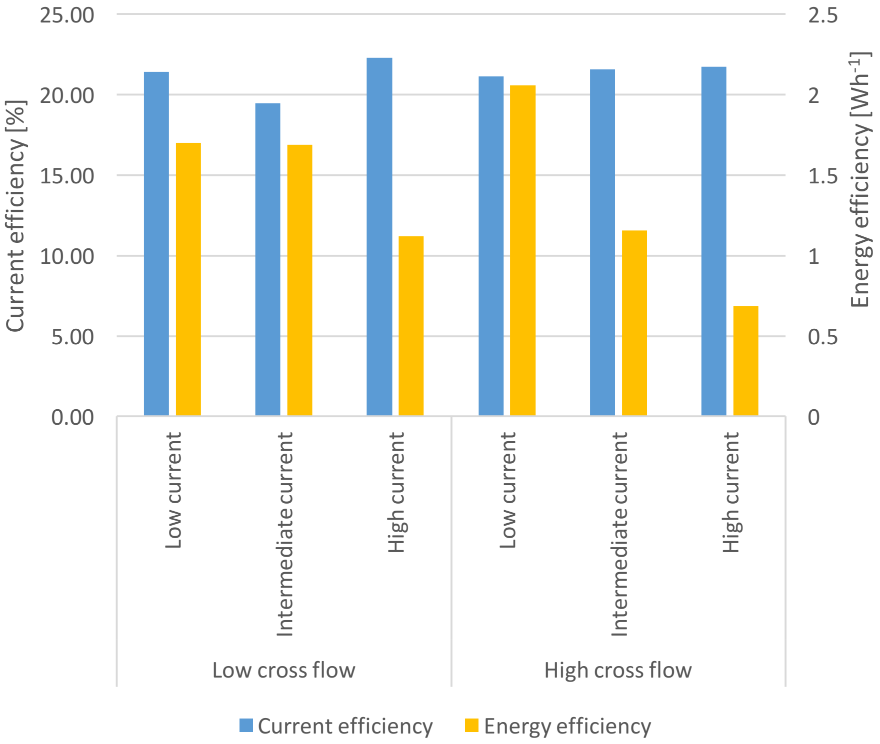


*Figure 13 – Current- and energy efficiency for different flow cross speeds and applied currents*

A maximum deviation of 2.81 can be observed in the current efficiency between the different input parameters. As the operation of the ED is stopped at the same EC value, namely 1 mS/cm, and the start concentration is also equal for all runs, it can be assumed that the concentration at the end minus the initial concentration is equal for all experiments. Moreover, the charge of the ion, Faraday constant and number of cell pairs in the ED setup also stays equal. It can therefore be concluded that the time spend to move a certain amount of salts through the membrane is linear related to the amount of applied current.

Current efficiencies between 19.5% and 22.3% are found when conducting these experiments. These values seem very low compared to the range of 61.3% and 67%, which were found in literature (Luther et al., 2015). However, the applied current does not only induce the transfer of ammonium through cation exchange membranes, but also the transport of bicarbonate through anion exchange membranes. If the transfer of bicarbonate is also taken into account, efficiencies between 85% and 96% can be found. These high values can be reached due to a very idealistic solution, with only containing one salt, and the operation where the current never exceeds the LCD values.

As mentioned before, this thesis focusses on the utilization of energy by electrodialysis, and not only the used current. Compared to the current efficiency values, large deviations between the different input parameters can be observed for energy efficiency. Energy efficiencies between 0.7 and 2.1 $Wh^{-1}$ are observed, for the concentration of the same ammonium mass. Generally, it can be concluded that the increase of current decreases the energy efficiency. Moreover, there is no clear relation between the high and low cross-flow tests. According to Figure 13 a high cross-flow (HCF) with a low current (LC) of respectively 11.6 mm/s and 15.63 $A/m^2$ uses energy as efficient as possible for the concentration of ammonium.

### 4.1.2 Pump energy

However, besides the electrical energy used for the operation of electrodialysis, also energy is needed to transport the electrolytes through this stack. The energy consumption of the pump is neglected in this graph, but could influence the outcome significantly. Operation times vary greatly from 32 to 178 minutes.

The pressure loss over the ED cell is calculated by assessing the pressure after the pump, but before the ED cell, while the pressure after the ED cell is equal to zero (adjusted for atmospheric pressure). These experiments are conducted for cross-flow speeds of 11.6, 7.7 and 3.9 mm/s. From hydraulics, the relation between pressure drop can be related to the flow and the power demand.

$$P = Q \cdot \Delta p$$

Where:

P: power [W]

Q: Flow [$m^3 \cdot s^{-1}$]

$\Delta$p: pressure loss [Pa]

The results from these experiments are shown in Figure 14.

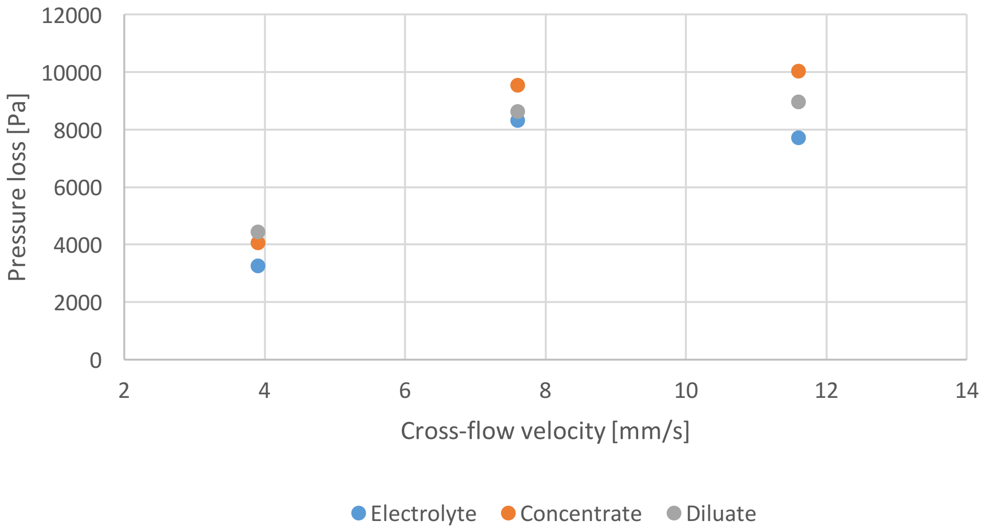


*Figure 14 – ED cell pressure losses for different cross-flow velocities*

The pressure loss for all streams are almost equal, as can be seen from this figure, while the pressure loss between a cross-flow velocity of 3.9 mm/s and 7.7 – 11.6 mm/s is about 5 kPa. When using these values, in combination with the data gathered in paragraph 4.1.1, the new energy efficiency of the several input parameters can be determined. In Figure 15 the energy efficiencies, including and excluding the pump energy, are shown. The preferable settings, with a high cross-flow and a low current, uses a significant amount of pump energy, leading to a lower energy efficiency. However, still more energy is consumed for low cross-flow with low current and low cross-flow with intermediate current.

It should be mentioned that the energy consumption of the transport of volumes is determined theoretically, with a pump efficiency of 100%. Taking into account a more realistic pump efficiency will lead to a lowering of energy efficiency for all settings. As the total energy demand only consist of a relative small part of pump energy, this will not lead to a higher energy efficiency for different input parameters. Moreover, a pump efficiency of 40% or less will lead to preferable settings with low cross-flow speed and low current.

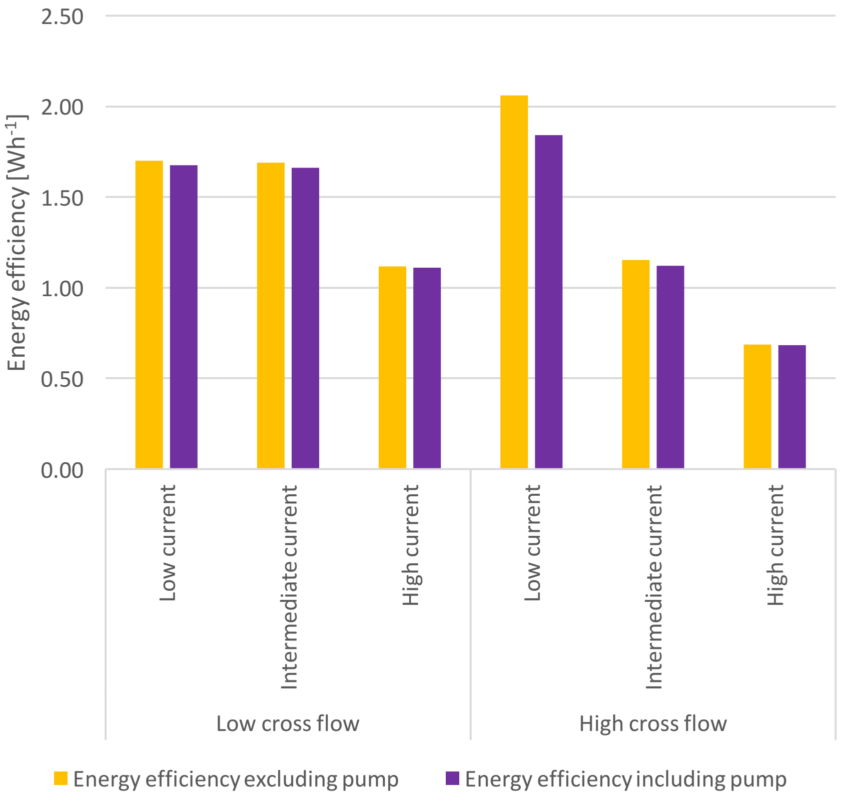


*Figure 15 - Energy efficiency for different flow cross speeds and applied currents including and excluding pump energy*

### 4.1.3 Effect of cross-flow speed on energy consumption

In the latter paragraph, the influence of cross-flow speed on the energy efficiency is stressed by including the energy demand for the transport of volumes through the ED stack. As the transfer of current is limited by the flow with the lowest electrical conductivity, the diluate stream, this flow needs the highest recirculation of volume to increment the number of ions in the solution. Hence, the electrode rinse and concentrate volume could be pumped through the system with a lower cross-flow velocity.

This principle is tested by decreasing individual streams while logging the energy consumption of the ED stack. The results of these tests are shown in Table 4. It can be concluded that lowering any individual stream leads to an increase in energy needed. However, decreasing the diluate cross-flow speed has twice as much influence on the energy consumption compared to the concentrate and electrode rinse speeds. On average, as these tests were performed in duplicate, the energy consumption increases with 0.07 Wh when the concentrate speed is lowered, 0.1 Wh when the electrode rinse speed is lowered, and finally 0.19 Wh when the diluate speed is lowered from 11.6 mm/s to 3.9 mm/s.

| Cross-flow speed Concentrate [**mm · s$^{-1}$**] | Cross-flow speed Diluate [**mm · s$^{-1}$**] | Cross-flow speed Electrode rinse [**mm · s$^{-1}$**] | Runtime [**min**] | Energy [**Wh**] |
|---|---|---|---|---|
| 11.6 | 11.6 | 11.6 | 145 ± 1 | 0.85 ± 0.01 |
| 3.9 | 11.6 | 3.9 | 143 ± 1 | 1.02 ± 0.02 |
| 11.6 | 3.9 | 11.6 | 152 ± 2 | 1.21 ± 0.02 |
| 3.9 | 11.6 | 11.6 | 143 ± 1 | 0.92 ± 0.01 |

*Table 4 – effect of cross-flow speed on energy consumption*

As the required pump energy for operating all three streams on 11.6 mm/s is equal to 0.1 Wh, it is not more advantageous to decrease any of the flows. Therefore, the tests in the remainder of this thesis will be performed with a cross-flow speed of 11.6 mm/s for all streams and a current density of 15.63 A/m$^2$.

## 4.2 Maximum ammonium concentration

In this paragraph the maximum concentration of ammonium will be assessed, while also the main relations between output parameters in the electrodialysis operation will be discussed. These tests are performed in a feed and bleed set-up as shown in Figure 12, elucidated in paragraph 3.2.2 and operated with the input parameters found in paragraph 4.1. It is important to emphasize electrodialysis operation will be stopped when a conductivity of 1 mS/cm, which is equal to 140 mg $NH_4$/L, is reached. Operations will be resumed after the preparation of a new diluate volume, containing an initial ammonium concentration of 1.5 g/L. These steps were repeated until no further increase in concentrate ammonium concentration is observed.

### 4.2.1 Mass imbalance

According to the theory of electrodialysis, salts transfer from diluate cell to concentrate, is recirculated through the system by means of the electrode rinse solution. Previous multi-diluate test have shown a mass balance that could not be closed due to the genesis of gaseous ammonia (Mondor et al., 2008). However, concentrations of ammonium in the electrode rinse solution or the formation of crystals due to high concentrations in the concentration are not reported.

In the tests performed in this thesis the ammonium bicarbonate concentration will not exceed 150 g/L, while its solubility can be up to 300 g/L. Moreover, the pH at which the tests are operated, almost all ammonium bicarbonate is ionized into ammonium and bicarbonate (see paragraph 7.2.5). The vaporization of high ammonia gas concentrations is therefore not likely and gives reason to measure the ammonium concentration in the electrode rinse solution.

### 4.2.2 Maximum ammonium concentration

With this consideration, the maximum ammonium concentration in the concentrate, taking ammonium concentrations in the diluate and electrode rinse solutions and its volumes into account, was determined. The ammonium measurements are shown in Figure 16 below.

This graph shows essential information about the ammonium concentration in the concentrate and electrode rinse stream within electrodialysis. Considering the concentrate flow, a steep increase in ammonium concentration can be observed for the first couple diluate volumes. However, a flattening occurs at an ammonium concentration of **7.3**-gram ammonium per liter. Ammonium ions can be removed from more diluate volumes, but do not contribute to the further increase of the ammonium concentration in the concentrate. However, as already indicate above, the accumulation of ammonium in the electrode rinse solution has a serious contribution on the total mass balance of the system. Moreover, ammonium ions are still transferred trough the ion exchange membranes from the diluate- to the concentrate stream. A corresponding amount of water transfers along with these ions, leading to an equilibrium in ammonium concentration.

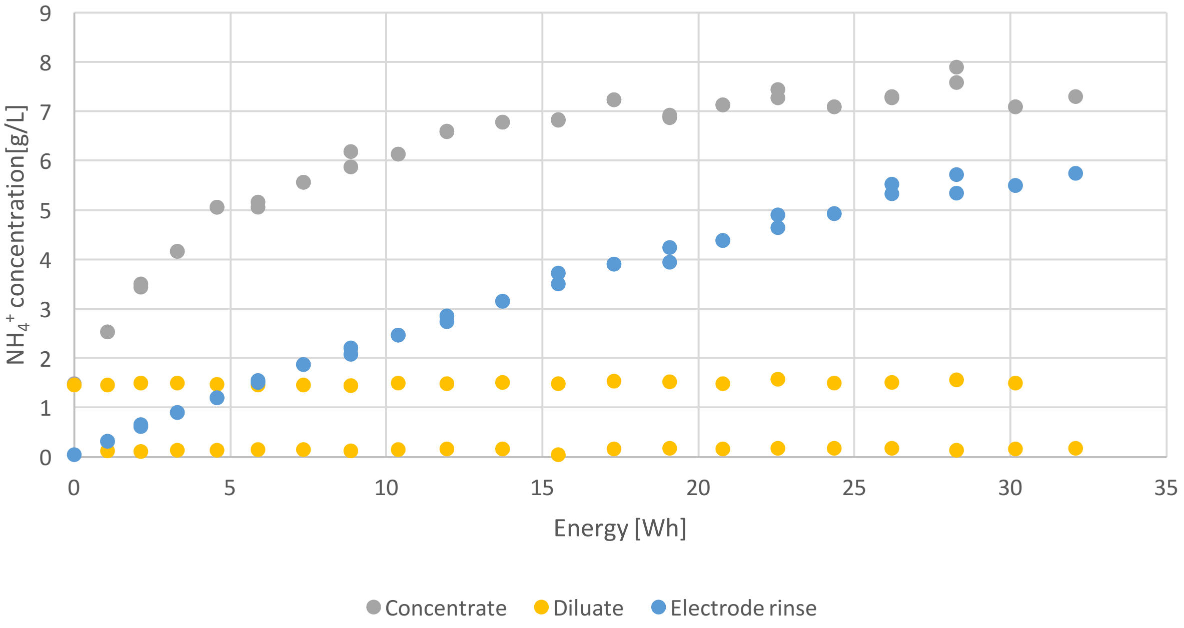


*Figure 16 – Ammonium measurements multiple diluate depletion experiment*

### 4.2.3 Mass balance

A simple mass balance can be performed over this system.

$$V_{total} \cdot C_{total} = V_{concentrate} \cdot C_{concentrate} + V_{diluate} \cdot C_{diluate} + V_{electrode\ rinse} \cdot C_{electrode\ rinse} + E$$

Where:

V: volume [l]

C: ammonium concentration [g · $L^{-1}$]

E: evaporation of ammonia [g · $L^{-1}$]

Deviations range from 37 mg $NH_4^+$ in the low concentration ranges to 3077 mg $NH_4^+$ in the higher segments. These deviations could be a result of measuring errors in the ammonium kit photo-spectrometer, or the preparation of these samples, the volume measurements and the initial weighing process of the ammonium bicarbonate salt. It can therefore not be stated that this deviation in ammonia is evaporated. The relative average deviation is equal to 3.98% respectively to the total mass in the system per measuring step.

### 4.2.4 Electrochemical potential

The minutely logged electric conductivity values are used as indicator for the concentrations in the concentrate and diluate stream, which are needed to calculate the electrochemical potential. Furthermore, the power supply log file, containing minutely current and potential measurements, is used to determine the electrical potential. Both potentials are shown in Figure 17.

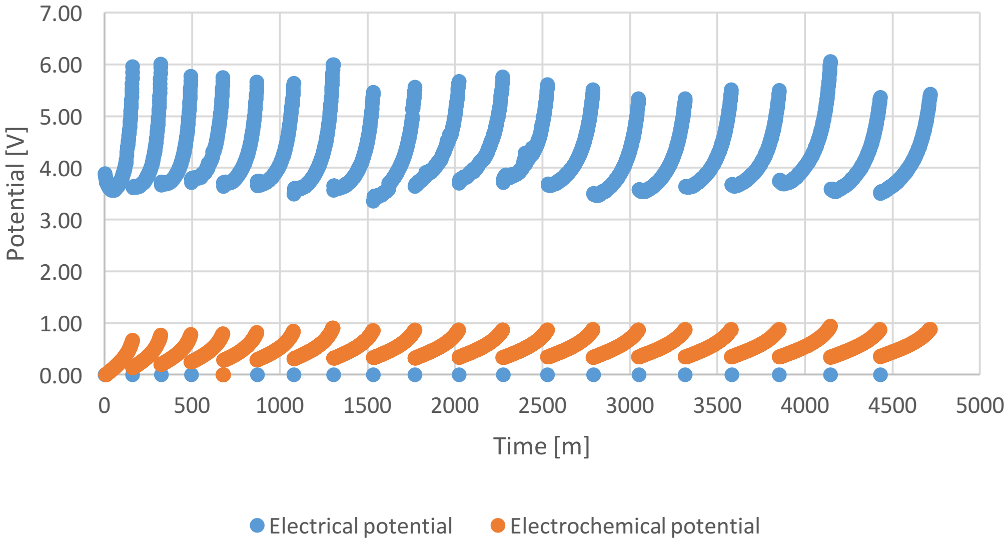


*Figure 17 - Electrical and electrochemical potential for multiple runs*

This plot shows both potentials for the multiple diluate experiment, and therefore consist out of twenty electrical potential lines and twenty electrochemical potential lines. The total potentials show a small decrease in the beginning of the experiment, where after an increase in cell resistance (due to the depletion of ions in the diluate flux) is accompanied by the increase in potential. As the limiting flow, the concentration of ions in the diluate flow, is equal for all experiments, no differences are observed for the electrical potential. As the experiments continues, the difference in concentration between the diluate and concentrate stream increases, leading to higher electrochemical potentials. Moreover, the start point of the electrochemical potential lines starts higher for every run, due to this bigger concentration difference.

Between the electrical potential lines an initial horizontal trend can be observed. As these initial electrical currents values are not increasing, it can be concluded no fouling of the membranes occurs.

The electrochemical potential amounts fifteen percent of the electrical potential used during an electrodialysis experiment. The theoretical electrochemical potential is lower as it does not take the resistance of the ion exchange membranes, the transfer of electrons from electrodes to solution and the resistance due to depletion of ions in the diluate stream, into account.

### 4.2.5 Volume displacement

Besides the transfer of salts from diluate- to concentrate stream, also the transfer of water occurs. This flux can be subdivided into the flux of water due to co-migration of water molecules with salt ions, and naturally occurring osmosis. These processes are further elaborated in paragraphs 4.3.2 and 4.3.3.

In appendix 7.4 a table with the measured water volumes of the concentrate, diluate and electrode rinse streams can be found, for the operation of the multi diluate experiment. This data is used to investigate the relation between electrical conductivity and water transfer. From Figure 18 it can be concluded that the amount of water flowing out of the diluate stream increases with every experiment, as the dissimilarity in ammonium concentration between concentrate and diluate streams increases.

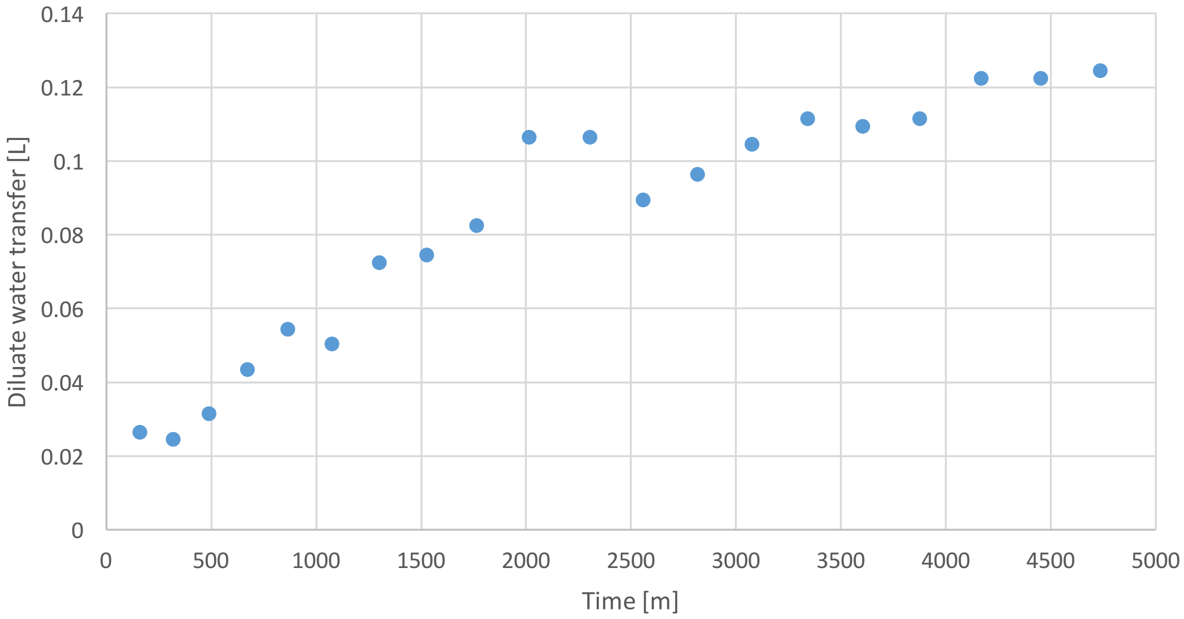


*Figure 18 – Water transfer over time*

As osmosis is mainly driven by the difference in salt concentration, the water transport is compared to this difference. These results are shown in Figure 19. An exponential relation between the delta EC and diluate water transfer can be observed. Membrane theory, as discussed in paragraph 2.3.3, shows the linear relation between flux through a membrane and the osmotic pressure difference and is shown in the equation below.

$$J = \frac{1}{\mu \cdot \mathrm{R}} \cdot \Delta\pi$$

The relation between the osmotic pressure difference, or in this case the difference between EC in both cells, and the flux through the membrane should be linear. However, the slight increase of temperature influences the viscosity of the water and also the time of an experiment plays a role. Moreover, the amount of co-migrated water has a larger influence for smaller diluate water transfer rates compared to higher values. If the water flux over delta EC is considered, still an increase in flux can be seen when delta EC increases. Physical properties of the ion exchange membranes can influence the flux through the membrane and limit the maximum water passage.

As the formula shown above describes the water flux, a transfer of volume over time, while Figure 19 shows the total diluate water transfer per experiment, temporal variations influence water transfer significantly. Higher currents lead to quicker transfer of salt, but also lower osmotic fluxes, while the amount of co-migrated water stays equal. Therefore, higher current densities utilize potential less efficient, having a negative effect on the energy efficiency. While on the other hand higher current densities lead to quicker transfer of salts, lower operation times, less volume transfer and therefore a positive effect on the energy efficiency. The consequence of applying higher current densities on the energy efficiency is not tested in this thesis.

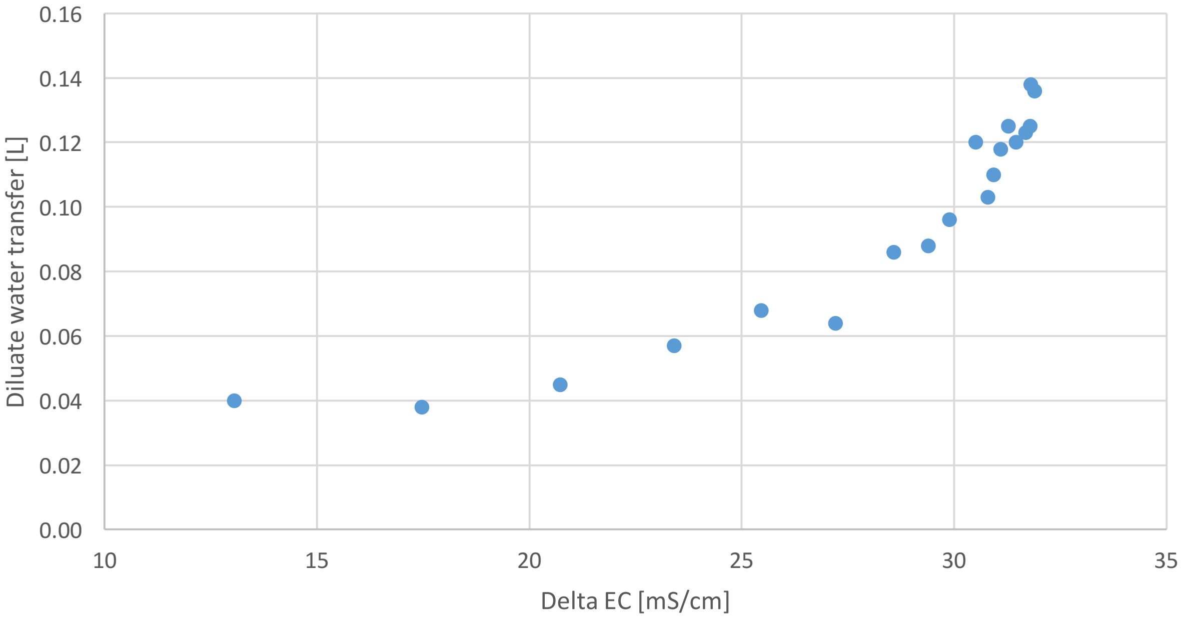


*Figure 19 – Water transfer over the difference in electrical conductivity for multiple jars*

It should be noted that the amount of water in the whole system increases every run, as the final volume in the diluate stream is always less than one liter. Due to the water transfer as a whole, the volume ratio between concentrate and diluate will not be equal to one. Effects of this inequality are discussed in paragraph 4.5.4.

### 4.2.6 Relation concentration, mass and energy consumption

An important part of this research is achieving a high concentration factor with an optimal utilization of the process energy. In Figure 16 the ammonium concentrations are plotted against the energy consumption. As the concentration in the concentrate stream flattens, while energy is still used for operating the ED stack, the utilization of energy is ineffective. As discussed in paragraph 4.2.4, the flattening of this concentration is accompanied with the transfer of solvent. Below, in Figure 20, both concentration- and mass factors are plotted against the energy consumption for the concentrate volume. Hence, these factors are the respective concentration or mass at the end of an experiment, divided by the initial concentration or mass.

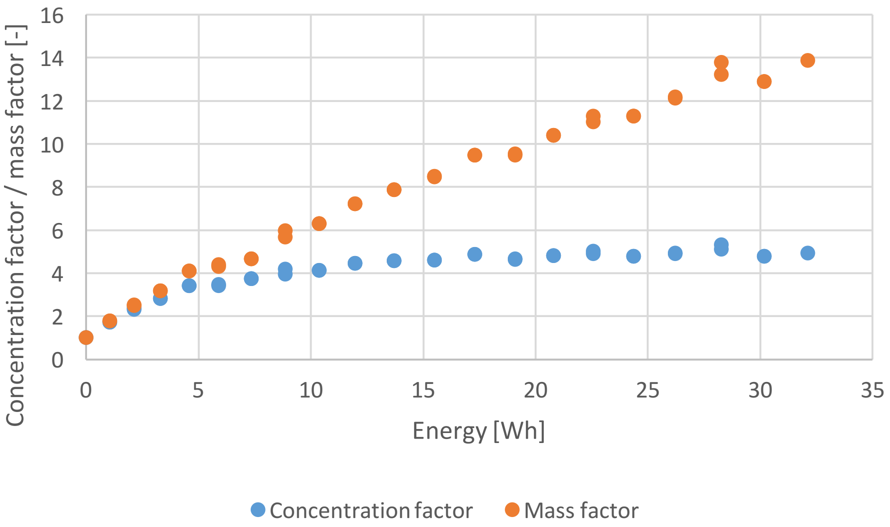


*Figure 20 – Relation between Concentration factor, Mass factor and energy consumption in the concentrate stream*

As the concentration factor shows similar behavior as the ammonium measurements shown in Figure 16, the mass factor has a linear relation with the applied energy. In conclusion, not only the same mass is transferred through the ion exchange membranes out of the diluate stream, also an equal increase in ammonium mass in the concentrate stream over the applied energy is observed. Idealistic, no volumetric differences are observed in the concentrate streams, giving a higher ammonium concentration for the same applied energy.

Moreover, it can be concluded that the amount of energy needed to increase the ammonium concentration in the concentrate stream increases when reaching a concentration factor of five.

Therefore, current- and energy efficiency both decline for a larger concentration difference between diluate and concentrate stream.

### 4.2.7 Relation maximum concentration and EC

A more interesting relation can be found when not considering the concentration ratio, but the ratio in electrical conductivity. As the maximum electrical conductivity in the experiments conducted in this paragraph is equal to 33 mS/cm while the initial conductivity is 8 mS/cm, a factor four can be distinguished.

Found literature shows the same factor four between the initial and final EC in the concentrate stream (Mondor et al., 2008). In this paper, a swine manure, consisting mainly of with ammonium, phosphorus and potassium, is treated with electrodialysis. Also other experiments show this relation, see appendix 7.3.4.

In conclusion, the final concentration, and thus the final electrical conductivity, is highly depended on the initial conductivity in the diluate stream. As discussed in paragraph 4.2.4, the difference in EC between concentrate and diluate stream on any time in electrodialysis induces an osmotic pressure over the ion exchange membranes, leading to higher volumetric flows. This transfer of water from one stream to another reaches a certain limit, with respect to the transfer of ions, leading to a stabilization of its concentration.

## 4.3 ED processes

In this paragraph the main processes occurring during the electrodialysis will be discussed, using the data gathered in the multiple-diluate run shown in paragraph 4.2. Quantifying fluxes is not the main goal of this thesis and is therefore only addressed shortly. However, proving, dividing and linking certain parameter to these fluxes is of crucial importance for the understanding of the processes in the ED stack. Moreover, their influence on the energy efficiency can be used in order to optimize the process and reduce the energy consumption.

### 4.3.1 Migration of salts

The main reason for using electrodialysis is the transfer of ions from a diluate stream, and concentrating this mass in a concentrate stream. Conducted tests shows a linear relation between the transfer of mass and the applied current. In Figure 20 this relation is already shown for the concentrate, while it is not possible to produce this trend for multiple diluate volumes. An average mass factor transfer rate of 0.44 $Wh^{-1}$ is found from the trend in this figure. However, if the first experiment is considered, see Figure 21, higher transfer rates per energy consumed can be found.

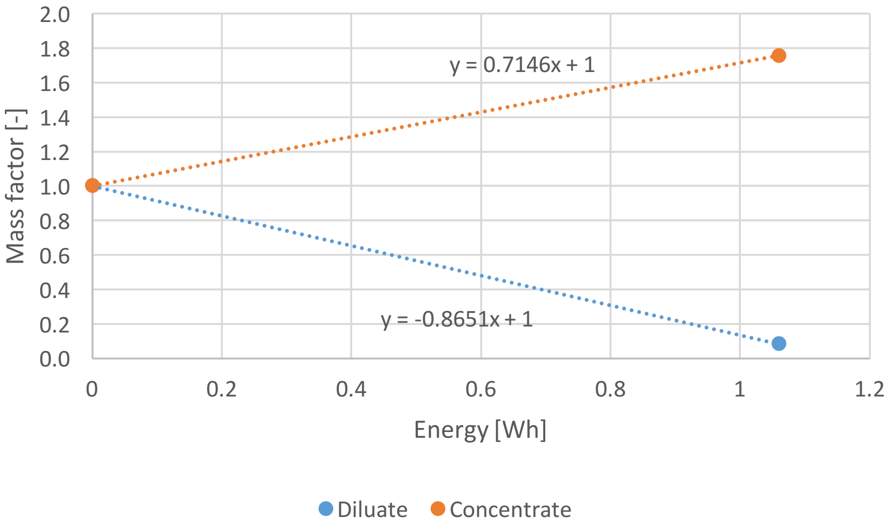


*Figure 21 – Mass transfer factor versus consumed energy for the first experiment*

Remarkable is the difference in slope between the diluate and concentrate trend line. However, the accumulation of ammonium ions in the electrode rinse solution explains the lower increase in mass compared to the decrease of the mass in the diluate stream. The values found in Figure 20 for concentrate and diluate streams are correspondingly equal to transfer rates of 1.06 and 1.26 mg $NH_4$/Wh. This is, for now, considered as the idealistic operation of concentrating ammonium with electrodialysis.

The slow decline in mass transfer per energy usage, when concentration differences between concentrate and diluate increases, is due to back migration of ions, and is discussed in paragraph 4.3.4.

### 4.3.2 Electro-osmosis

Co-migration of water molecules with ammonium and bicarbonate ions is a process that cannot be prevented and highly depended on the ion exchange membranes used in the ED stack (Gain et al., 2002). Limiting water fluxes from diluate to concentrate cells will lead to higher ammonium concentrations in the concentrate volume. The preferable minimum flow exists only of the co-migration of water molecules with salt ions.

However, detailed information from the membrane supplier should be made available and even then it would be hard to quantify the percentage of the total water flux through the membrane belonging to electro-osmotic processes. During ED operations, ammonium bicarbonate is transferred together with water molecules, but also directly creates a discontinuity between the conductivity in both cells. In paragraph 4.3.1 the transfer rate of ammonium is determined per amount of energy consumed. It is also possible to calculate the relation of ammonium transfer over time. In this case, an accurate amount of ammonium bicarbonate needs to be added in a very small temporal grid, keeping electrical conductivities equal in both streams. Two assumptions have to be made in order to quantify electro osmosis with this experiment:

- the co-migration flux is relatively small compared to the total volume, so it does not have a big influence on the volume and therefore the concentration of the concentrate volume;
- the increase in electrical conductivity is relatively small, so the electrical resistance in the cell stays equal, leading to an equal ammonium transfer rate over time.

As example a value of 10 moles water per mole ammonium bicarbonate, as found in literature, is chosen as example. It should be noted the range found in literature deviates between 2 and 13 moles water per mole ammonium bicarbonate (Lee et al., 2002; Ling et al., 2002).

As mentioned in the materials and methods chapter, the initial concentration of the diluate volume equals 1.5 g $NH_4$/L and end when the diluate stream reaches an electrical conductivity of 1 mS/cm. This corresponds with an ammonium concentration of 0.14 g $NH_4$/L and therefore a transfer out of the diluate volume of 1.36 g $NH_4$ per run. The transferred amount of ammonium bicarbonate is measured in the diluate stream, as this is the steadiest stream for measuring start and end concentrations over multiple runs.

In order to calculate the mass of water transferred, the molecular weight of ammonium and water and the density of water need to be known. As the molecular weight of water is equal to ammonium, and the ratio water transfer over ammonium transfer is 10, the weight of water transferred is equal to 13.6 grams per experiment. Assuming a water density of 1000 kg/$m^3$ for a temperature of 20 degrees and low salt concentrations, a water flux of 13.6 ml per run can be calculated. Small discrepancies due to the change in salt transferred and the decreasing amount of final diluate volume are neglected.

Electro-osmosis influences the concentration factor, and therefore also the energy efficiency. If this process would not occur, which is not very realistic to assume, the energy efficiency would be increase with respectively 0.02 and 0.06 $Wh^{-1}$ for the first and last experiment.

### 4.3.3 Osmosis

Besides the conceptual amount of water transferred by electro-osmosis, which will be equal for all experiments, also osmosis influences the water transfer. This water transfer is induced by an ion concentration gradient between the concentrate and diluate stream.

In order to investigate the transfer of water better, an electrical conductivity dissimilarity is created by adding respectively 13 and 0.2 grams of ammonium bicarbonate to half a liter of demineralized water. Corresponding conductivities of respectively 25.8 and 0.8 mS/cm for the concentrate and diluate cells are observed. Both streams where pumped through the ED cell for 18 hours resulting in a decrease in ammonium bicarbonate concentration for the concentrate cell and an increase in ammonium bicarbonate concentration for the diluate cell. The time depended electrical conductivity of these two streams are shown in Figure 22.

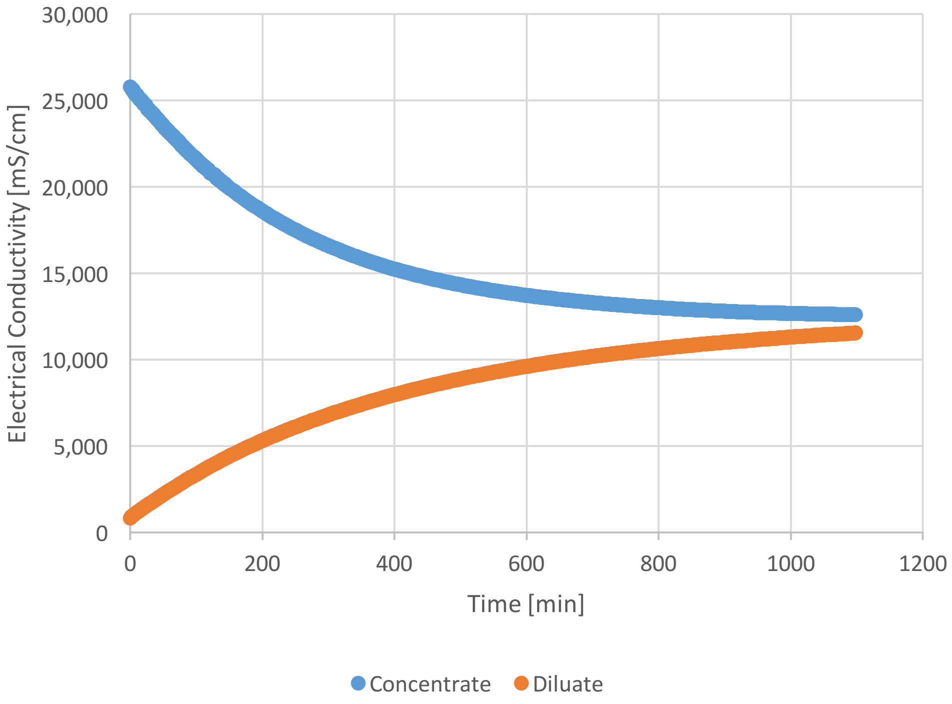


*Figure 22 – Osmosis experiment with large initial electrical conductivity difference between concentrate and diluate cells*

It can be concluded that solvent transport is an important factor in the electrodialysis its operation, as the final volumes in the concentrate and diluate cells are respectively 343 and 621 ml. In this experiment the electrode rise solution is not taken into account. Apparently, as there is conservation of volume, a flux of 36 ml transfers to the electrode rinse. However, the relation between electrical conductivity difference and water flux cannot be concluded from this figure, as beside the change of the EC also a change in volume takes place. Therefore, a verification experiment, with the same initial elements, the weight of the two jars was constantly logged. As can be seen in Figure 23, the transportation of water is linear related to the development of the electrical conductivity and thus the osmotic pressure over the membranes.

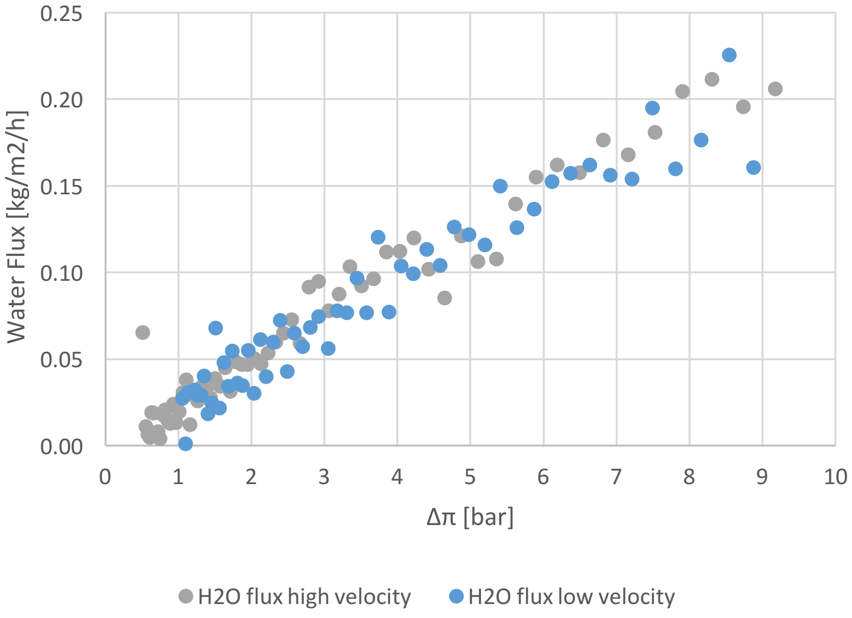


*Figure 23 – Relation between the osmotic pressure and water fluxes for the concentrate cell, with a cross-flow speed of 11.6 mm/s*

The results from this experiment are substantiated with the formula shown in paragraph 4.2.4, which shows a linear relationship between the osmotic pressure difference and the water flux through the membranes.

Moreover, the same experiment was repeated with a lower cross-flow speed of only 3.9 mm/s. When the data is compared to the data with a cross-flow speed of 11.6 mm/s, some important conclusions can be drawn. The development of electrical conductivity shows the same relation to time for both cross-flow velocities. Hence, the transport of water through the membrane show identical behavior. Therefore, it can be concluded that osmotic fluxes occur when the EC in two adjacent concentrate and diluate cells are not equal, but is not influenced by the cross-flow speed applied.

During the experiments, no electrical potential was delivered to the ED stack, however an electrical current was observed during the experiments. This indicates a flow of electrons, and therefore a flow ammonium and bicarbonate ions through the membranes. This process will be discussed in paragraph 4.3.4 Back migration of salts.

It is possible to calculate the amount of osmosis with the information from appendix 7.4.1 and a co-migration rate of 13.6 ml per run. The water transfer due to osmosis yields between 26.4 and 124.4 ml for respectively the first and last experiment. As osmosis is almost ten times bigger compared to co-migration, ED operations will be enhanced when osmosis is limited.

Osmosis influences the concentration factor negatively, and therefore the energy efficiency by respectively 0.03 and 0.65 $Wh^{-1}$ for the first and last experiment.

### 4.3.4 Back migration of salts

The last identified process is the back migration of salts from high concentration concentrate to low concentration diluate. (Lee et al., 2002) mentions the back diffusion of salts is neglected as its contribution is small compared to salt transfer. Quantifying the amount of back migrated salts, literature shows different mass transfer coefficients for different salts and used membranes (Izquierdo-Gil et al., 2012; Rottiers et al., 2014).

During the osmosis experiment described above, not only the transfer of water but also transfer of ammonium bicarbonate, from the high concentration to the low concentration cell, was noticed. In order to get a better understanding of this process, the osmosis experiment was repeated with different salts stocks. Two half liter volumes were prepared as concentrate and diluate volumes, with respectively 1 gram of sodium chloride and 9 grams of ammonium bicarbonate. Peristaltic pumps have pumped these stock solutions for 25 hours through the ED cell.

Below, in Table 5 the results of this experiment are shown. Also 208 ml of water has been transferred out of the diluate cell, while the concentrate volume only increased with 94 ml. As the final volume of the electrode rinse solution is not measured, it is hard to conclude this volume is transferred to this stream.

| Time [h] | $NH_4$ concentration concentrate [mg/L] | $NH_4$ concentration dilute [mg/L] |
|---|---|---|
| 0 | 3522 | 223 |
| 2.25 | 2478 | 357 |
| 5.5 | 1911 | 506 |
| 25.25 | 1100 | 1001 |

*Table 5 – results osmosis experiment with 2 g/L NaCl diluate and 15 g/L $NH_4HCO_3$ concentrate*

The results show a steady increase of ammonium in the diluate, while the concentration in the concentrate decreases. Correcting the final ammonium concentration for the water transfer, 535 mg/L $NH_4^+$ is already present from the start. However, this still proves ions transfer from a high concentration to a low concentration cell.

This effect can be quantified by considering the data acquired during the multiple diluate experiment. In paragraph 4.3.1 it is concluded that the migration of ammonium has a linear relation to amount of applied current. In this context, correcting for the decrease of the diluate volume, the time of one experiment should be equal for all diluate volumes. However, during the experiment the time to transfer the ammonium from the concentrate to the diluate increases. Therefore, the amount of energy required to perish the ammonium bicarbonate concentration in the diluate stream will increase, as the current is equal during one experiment.

The increase in time and energy can also be concluded from Figure 24. Here, both the electrical conductivities for the first and last experiment are shown. The twentieth diluate volume requires almost twice as much energy compared to the first run due to the increase in electrical conductivity difference.

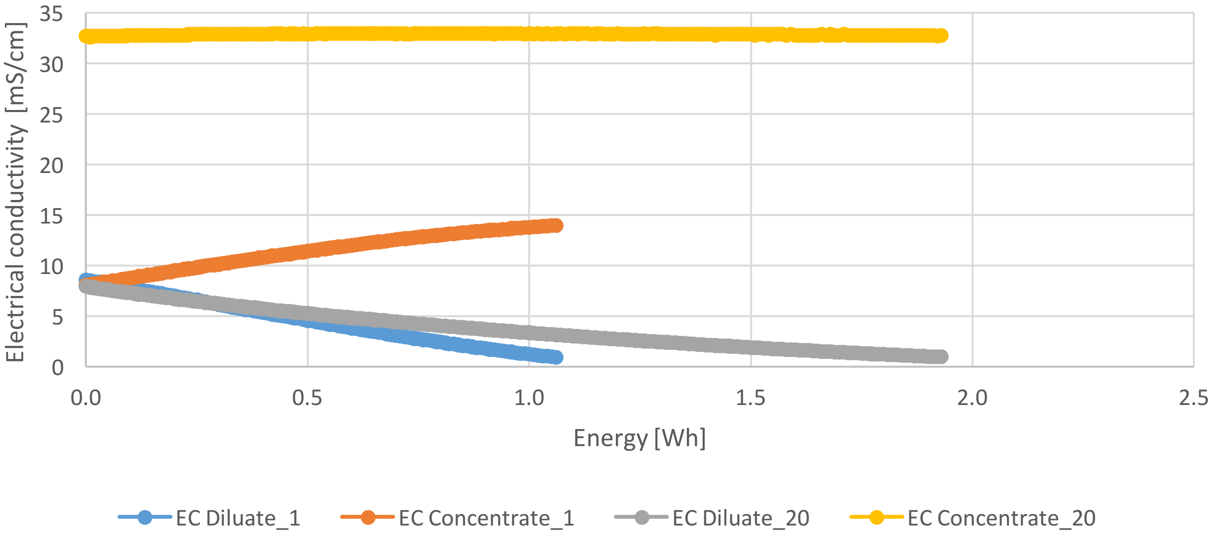


*Figure 24 – Energy comparison between experiment 1 and run 20*

The ratio between migration of ammonium bicarbonate from the diluate stream and the used amount of energy will always be constant as substantiated in the introduction of this chapter. From the first run, a transfer rate of 1.26 grams $NH_4^+$/Wh can be found, while the last run only 0.7 grams $NH_4^+$/Wh is transferred. Therefore, it can be concluded that the amount of back migration of ammonium is 0.56 grams $NH_4^+$ for the last diluate volume. Logically is the increase of back migration between every run, until the EC in the concentrate reaches a steady state. This trend is shown in Figure 25.

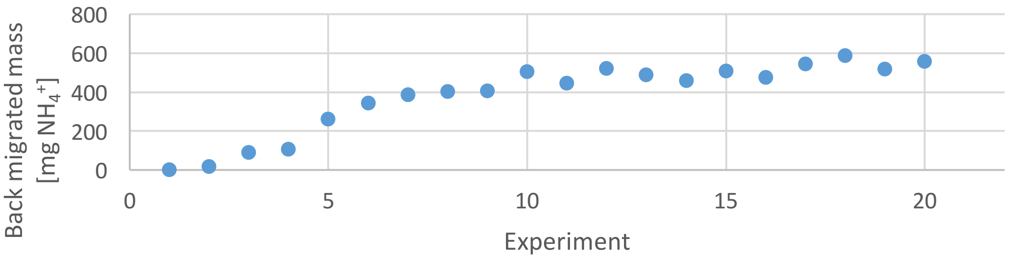


*Figure 25 – Back migration ratio of ammonium over multiple runs*

The back diffusion of ions does not influence the concentration factor, but the amount of used energy. The increase due to this process leads to a decrease in energy efficiency of 0 and 0.44 for respectively the first and last experiment.

## 4.4 Influence of other salts

All experiments conducted so far had idealistic initial parameters, as the volumes treated only consisted of demineralized water and ammonium bicarbonate. The treatment of real reject water from digested sludge also contains other ions, as shown in Table 1. A distinction can be made between monovalent and multivalent ions.

For these experiments monovalent selective exchange membranes are used. As these membranes have different electrical resistances, as shown in Table 2, it is not possible to compare results from this paragraph with data gathered during experiments with normal ion exchange membranes.

### 4.4.1 Monovalent ions

In the composition of reject water, ammonium is the most important (monovalent-) ion. Hence, reject water is fresh, and therefore contains a low amount of ions. In Table 6 the results of these experiments are shown.

| Experiment | Energy used [Wh] | CF [-] | Energy Efficiency [$Wh^{-1}$] |
|---|---|---|---|
| **Blanco** | 0.85 ± 0.01 | 1.63 ± 0.01 | 1.92 ± 0.01 |
| **Low concentration** | 0.85 ± 0.01 | 1.52 ± 0.00 | 1.77 ± 0.01 |
| **High concentration** | 1.00 ± 0.00 | 1.57 ± 0.01 | 1.57 ± 0.01 |

*Table 6 – relation energy consumption and concentration factor for additional monovalent salts*

It should be noted that the values shown in Table 6 are averages from three identical experiments, and a small difference in concentration factors between multiple experiments occurs. The experiments are ended when the diluate volume reaches an electrical conductivity of 1 mS/cm, however, the EC is not only determined by the concentration of ammonium bicarbonate, but also sodium bicarbonate. Therefore, the chance of transferring a sodium ion through the membrane increases when its concentration increases. This leads to lower transport of ammonium and therefore a lower concentration factor.

However, comparing the concentration factor of the high concentration and the low concentration experiment, this does not occur. The concentration factor of ammonium in the concentrate stream is bigger for higher concentrations of sodium. However, the addition of higher concentrations sodium also leads to a higher EC in the diluate volume, and therefore a lower electrical resistance in the passage of current in the ED stack. Summarized, the operation of electrodialysis takes longer as the initial electrical conductivity value is higher. Comparing all experiments over a fixed interval shows an equal consumption of energy (0.85 – 0.65 Wh).

However, it can be concluded from this data that the influence of other monovalent salts is negative on the performance of electrodialysis for concentrating ammonium ions. Presumably due to the current that is used to transfer sodium through the membranes. Higher concentrations of sodium lead to lower concentration factors per energy consumed. Finally, a linear increase in concentration factor over energy consumption is expected, as shown in Figure 20.

### 4.4.2 Bivalent ions

Besides monovalent ions, also multivalent ions are present in the reject water. As multivalent ions are rejected by monovalent selective membranes, the concentration of these ions stays equal in the diluate stream. Hence, this leads to a relative higher electrical conductivity and thus a lower resistance.

The influence of these salts on the energy consumption is again tested by adding high and low concentrations. The results are shown in Table 7.

| Experiment | Energy used [Wh] | CF [-] | Energy Efficiency [$Wh^{-1}$] |
|---|---|---|---|
| **Blanco** | 0.96 ± 0.02 | 1.48 ± 0.01 | 1.54 ± 0.01 |
| **Low concentration** | 1.01 ± 0.01 | 1.57 ± 0.01 | 1.55 ± 0.02 |
| **High concentration** | 1.03 ± 0.00 | 1.64 ± 0.00 | 1.59 ± 0.00 |

*Table 7 – Relation energy consumption and concentration factor for additional multivalent salts*

Only small deviations in energy efficiency can be observed, ranging from 1.54 to 1.59 $Wh^{-1}$. Due to the same factors as mentioned in the monovalent ions section, and the small deviations of the dataset, no clear conclusion can be drawn. An increase in energy efficiency was expected as higher multivalent salts concentrations were present in the diluate volume. Multivalent ions enhance the electrical conductivity of the electrolytes greatly, and should therefore have a positive effect when contained in the diluate volume. Understanding how this process can be optimized, the selectivity of its membranes should be investigated.

### 4.4.3 Selectivity of monovalent ion exchange membranes

The goal of using monovalent selective ion exchange membranes is the separation of monovalent and bivalent ions from each other. This thesis focusses on the concentration of ammonium, where no limits are set for ion concentrations. As it is determined in paragraphs 4.3.1 and 4.4.1, the migration of ammonium is linear related to the applied current, while the presence of other ions decreases the energy efficiency of electrodialysis. Therefore, it is beneficial to use membranes only selective for ammonium. As these membranes are not yet available, monovalent selective ion exchange membranes are used. However, the selectivity of these membranes has to be determined to justify the use of these membranes.

The experiments conducted with bivalent magnesium sulfate (paragraph 4.4.2) are used to determine this selectivity. Samples are taken before and after operation of the ED stack from concentrate, diluate and electrode rinse volumes and analyzed with Ion Chromatography (IC).

The following conclusions can be drawn if considering only calcium ions.

i. There are big deviations in the mass balance for calcium. However, preservation of ammonium and other ions occurs.
ii. The decrease of calcium concentration in the diluate cell ranges between 57% and 75% compared to initial concentrations.
iii. The increase of calcium in the concentrate volume ranges between 5% and 10% compared to initial concentrations.
iv. The amount of calcium ions in the electrolyte is increased significantly. However, no trend can be found in the amount of transferred calcium. Concentration increases with a range of 20 and 50 mg/L.

The transfer of calcium through the non-monovalent selective cation end exchange membranes (CEEM) to the electrode rinse volume removes all benefits assumed above. This is probably the reason the energy efficiency did not increase more for higher calcium sulfate concentrations. Moreover, the incontinuity of mass preservation is rather particular, and cannot be explained easily. It could be assumed the calcium precipitates with bicarbonates left on the exchange membranes of former experiments. However, no visual proof of that was found on the membranes.

## 4.5 Optimization electrodialysis process

The tests performed during this thesis shown three factors influencing the energy efficiency of electrodialysis negatively. The transport of water through the membranes between concentrate and diluate stream leads to lower concentrations in the concentrate stream. This transport of solvent can be divided into co-migration of water and osmosis. The latter is induced by concentration differences between the two streams. Moreover, this difference also leads to an electrical potential gradient and therefore the back diffusion of ions from high to low concentrate solution. Lastly, ammonium ions accumulate in the electrode rinse stream, retain them from entering the concentrate stream. This paragraph will discuss these problems and two possible solutions.

### 4.5.1 Staging

Concentration differences between two adjacent cells, concentrate and diluate flow, leads to several negative effects considering the energy efficiency of electrodialysis. This difference increases due to an increase in concentrate concentration while the initial diluate concentration stays equal. In a staged operational scheme, concentration differences are minimized.

### 4.5.2 Experimental procedure

This scheme is shown below in Figure 26. In this figure only the first three steps of the staged layout are shown, while the experiment is conducted with 7 stages.

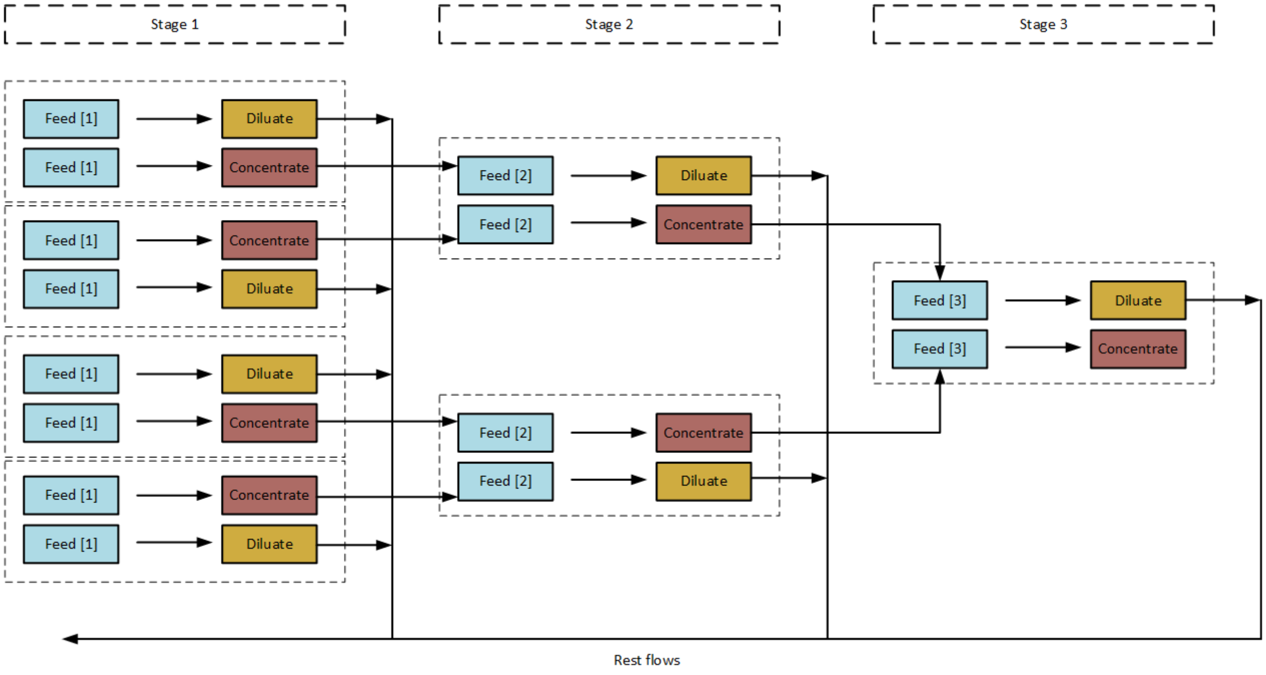


*Figure 26 – The first three steps of a staged ED operation*

The initial condition of the diluate and concentrate volumes of the first step are equal to all other performed experiments, as discussed in paragraph 3.2.2. In order to investigate the operational parameters of electrodialysis, final conditions are set to always transport the same amount of ammonium mass from the diluate to concentrate and electrode rinse volumes.

It would be beneficial if the ammonium concentration in the diluate of the second step had the same concentration as the initial concentrate/diluate concentration of the first step. In this way, it would be easier to compare this system to the multiple diluate experiment, as a fixed amount of concentrate and diluate would be produced. However, due to the transfer of ammonium bicarbonate to the electrode rinse, and a contrary flux of sodium nitrate to the concentrate flow, the increase of the ammonium concentration in the concentrate reduces. Therefore, a lower total amount of ammonium is transferred out the diluate volume. As a flux of water, due to co-migration of water molecules with the ammonium bicarbonate, is expected from low to high concentration cells, it also not possible to stop at a fixed EC value. In this matter, more mass will be transferred when the solution consists of more volume.

The final ammonium concentration can be determined using the data gathered in paragraph 4.3.1. As the ammonium concentration cannot be known at every time, this value is converted to an EC value, using the relation shown in paragraph 7.3.2. It must be noted that due to (electro-) osmosis also water is being transferred, influencing the EC and total mass in the concentrate volume. A substantiated assumption of the water transport, according to previous experiments, is made to be 25 ml. In this way, the final electrical conductivity can be approximated. Small deviations in ammonium mass transfer can occur due to the presence of sodium ions in the concentrate flow, which have a different influence on the EC as ammonium ions.

Ammonium concentrations in all streams are measured before and after the experiment is operated. The diluate volume is corrected for the water transport in the previous experiment, ensuring a volume ratio between concentrate and diluate of one.

### 4.5.3 Preliminary results

The energy requirement for the staged concentration of ammonium is shown in Figure 27. A straight line can be observed for the ammonium concentration in the concentrate, while Figure 16 shows a clear smoothing. If the data is studied, a clear decrease in electrical potential can be observed over multiple experiments, ranging from 3.61 W for the first experiment to 2.53 W for the last experiment. Also, operation times of the experiments show a decrease for higher ammonium concentrations. The migration rate, as determined in paragraph 4.3.1 are therefore underestimated and have maximum values for these experiments equal to 1.32 and 2.31 mg $NH_4^+$/W for respectively concentrate and diluate ammonium migration. The migration of ammonium to the electrode rinse flow has the same linear trend to time and energy compared to the multiple diluate experiment. However, the accumulation rate of ammonium in this stream is for this experiment 2.5 times as high.

All parameters indicate a higher energy efficiency compared to the multiple diluate experiments. Energy efficiencies of 0.15 and 1.21 $Wh^{-1}$ can be determined for respectively the multiple diluate experiment and the staged experiment. However, only the concentration factor is taken into account in this efficiency, the produced diluate and concentrate volumes are neglected.

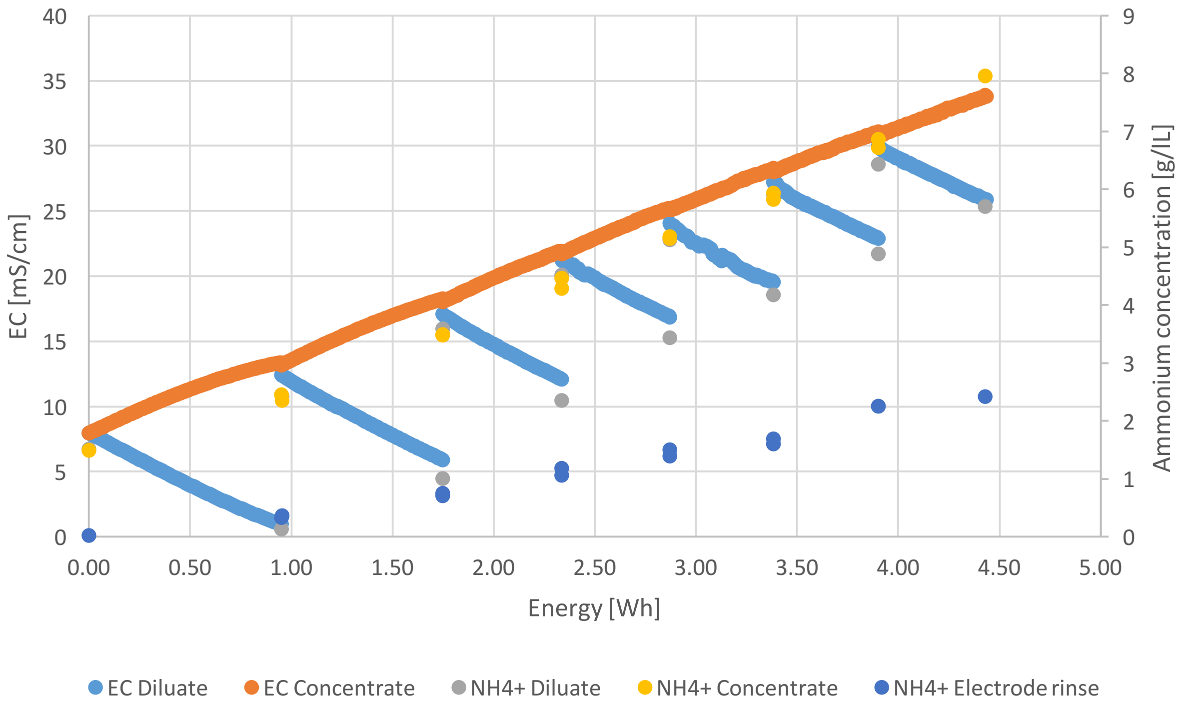


*Figure 27 – Energy requirements for staged concentration of ammonium*

If these volumes are taken into account, two possible comparison scenarios can be considered. In the first scenario, the energy consumption of treating the diluate streams shown in Figure 27 is estimated. The multiple diluate experiment produces, from an initial volume of 22.83 liters, 19.06 liter diluate and 2.83 liters concentrate and needs 32.10 Wh. With a same amount of influent, 20.83 liters of diluate is produced and 2 liter of concentrate with an energy consumption of 33.26 Wh. In this comparison, not only less concentrate volume is produced, also its energy requirement is higher.

As the production of clean diluate volumes is not the focus of this thesis, also a second comparison can be made. In this case, we take the point in the multiple dilute experiment where the ammonium concentration in the concentrate does not increase further. An energy consumption of 20.79 Wh is needed to produce 2.17 liter of concentrate and 13.85 liter of diluate from an influent volume of 16.02 liters. The same amount of influent, when treated in stages, only needs 11.56 Wh for the production of 0.125 liter concentrate, 8.01 liter diluate and almost 8 liter of volumes with different ammonium concentrations.

It can therefore be concluded that concentrating streams in stages is only beneficial if the production of "clean" water streams is not the main goal, and also the volumes of the concentrate can be neglected. Only when the concentration ratio over energy consumption is considered, this set-up is more beneficial compared to normal operation.

Due to the reduction of ion concentration gradient, the above discussed processes will also reduce. The possible energy efficiencies increase will be 0.04, 0.11 and 0.04 $Wh^{-1}$ for respectively the influence of electrode rinse leakage, osmosis and electro osmosis for the last experiment of the staged experiment.

### 4.5.4 volume ratios

In paragraph 4.2.5 the volume displacements in the diluate stream are examined. An important conclusion from this section suggests the temporal influence of osmotic fluxes on the energy efficiency. Lowering operation times by Increasing the current density is not investigated as this will also lead to a decrease in energy efficiency due to the lower utilization of the potential. Decreasing the operation time can also be achieved by applying volume ratios.

### 4.5.5 Preliminary results

Literature showed a decrease of used energy, for an increase for relative diluate volume versus concentrate volume. As already encountered, a higher diluate volume leads to more ions in the limiting solution, a slower decrease of the electrical conductivity in this stream and therefore a lower electrical resistance. However, on the other hand, a smaller concentrate volume leads to a quicker increase of ion concentration, electrical conductivity and concentration gradient between concentrate and diluate streams. This results in a bigger flux of solvent from low to high concentration cells.

Experiments have been conducted with different volume ratios for different membrane types. In order to compare the test results with the multiple diluate experiment, only the standard anion – cation membranes are described here. Due to practical limitations, concentrate volumes cannot be smaller than 0.10 liter. As twenty diluate volumes are used in the multiple diluate experiment, the volume ratio of 20 would be interesting. Therefore, the total diluate volume for the experiments discussed in this paragraph will consists of 2 liter. In Figure 28 the relation between electrical conductivity over the consumed energy is shown for multiple volume ratios.

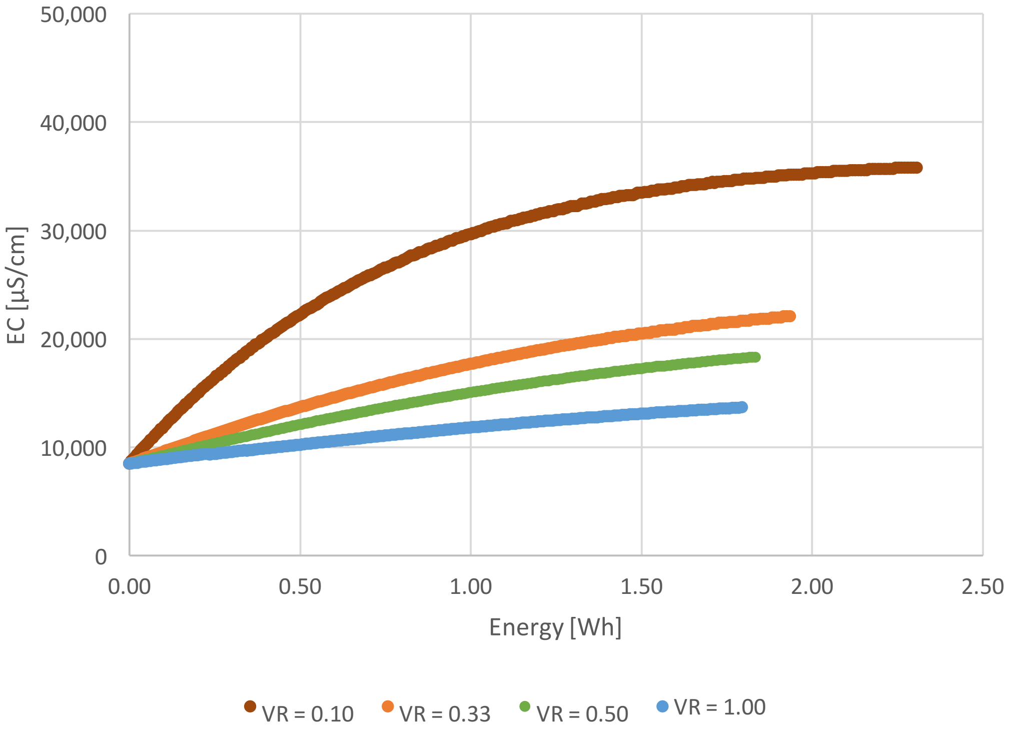


*Figure 28 - Electrical conductivity progression versus the used amount of energy for different volume ratios, with a diluate volume of 2 liter and STA-STK membranes*

In this graph volume ratios between 0.1 to 1.0 are examined, with a diluate volume of 2 liter. Evident to the decrease of time is the increase of electrical conductivity over the amount of energy used. If all volume ratio experiments are considered at the same energy consumption, it can be seen a smaller concentrate volume leads to a higher electrical conductivity. Hence, the ammonium concentration, as we assume the electrical conductivity is mainly influenced by the ammonium bicarbonate concentration. The 0.10 volume ratio experiment shows the same trend as the multiple diluate experiment in Figure 16.

In order to reach the same electrical conductivity for both tests, the 0.10 volume ratio experiment requires 1.36 Wh, while the multiple diluate experiment needs 32.1 Wh. However, the produced concentrate volume only consists of 0.38 liter, while the multiple diluate experiments produces 2.83 liter. Correcting the energy consumption for an equal amount of produced concentrate leads to a consumption of 10.1 Wh. Moreover, a 0.05 volume ratio experiment is conducted with monovalent membranes, which are newer but have a higher electric resistance. Experiments with these membranes have a lower energy consumption compared to the standard anion – cation membranes. The 0.05 volume ratio experiment consumes 0.46 Wh in order to reach the same electrical conductivity, and 7.7 Wh if corrected for the produced concentrate volume.

Moreover, from the 0.1 volume ratio in Figure 28 (and also the 0.05 volume ratio with MVM membranes) higher electrical conductivities are achieved compared to the multiple diluate experiment. Electrical conductivities of 42 mS/cm are achieved for a volume ratio of 0.05.

Within the volume ratio 0.05 experiment, for a same electrical conductivity as reached in the multiple diluate experiment, an energy efficiency of 10.00 $Wh^{-1}$ is reached. This is mainly due to the lower amount of salts transported through the ion exchange membranes.

As already discussed above, and shown in Figure 28, is the increase in energy efficiency when decreasing the concentrate volume. These values are shown in Figure 29.

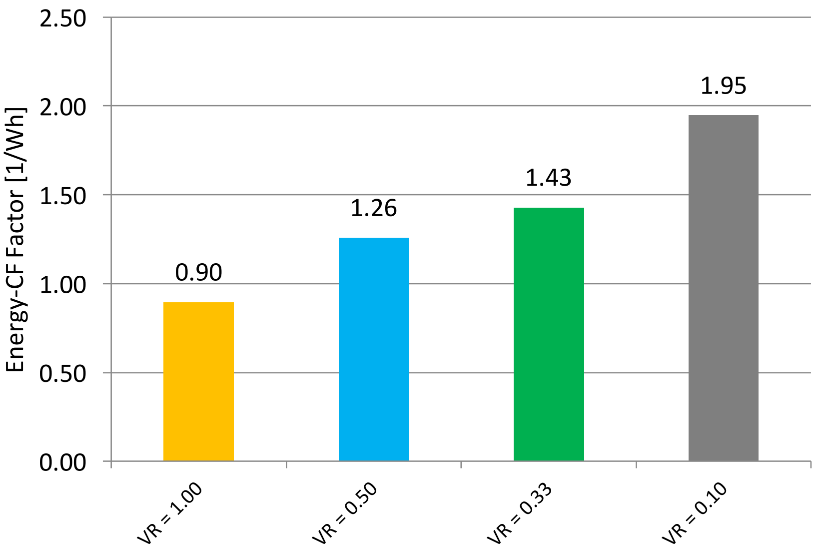


*Figure 29 - Energy efficiencies for multiple volume ratios, with a total diluate volume of 1 liter*

However, the migration of ammonium mass per consumed energy over the ion exchange membranes decreases for decreasing volume ratios. These results are shown in Figure 30. Comparable to the multiple diluate experiment, a maximum electrical conductivity is expected, leading to an optimum utilization of energy for the concentration of ammonium. Decreasing concentrate volumes further will lead to more osmosis, no increase in maximum ammonium concentrations and therefore lower energy efficiencies. This optimum is not yet reached for the volume ratios between 1.0 and 0.05.

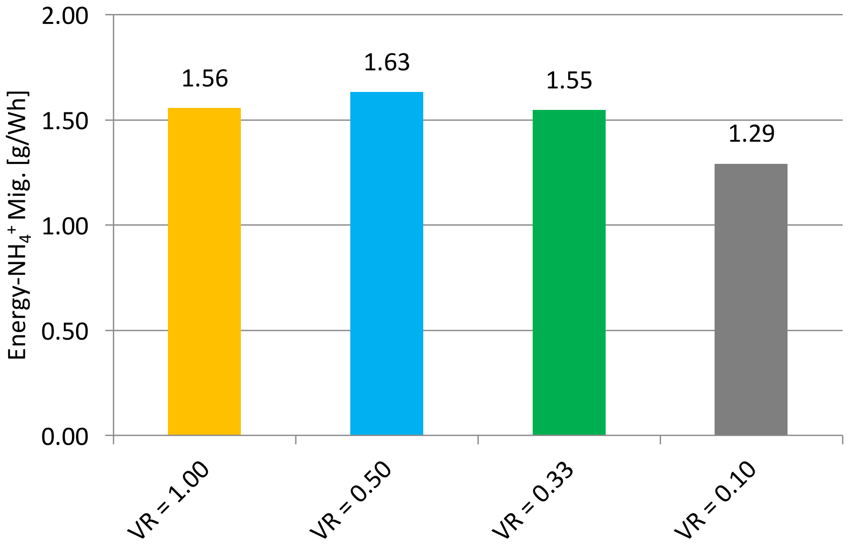


*Figure 30 – Ammonium mass transfer over energy consumption for multiple volume ratios, with a total diluate volume of 2 liter and STA – STK membranes*

Lastly, experiments with the same volume ratio but a different diluate volume, respectively 1.0 and 2.0 liter, are compared. The following conclusion can be drawn:

i. Lower values for the energy efficiency can be found for tests performed with 2 liter diluate volume. Correcting these values for a double ammonium transport leads to smaller decreases in energy efficiency.
ii. There is more ammonium transport per amount of consumed energy for test performed with the 2 liter diluate volume.

It is more efficient to use small volume ratios while keeping the total feed volume, and thus the electrical conductivity, high when operating electrodialysis for the concentrating of streams.

# 5 Conclusions

In this chapter the sub-questions are used to answer the research question.

1. *Is there a conceptual difference between current- and energy efficiency?*

Yes, as already found in literature, current efficiency measures the operation efficiency of an electrochemical process by considering the share of electrons that is usefully used. However, the used electrical current and operation times are neglected. Energy efficiency is often used for the combustion of energy carriers, or relates to the share of electrical energy usefully used. In this thesis, the performance of electrodialysis is measured by dividing the useful energy, for concentrating ammonium ions in the concentrate stream, by the total used energy.

Experiments conducted with different cross-flow speeds and electrical currents show, as tests are performed with only ammonium bicarbonate and are operated below limiting current density, current efficiency values in the same range. However, these experiments also show the utilization of current is not a good standard for testing energy efficiency.

2. *What is the maximum achievable ammonium concentration, using digested sludge reject water with an ammonium influent concentration of 1.5 g/L?*

The maximum achieved ammonium concentration was determined by performing a multiple diluate experiment with 20 diluate volumes. The final ammonium concentration seemed to reach a maximum concentration after 14 experiments. In the last experiments ammonium was still transferred from the diluate to the concentrate stream. Due to the equal direction of the solvent transport, the concentration did not increase further. This ammonium concentration is equal to 7.3 g/L. Literature found on the final ammonium concentration when treated with electrodialysis is equal to 16 g/L. Found literature and experiments with other salts in other concentration ranges show a clear relation between initial and final electrical conductivity values. The interrupting processes, (co-) migration of water and back diffusion of ions, are mainly influenced by the ion concentration gradient between concentrate and diluate stream and therefore limits the maximum ammonium concentration. This ratio between initial and final electrical conductivities is found to be a factor 4.

3. *To which extent is the energy efficiency influenced by back diffusion of ions?*

The diffusion of ammonium bicarbonate ions from high to low concentration influences the energy consumption to transfer ions, but does not influence the maximum ammonium concentration. The performance of back diffusion of ions is tested in an osmosis experiment and quantified with the data of the multiple diluate run. As the back diffusion of ions is induced by the ion concentration gradient between concentrate and diluate stream, its influence on the consumed energy increases for more experiments during the multiple diluate experiment. Assumed is the back diffusion of ions in the first experiment to be zero, so back diffusion rates for experiment two and twenty are respectively equal to 0.018 and 0.557 g $NH_4^+$/L. If back diffusion could be prevented, ammonium concentrations in the concentrate will be between 1.3% and 40% higher. As the energy consumption is equal, also the energy efficiency will increase.

4. *To which extent is the energy efficiency influenced by (electro-) osmosis?*

This stabilization of ammonium concentration in the concentrate stream is largely influenced by the transfer of solvent. This transfer can be sub-divided in osmosis and electro-osmosis. Electro-osmosis can only be calculated theoretically as the amount of molecules water per ammonium or bicarbonate ions cannot be determined experimentally. This water flux through the ion exchange membranes is induced by the transfer of ions and therefore only influenced by the current density applied in the electrodialysis process. Total solvent differences can be measured in order to determine the osmosis water flux, which is related to the osmotic pressure differences between concentrate and diluate stream. Solvent transfer due to osmosis is ten times larger compared to electro-osmosis. The osmotic volume transferred is influenced by the time of an experiment and can therefore be minimalized by applying a higher current densities or lower concentrate to diluate ratios. The application of hydrophobic membranes reduces solvent flux and therefore has a high potential for increasing the energy efficiency.

5. *Do residual streams with mono- and bivalent salts have a positive or negative influence on the energy efficiency?*

The addition of sodium bicarbonate has a negative effect on the effect on the energy consumption for concentrating ammonium bicarbonate. As the concentration of sodium bicarbonate increases, the energy efficiency decreases.

The experiments conducted with bivalent salts (magnesium sulfate) show no clear relation between the concentrations of bivalent salts and the energy efficiency. However, the selectivity of the end membranes influences this result, as these membranes are not monovalent selective and therefore allow magnesium sulfate to transfer into the electrode rinse solution.

6. *Can the performance of electrodialysis be increased by staging or applying different volume ratios?*

It is hard to compare results from staging experiments with the multi diluate experiment, as multiple residual streams with different ammonium concentrations are produced during staged operations. As this thesis considers the energy efficiency, concentrations and consumed energy are more important than the total concentrate and diluate volume produced. Figure 31 shows the relation between ammonium concentration in concentrate-, diluate- and electrode rinse stream and the used energy for both the multi diluate experiment (shown in this figure as MDE) and the staged experiment. From this figure it can clearly be concluded, less energy is needed for reaching the 7.3 g/L ammonium concentration. Moreover, as no flattening can be seen for the staged experiment, combined with the conclusion the maximum ammonium concentration is very dependent on the initial concentration, higher ammonium concentrations can be reached using the staged set-up. Moreover, resistance decreases when ion concentrations in the diluate increase.

Additional is the transport of ammonium to the electro rinse solution, which is higher for the staging experiment.

Volume ratios occur during experiments due to the transfer of solvent from diluate to concentrate stream. However, also man-induced volume ratios can be applied, in order to optimize the energy efficiency. Using lower volume ratios, were the concentrate volume is smaller compared to the diluate volume, lead to a quicker increase in concentration factor and therefore a higher energy efficiency. However, an optimum volume ratio can be found as the transfer of ammonium bicarbonate from diluate to concentrate stream needs more energy when volume ratios decrease.

Moreover, an increase of the total feed volume also influences the efficiency of electrodialysis positive. Summarized, a small volume ratio in combination with a high feed volume, is most beneficial for the energy efficiency.

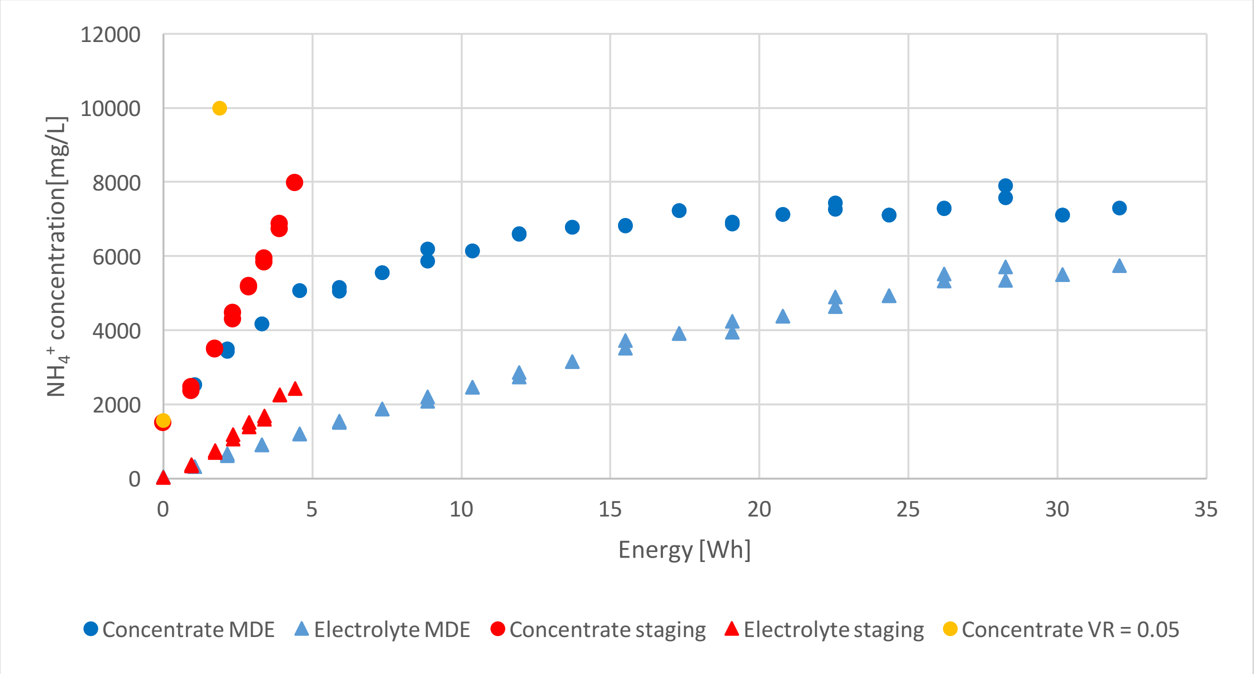


*Figure 31 – Energy efficiencies for multi diluate experiments and staging experiments*

The research question, which were drafted in the introduction, can be answered when al conclusions of sub-questions are taken into account. These results are summarized in Table 8 below.

| | | First experiment | Multiple diluate experiment | Staging | Volume ratio = 0.05 |
|---|---|---|---|---|---|
| CF | [-] | 1.71 | 1.03 | 1.16 | 4.60 |
| Energy | [Wh] | 1.06 | 1.93 | 0.54 | 0.46 |
| EE | [$Wh^{-1}$] | 1.61 | 0.53 | 2.15 | 10.00 |
| **Possible increase in EE when neglecting processes (shown below)** | **[$Wh^{-1}$]** | **0.22** | **1.16** | **0.19** | **7.10** |
| Electrode rinse leakage | [$Wh^{-1}$] | 0.17 | 0.02 | 0.04 | x |
| Back diffusion of ions | [$Wh^{-1}$] | 0 | 0.44 | x | x |
| Osmosis | [$Wh^{-1}$] | 0.03 | 0.65 | 0.11 | x |
| Electro osmosis | [$Wh^{-1}$] | 0.02 | 0.06 | 0.04 | x |

*Table 8 – Electrodialysis processes and its influence on the energy efficiency*

The energy efficiency in the multiple diluate experiment decreases mainly due to osmosis and back diffusion of ions. In the staging experiment these factors are reduced, leading to a lower possible increase in energy efficiency. Moreover, applying a volume ratio has the highest energy efficiency as its concentration factor is highest. However, due to a quick increase in ammonium concentration in the concentrate stream, the possible increase in energy efficiency is over a factor of 4. The potential of combining staging and volume ratios is therefore high.

The goal of this thesis is defined as:

*How can the maximum ammonium concentration from residual stream be optimized, utilizing energy as efficient as possible for the concentration of ammonium in an electrodialysis setup?*

- The maximum ammonium concentration is influenced by the initial feed concentration.
- The presence of other (monovalent-) ions in the residual stream lead to a less energy efficient transfer of ammonium.
- Small volume ratios, combined with a high feed volume, can be used to increase the utilization of energy for the concentration of ammonium.
- Staging is a possible alternative to achieve higher maximum ammonium concentrations and reduce limiting factors, leading to higher energy efficiencies.

# 6 Recommendations

## 6.1 Electrode rinse composition

During all experiments an accumulation of ammonium ions was noticed in the sodium nitrate electrode rinse solution. Ammonium is transferred from a diluate cell through the CEEM and recirculated to the other side of the ED stack, where it is once again transferred through a CEEM into the concentrate flow. As the concentration of sodium ions is higher in the electrode rinse solution compared to the ammonium ions, while the charge and masses of these molecules are nearly equal, the chance is higher a sodium ion is transferred through the CEEM. In this context, a salt with ammonium as cation would be more suitable for this application.

### 6.1.1 Possible alternatives

If the sodium nitrate solution was to be replaced by an ammonium holding solution, an applicable counter anion should be chosen. Besides a high solubility of this salt in water, also other factors like explosion danger ($NH_4NO_3$) and gas forming ($NH_4Cl$) should be prevented. Moreover, as it is possible for mono- and bivalent ions to move to the electrode rinse solution, also precipitate products should be taken into account. Concentrate and diluate feed solutions contain calcium and magnesium ions, which can easily exceed the solubility product if sulfate ($(NH_4)_2SO_4$) or phosphates ($(NH_4)_3PO_4$) are present. As the influent mostly consists of ammonium bicarbonate, this would be an obvious suitable replacement for the current electrode rinse solution. Other salts, which are present in the diluate/concentrate flow and therefore also in the electrode rinse solution, have a relative low concentration compared to the ammonium bicarbonate. Therefore, the chance is very high an ammonium ion is transferred from the electrode rinse, back into the concentrate flow. Over time, concentrations of potassium and sodium will increase, requiring a replacement of the electrode rinse volume.

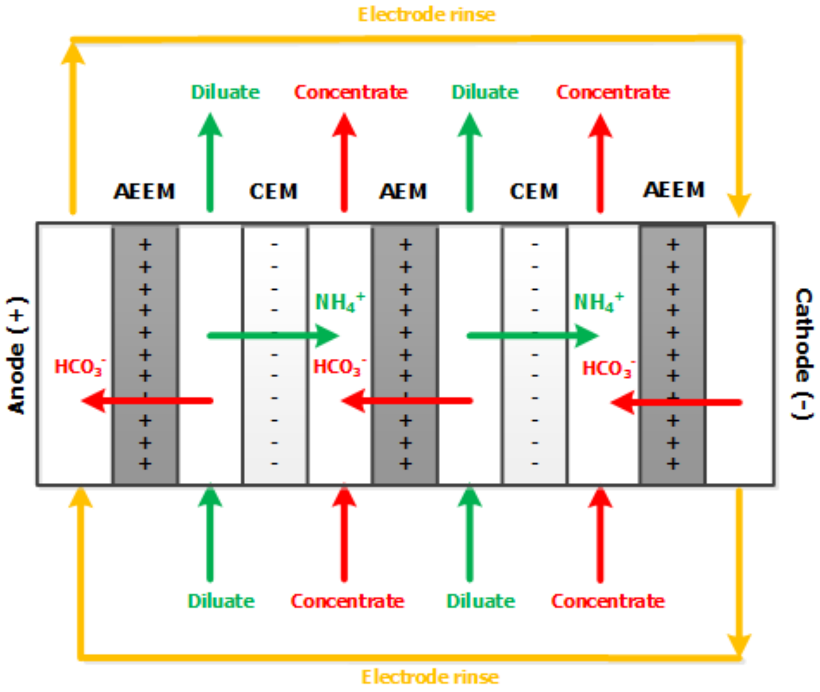


*Figure 32 – Processes in a ED stack with anion exchange end membranes (AEEM)*

Another possible alternative is not focused on the change of electrode rinse solution, but to the sequence of membranes in the stack. For the experiments conducted above, cation exchange end membranes (CEEM) are used, making it possible for cations to pass into the electrode rinse solution. If these membranes were to be replaced with anion exchange end membranes (AEEM), all cations would be retained in the solution. This can be compared to the exchange of nitrate from the electrode rinse stock solution to the concentrate cell, for the multiple diluate experiment. After an operation time of 78 hours, 0.62 grams of nitrate are found in the concentrate flow. The initial concentration of nitrate in the electrode rinse flow equals 62 grams of nitrate.

Moreover, the accumulation of ions in the electrode rinse solution is never preferred, as this to washing out the electrode rinse solution and therefore leads to higher chemical costs. In combination with the AEEMs, sulfonate groups can be applied as they have a molecular composition that makes them very unlikely to be transferred through the exchange membranes. The big disadvantage of these groups is the high investment costs for the purchase of the chemical.

## 6.2 Scaling to full plant level

When scaling a laboratory experiment to a full plant level, also operation parameters should be taken into account. Within this context, mainly the membranes are a point of interest.

In the introduction it was already stated, this thesis only focusses on the electrical energy utilization, and not on financial aspects. However, literature shows the biggest disadvantage of using electrodialysis, is the price of the membranes. As membrane prices are decreasing last years, ED starts to become a better treatment technique than, for example reverse osmosis.

With the used current density in this thesis the energy efficiency is high, while operation times are relatively long. Increasing the current density also increases the mass transfer of ammonium ions through the ion exchange membranes per time, and therefore shortens the operation time. In conclusion, higher current densities require less membrane surface. A consideration between investment costs for the membrane, lifespan of these membranes and electrical requirement by induced electrical potential difference should be further researched.

Moreover, during laboratorial experiments membranes with an effective surface of 0.08 by 0.08 $m^2$ are used. In a full-scale setup, the cross-flow distance will be larger, leading to a significant concentration difference between in- and outlet of the concentrate and diluate stream. In co-current flow, both concentrate and diluate flow in the same direction along the membranes, the concentration difference between both streams increases linear with the traveled distance. The potential of using counter-current flow, concentrate and diluate flow in opposite direction along the membranes, should be investigated. It is likely counter-current operations lead to smaller water fluxes, as concentration differences are oppressed.

## 6.3 Discharging the diluate

Depended on the used stack, ammonium concentrations in the diluate effluent range between 80 and 140 mg/L. However, these flows cannot be discharged in natural water bodies due to an ammonium discharge regulation set by the European framework directive (EFD) of 2.2 mg N/l (corresponding to 2.83 mg $NH_4^+$/l). As the relation between electrical conductivity and ammonium concentration is inaccurate for low ammonium concentrations, as the influence of other salts present in the solution have a high influence on the conductivity, it is hard to convert the concentration to a corresponding EC. If the regular relation is used, as shown in 7.3.2, an EC value of 20 µS/cm can be calculated.

Electrodialysis is known not to be the most suitable technique for treating low conductivity flows, due to high electrical resistance in the ED stack. This can also be seen from Figure 33, where the slope of the EC versus energy relation declines greatly. The energy needed to decrease the ammonium concentration in the diluate from 1500 g/L to 140 g/L is approximately 0.96 Wh, while a further decrease to 3 mg/L requires another 0.64 Wh. It should be noted that this process can be optimized by using stages, which will also lead to a higher volume of diluate produced.

However, the potential of treating these low conductive flows with other techniques should be investigated. In this matter, energy efficiencies of reverse osmosis or ion exchange should also be taken into equation.

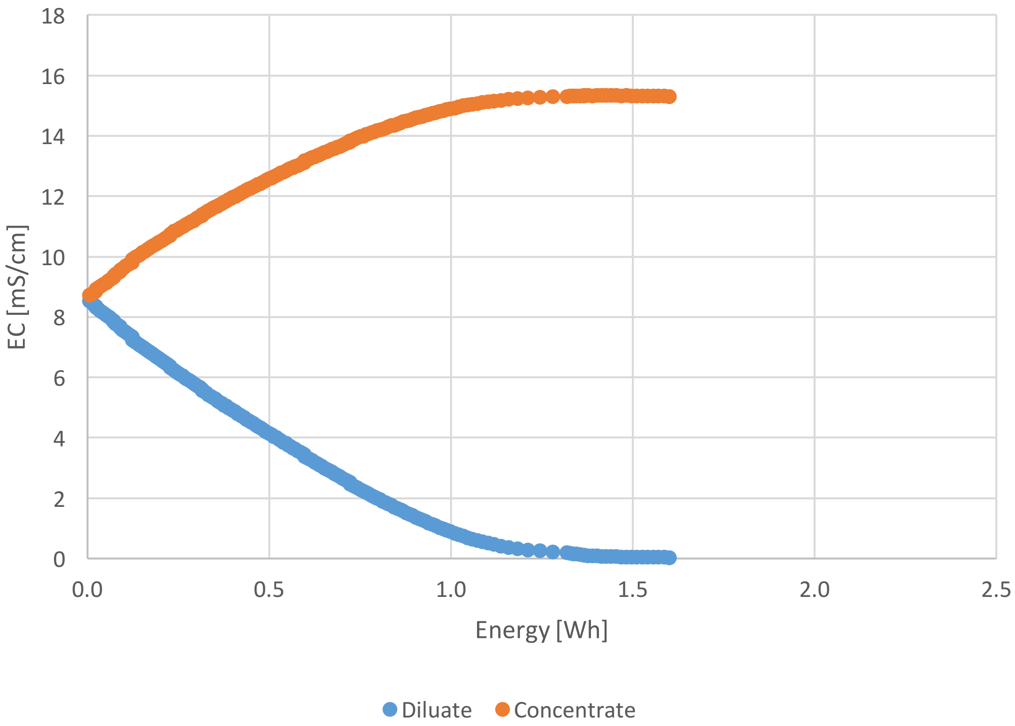


*Figure 33 – Relation EC versus energy for producing dischargeable diluate*

## 6.4 Bipolar membranes

Within the boundaries of the N2kWh project, the potential of bipolar membranes (BPM) should be investigated. Bipolar membranes consist of two ion exchange membranes (used in regular ED operations) so that one surface is an anion exchange layer, and the opposite surface is a cation exchange layer. These exchange layers are packed very closely together, making it able to split water molecules into protons and hydroxyl ions (F.G. Wilhelm, 2001; Y. Tanaka, 2015). New developments resulted in a three layered structure, where the cation- and anion exchange membrane are transition layer containing a weak acid or base catalyst.

In the operations of an ED stack with normal or monovalent membranes three streams can be distinguished, namely the concentrate, diluate and electrode rinse solution. Operating an electrodialysis cell with BPMs has four flows, namely the feed salt solution, a base stream, an acid stream and the electrode rinse solution. The layout of such an ED cell is shown in Figure 34.

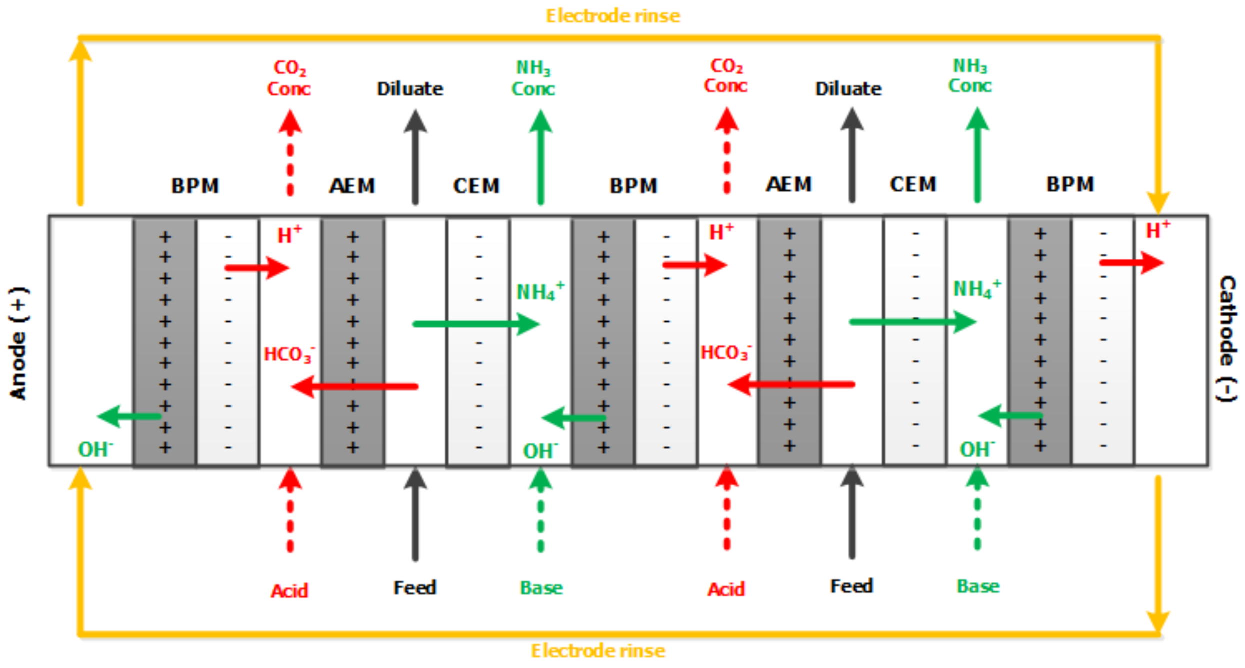


*Figure 34 – Positioning of membranes and occurring transfers in an ED stack with bipolar membranes (BPM)*

### 6.4.1 Preliminary results

The application of bipolar membranes results in one dischargeable diluate stream, while the base, acid and electrode rinse streams can be reused. In Figure 35 the evolution of pH can be seen for the salt, acid and base stream. Due to the membrane sequence, shown in Figure 34, ammonium is transferred to the base stream, leading to a transition of ammonium to ammonia. Ammonium measurements of the three fluxes, shown in

Figure 36, show a clear decrease of ammonium concentration in the salt stream, while the ammonium concentrations in other streams do not increase in the same quantities. The test kits used to measure ammonium operate at a low pH, converting all ammonium into ammonia before measuring. Therefore, it can be concluded that due to the increased pH in the base stream, ammonium is converted into gaseous ammonia. Due to the transition of ammonium to ammonia gas, the electrical conductivity of the base stream will only slightly increase. However, the difference in EC between feed and base stream is lower compared to an ED stack with normal or monovalent membranes. Therefore, lower solvent fluxes through the membranes are expected.

With this application, the ammonium is concentrated but also converted to ammonia gas, making it unnecessary to use a gas production phase. However, the energy requirement to extract 1.6 gram ammonium from the feed equals 2.29 Wh, while regular operations use approximately 1.05 Wh. The difference in energy requirement can be allocated to the dissociation of water molecules and the extra membrane resistance. Further research should be conducted to see if this setup utilizes energy more efficient than the gas production step.

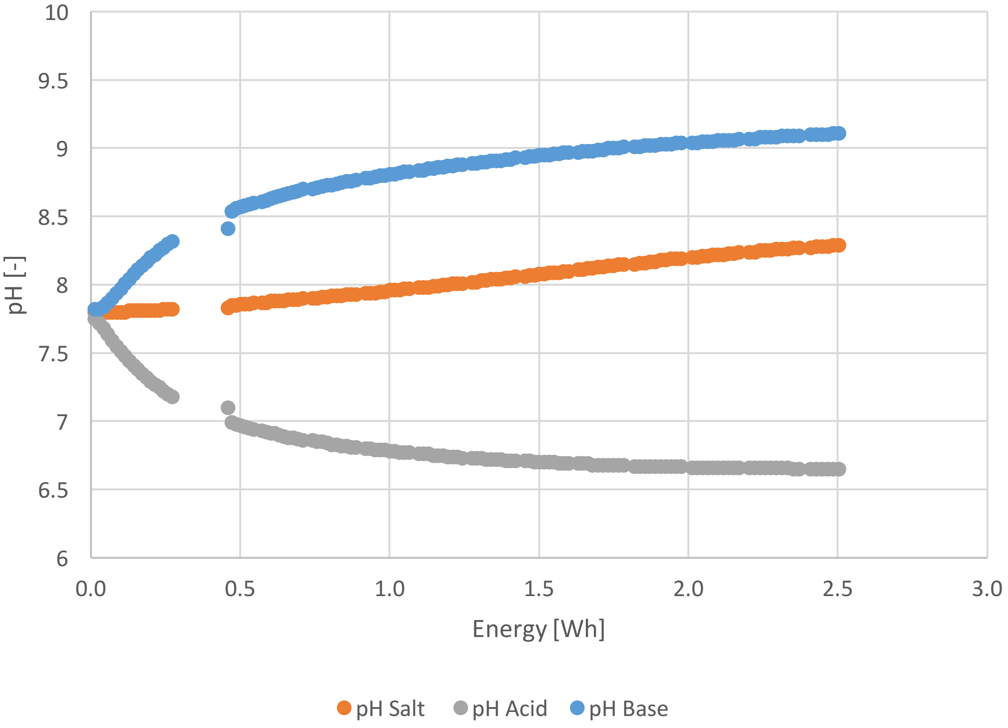


*Figure 35 – Evolution of pH over energy for ED operations with BPMs*

Besides the transfer of ammonium through cation exchange membranes into the base stream, also the transfer of bicarbonate (and other anions) are transferred through the anion exchange membranes into the acid stream. Due to a low pH, the equilibrium will shift to carbonic acid ($H_2CO_3$), which is in equilibrium with carbon dioxide and water. The application of BPM therefore produces the greenhouse gas carbon dioxide ($CO_2$).

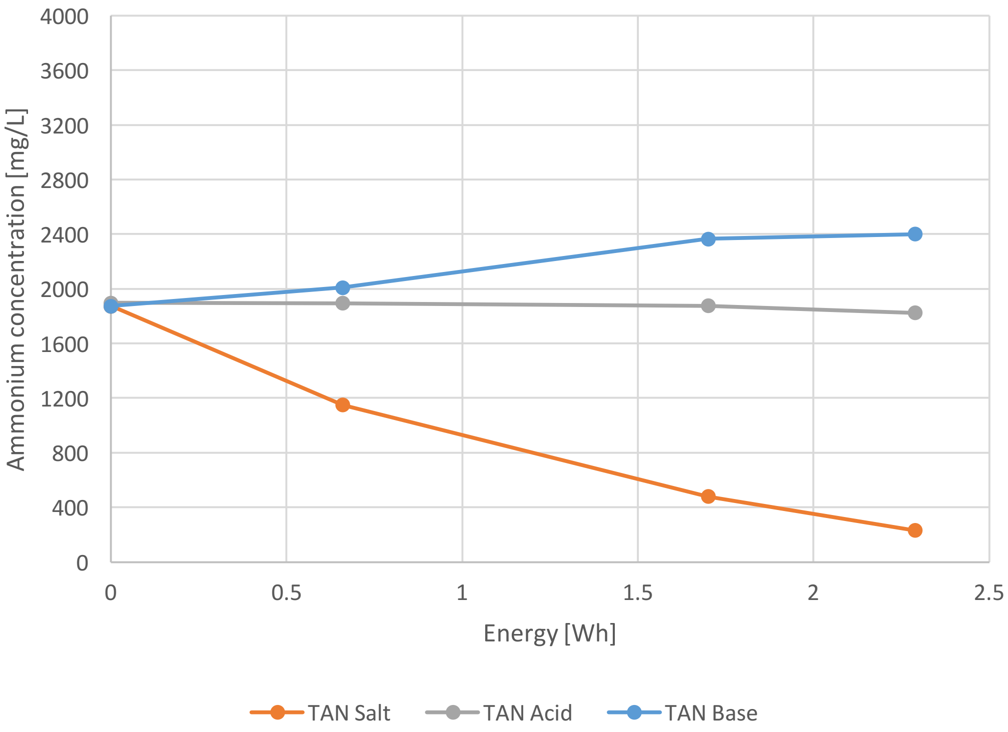


*Figure 36 – Evolution of ammonium concentration over energy for ED operations with BPMs*

The direct treatment of reject water with an ED stack containing BPM might not be highly effective, as the hydrogen and hydroxyl ions also react with other ions in solution. It would be beneficial to selective concentrate ammonium with MVM before using BPM. The application and potential of such layout should be further researched.

## 6.5 Fouling

In this thesis the influence of fouling components, as monovalent and bivalent salts, on the energy efficiency were tested. However, another important component in the influent of digest sludge reject water is neglected, organics. In the multiple diluate run experiment a horizontal trend could be seen when looking at the driving force for electrodialysis. No fouling takes place in these experiments. However, biological and organic fouling will occur when using real digest sludge reject water. This fouling will have a negative effect on the energy efficiency and also on the operation of the processes, as during electrodialysis reversal (EDR) or cleaning in place (CIP) the ED cell is not operational. The influence of these pollutions on the energy efficiency, and the consequence of pre-treatment, should be further investigated.

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# 7 Appendices

## 7.1 N2kWh background

### 7.1.1 From pollutant to power

During the climate conference in Paris in 2015 (COP21), all members agreed that action was needed to limit global warming before climate change would reach dangerous levels. One of the adaptions needed is the reduction of greenhouse gas, like carbon dioxide and methane, emissions. New established regulations aim for the reduction of greenhouse gasses by 40%, compared to the levels in the year 1992, before the year 2030. Therefore, the need for alternative energy sources is substantial.

The N2kWh project aims for the introduction of a new, widely available, energy source in the form of ammonia ($NH_3$). Besides the potential energy recovery, also alternative treatment techniques to remove nitrogen concentrations from residual streams are required. Within the boundaries of this project, a paradigm shift is provided: “from pollutant to power”. Not only will ammonia be seen as a valuable resource, rather than a pollutant, also the discharge requirement of nitrogen will be addressed. The paradigm shift is shown below in figure 37 as a part of the ammonia cycle.

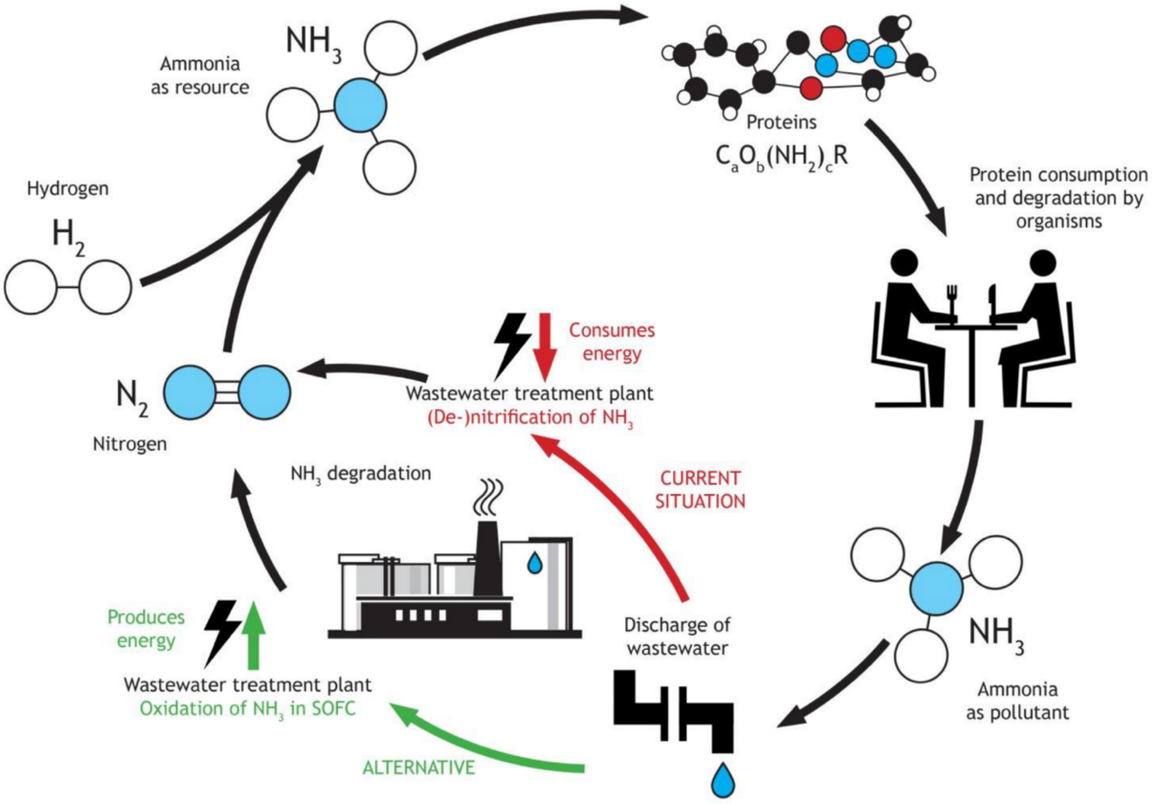

*Figure 37 – Paradigm shift for ammonia: from pollutant to power*

### 7.1.2 Solid oxide fuel cell

Consequently with the Kyoto agreement (and subsequently the Paris agreement) is the renewed interest in sustainable energy resources and its combustion. Fuel cells, which were already invented over 160 years ago, offer large environmental advantages over conventional power generation techniques (Ormerod, 2003). Moreover, high efficiency of these cells and the current commercial status make them very attracting.

#### Solid oxide full cell (SOFC)

Within the boundaries of the N2kWh project, solid oxide fuel cells (SOFC's) have the highest potential for recovering energy from ammonia combustion. These fuel cells are particular interesting for application where not only electrical energy (power) but also heat is required. This heat could be used to drive gas turbines in order to raise the electrical efficiency up to 80% (Ormerod, 2003). SOFC's operate at high temperature (between 700 and 1000 degrees celcius) and directly generate power by the electrochemical oxidation of a fuel. The high efficiency, and the clean and pollution free combustion of fuel are some of the big benefits of these fuel cells over traditional energy conversion systems (Singhal, 2000).

An SOFC consist of a solid oxygen conductor between two electrodes, one oxygen reducing cathode and a fuel anode reactant. In the anode the reduced oxygen reacts with the fuel leading to an electrical current and the production of heat. A simple representation of this cell is shown in figure 38.

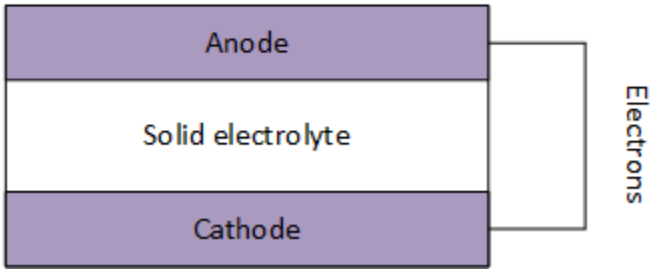

*Figure 38 – Schematic representation of the SOFC main parts*

#### Chemical thermodynamics

Chemical thermodynamic can be used to calculate the amount of energy which is stored within a chemical solution. Chemical reactions of these solutions can lead to the release of stored energy. In this thesis only electrical energy is considered, also referred to as work. The following reactions take place in the respectively the cathode and the Anode of the SOFC.

$$O_2 + 4\ \mathrm{e}^- \rightarrow 2\ \mathrm{O}^{2-}$$

$$NH_3 \rightarrow N_2 + 3\ H_2$$

$$H_2 + O^{2-} \rightarrow H_2O + 2\ e^-$$

This yields a total reaction where, as discussed before, no greenhouse gasses are produced (Fuerte et al., 2009).

$$4\ NH_3 + 3\ O^{2-} \rightarrow 6\ H_2O + 2\ N_2$$

Electrical energy calculations show that the combustion of one mole ammonia contains 4.86 kWh per kg-NH3 can be obtained combustion of ammonia. For the combustion of a pure $NH_3$ solution, cracked with a temperature between 700 and 800 degrees Celsius, an electrical efficiency up to 70% could be reached (Dekker & Rietveld, 2006). However, the long-term stability, leading to lower efficiencies, is not taken into account. Moreover, a pure ammonia solution yields a higher electrical efficiency compared to the residual streams considered in this thesis.

### 7.1.3 Research plan

This project focuses on residual streams containing high nitrogen levels and low carbon levels, for example reject water from the digested sludge step of a WWTP. However, the needed composition for the SOFC fuel does not match the water matrix of reject water. Therefore, a (selective) concentration step, and gas production step, are needed. A schematization can be found in Figure 39. Note that not only electrical energy, but also thermal energy is reused in this research scheme to reach the proper input quality for the SOFC.

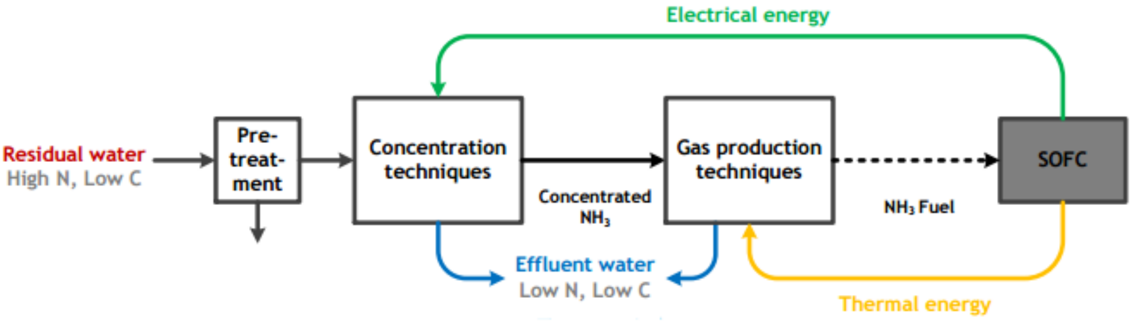

*Figure 39 - Schematization research plan N2kWh*

In the gas step, energy is required to bring the concentrated ammonia streams into a gas phase. The amount of energy required is depended on the concentration of ammonia in the liquid. The higher the concentration of ammonia in the liquid phase, the less energy is needed per volume ammonia gas. Moreover, as mentioned before, higher concentrations ammonia gas produces energy more efficient in the SOFC. Therefore, proper research needs to be conducted on the maximum reachable ammonia concentrations in the liquid phase.

More information about this project can be found in (Van Linden et al., 2016).

## 7.2 Technology review

### 7.2.1 Reverse osmosis

Osmosis is a natural phenomenon where solvent, often water, moves through a semi-permeable membrane from a low to a high solute concentration. This semi-permeable membrane retains ions, while water molecules can freely pass. An equilibrium is reached when the osmotic pressure difference over the membrane is zero. In reverse osmosis an external pressure is used to reverse the water flow from high to low concentration solutions. Due to this process there is no equilibrium, leading to an osmotic pressure difference. In order to keep the water flow in a natural reversed way, the applied external pressure should always be higher than the osmotic pressure. This phenomenon are shown below in figure 40.

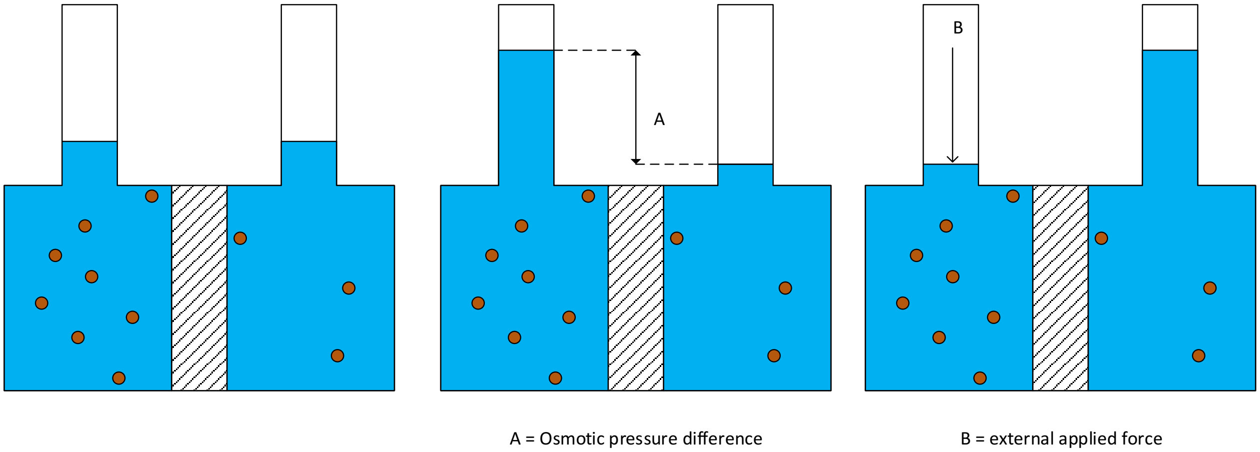

*Figure 40 – Reverse osmosis principle. From left to right: start conditions, equilibrium state and fresh water production after applying an external force.*

Reverse osmosis is a widely used technique to produce purified water from ground or surface water. In drinking water production these membranes are often used for the removal of salts, when desalinating sea or brackish water, or micro-pollutants, like organic or inorganic matter, for the production of fresh water. However, during these processes the fresh water production is important, while within the boundaries of this project, the focus lies on producing a concentrate stream.

The driving force for reverse osmosis is known as the difference between pressures over the membranes, better known as the transmembrane pressure. Correspondingly, the flux of water through a membrane can be calculated with the formula shown below.

$$J = \frac{1}{\mu * R} * (TMP - \Delta\pi)$$

Where:

J : volumetric flux [m/s]
R : membrane resistance [m$^{-1}$]
$\Delta\pi$: Osmotic pressure difference [pa]
$\mu$ : dynamic viscosity of water [pa*s]
TMP : transmembrane pressure [pa]

As high concentration differences between the concentrate en permeate side are expected for creating highly concentrated streams, the osmotic pressure difference between these two streams will increase significantly. To insure a water flow from concentrate to permeate, the applied pressure must exceed the osmotic pressure, leading to higher energy consumptions for pumps. Moreover, cleaning in place (CIP) is necessary to insure the membranes will not get clogged or (biologically) fouled. By taking out one reverse osmosis module, which is usually executed as a spiral wound membrane, the production of clean water will decrease. However, the high retention of salts and relatively low energy consumption are big advantages.

### 7.2.2 Ion exchange

Ion exchangers are insoluble materials, either natural occurring zeolites or manmade resins, which carry exchangeable cations or anions (Helfferich, 1962). Ion exchange is a reversible process which can be divided into cation exchange and anion exchange, where respectively positively and negatively charged ions are exchanged. The target ion in this research is ammonium, needs the same charge as the functional group of the resin, which is called the counter ion. Operating an ion exchange column starts with resins fully loaded with positively charged ions. When electrolyte with the target ion is pumped through the column, and the target ion has a higher ionic interaction with the materials surface, it will exchange with the counter ion. When there are no counter ions on the resins surface anymore, the flow will be reversed, using a highly concentrate electrolyte solution containing the counter ion. This process can be seen below.

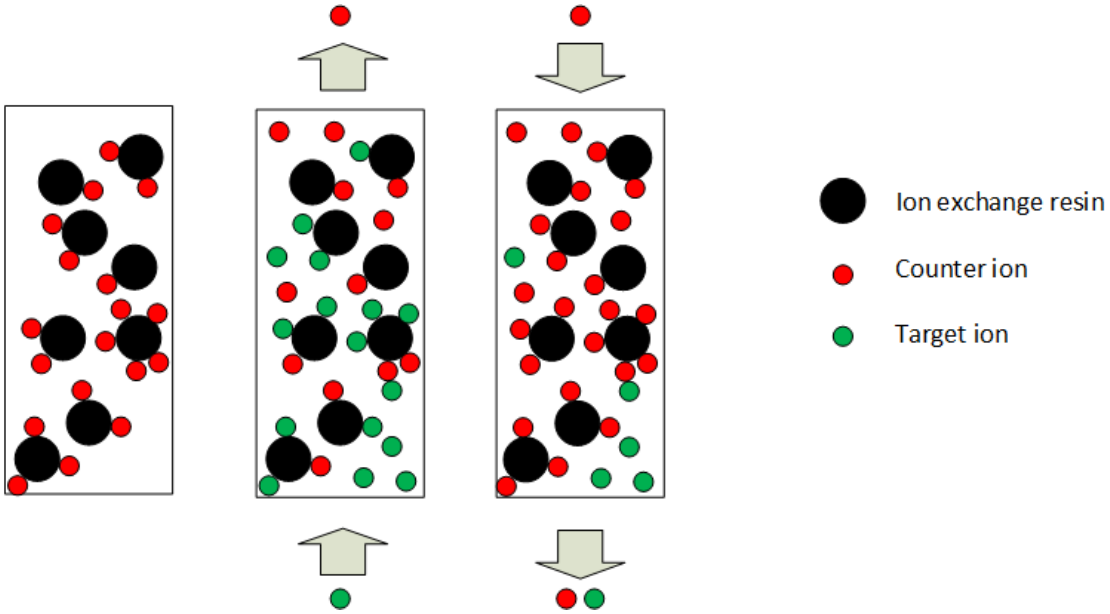

*Figure 41- Ion exchange principle. From left to right: start conditions, loading phase and regeneration phase.*

During the regeneration phase a stream with a high target and counter ion concentration is produced. In this way, almost no energy is needed to concentrate ammonium ions. However, high concentrations of target ions also required a high amount of counter ions, and therefore a high amount of ion exchange resin.

### 7.2.3 Electrodialysis

Electrodialysis is already presented in paragraph 2.1.1.

### 7.2.4 Technique consideration

In this paragraph, elementary information is given on three possible concentration techniques, for the concentration of ammonium from reject water. As the goal of this thesis is to optimize the energy efficiency for one of these techniques, and not to compare them to each other, the most promising technique is chosen after a literature review. Electrodialysis in this case has low amounts of literature available on the concentration of streams, while on the other hand has the highest potential as a concentration technique.

As explained in paragraph 7.1.3, a high concentration of ammonium is favorable for the operation of subsequent steps. This favorable concentration is presumably to high to have an effective ion exchange process, as the resin surface will be full with ammonium quickly.

Moreover, both electrodialysis and reverse osmosis seem good techniques to concentrate ions into one stream. Reverse osmosis creates low concentrate volumes, has much literature available on the technique and is often preferred over ED for treating brackish water (Walha et al., 2007). However, a higher salt concentration in the feed flow leads to higher osmotic pressures and therefore a higher energy consumption. On the other hand, in an electrodialysis process the water is not forced through the membranes, which is the case for all other membrane techniques, but only transfers ions over the membrane. The resistance in such a setup will be determined by the stream that has the lowest electrical conductivity, the diluate stream. Higher concentrations therefore lead to lower resistance and a better utilization of the energy. However, electrodialysis is limited by the properties of the ion exchange membranes and the high costs of electrodes and ion exchange membranes (Xu & Huang, 2008).

As this thesis only focuses on an effective utilization of energy for the concentration of salts, and not on the economic aspects as investment costs, electrodialysis is the most promising technique.

### 7.2.5 pH sensitivity of ammonium bicarbonate

Ammonium is a slightly positively charged ion and therefore does not exists on it's own, but is always part of a salt with a negatively charged ion. In this thesis ammonium bicarbonate is used, as this approaches the real water composition of biologically treated reject water (see paragraph 1.2.1). Both ions are kept together by ionic bonds, which will be interfered the moment they are dissolved in water. Moreover, Ammonium is always in equilibrium with ammonia, such as the equilibrium of bicarbonate with carbonic acid and carbon dioxide. These equilibria are depended on solute concentration, pH and temperature. Within the boundaries of this project the pH of digested sludge reject water ranges between 7.4 and 7.8 (STOWA, 2016). Below, in Figure 42 both equilibria graphs are shown. It can be concluded that at this pH, and a temperature of 25 degrees Celsius, almost everything is ionized in ammonium and bicarbonate.

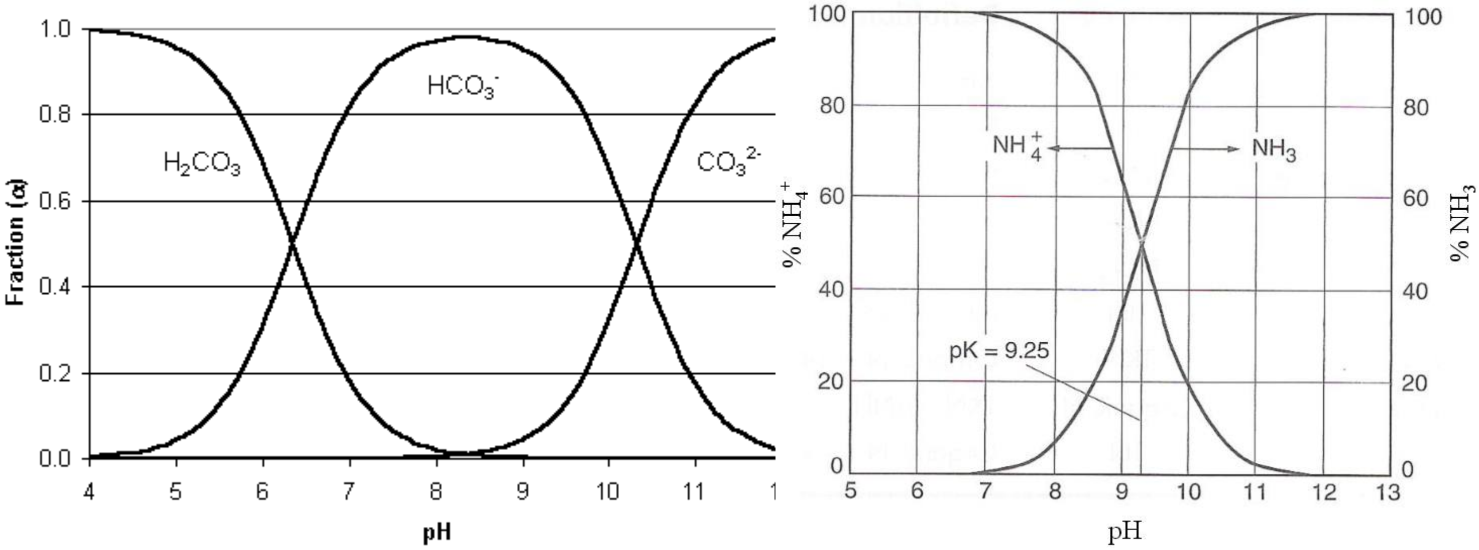

*Figure 42 - Equilibria of bicarbonate (left) and ammonium (right)*

## 7.3 Process parameters

### 7.3.1 Pump

The circulation of electrolyte solutions is induced by a Watson Marlow 520S pump and three 323 pump heads. The adjustment of speed is applied in revelations per minute (RPM) and calibrated by both measuring volume and weight for different settings. The trend between RPM and volume shows a linear relation with a high correlation factor. Small deviations are due to the low amount of bearings, only three, and therefore the corking circulation of flow at low flow speeds. Test are performed between 5 and 70 revelations per minute and show a relation of 0.0506 between the flow in milliliter per second and revelations per minute.

During experiments performed in this thesis a maximum flow speed of 11.6 mm/s (90 RPM) is applied, due to the physical barrier of the system. On the other hand, a minimum flow speed of and 1.3 mm/s (10 RPM) is applied.

### 7.3.2 Electrical conductivity and total dissolved salts

The electrical conductivity is constantly logged during the operation of the electrodialysis unit, as explained in the Materials and methods section. Electrical conductivity can be closely related to other operation parameters, such as the limiting current density and the electrical potential, and gives a good indication on the amount of ammonium in solution. In order to determine this relation, one liter of demineralized water was prepared, with addition of different ammonium bicarbonate quantities. Its results are shown in Figure 45.

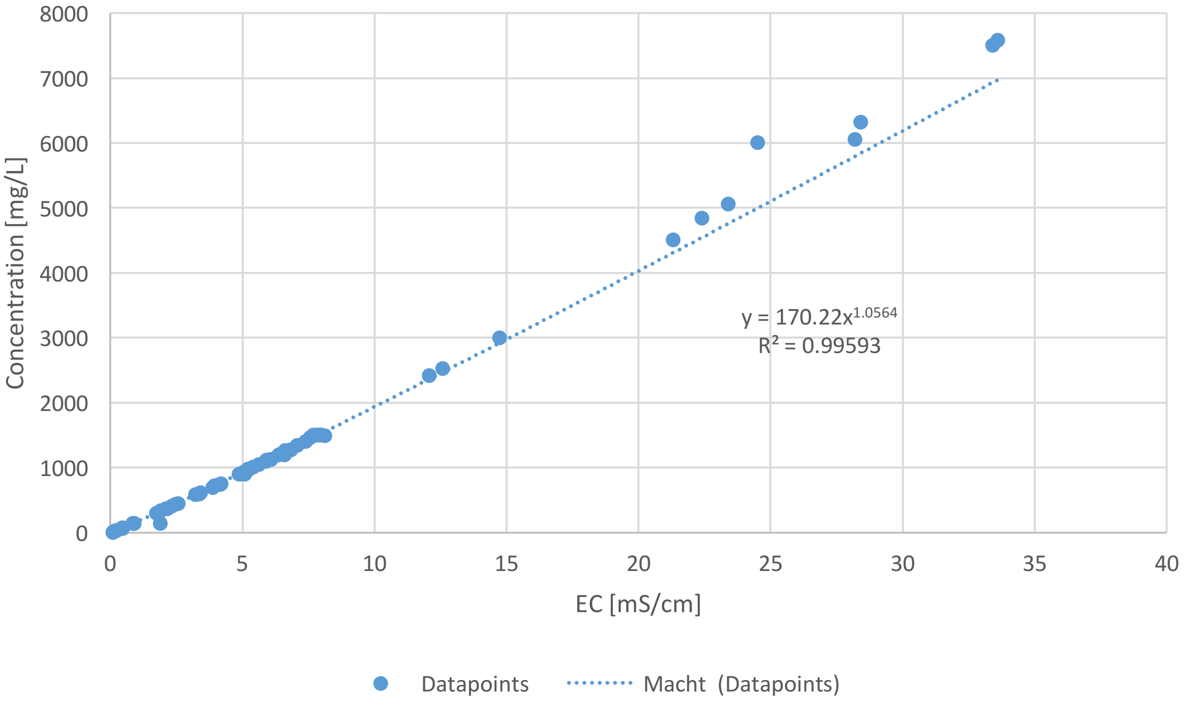

*Figure 43 - Relation EC and $NH_4^+$*

### 7.3.3 Limiting current density

By definition the LCD is the current where, for a given concentration, the resistance has its minimum. The procedure for determining the LCD can be found in paragraph 2.2.2, and is performed for 11.6 mm/s and 3.9 mm/s for different ammonium concentrations. An example for the determination of the LCD is shown in Figure 44. In this case, where 0.569 g/L of ammonium bicarbonate is dosed, the lowest resistance is 59 ohm and a corresponding amperage of 0.15.

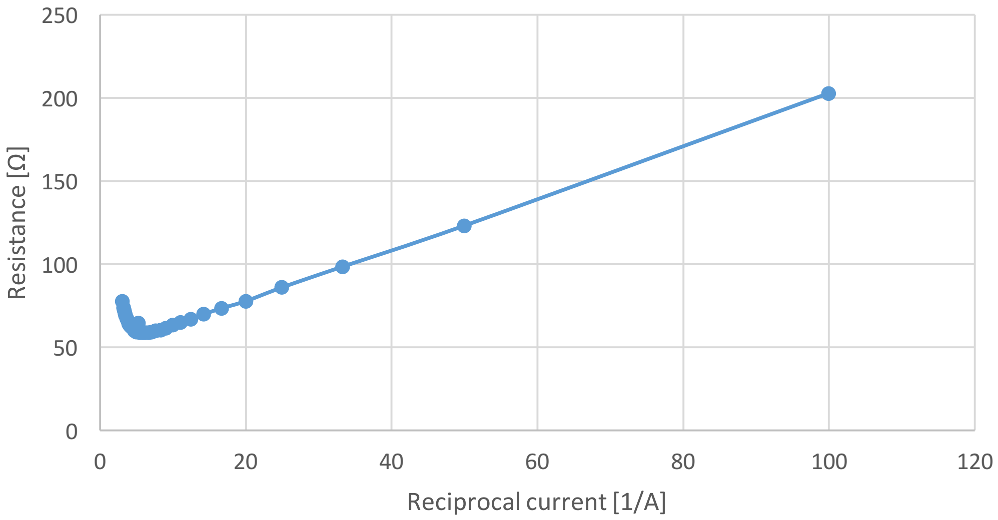

*Figure 44 – Determination of the LCD for 0.659 g/L ammonium bicarbonate and 11.6 mm/s*

Moreover, in literature it was shown that the pH dropped significantly when the current was increased after reaching the LCD. However, this change could not be observed in these experiments. A possible cause for this is the high alkalinity of the solution, due to the dosing of bicarbonate.

Literature research also showed a linear relation between the concentration in the diluate cell and the corresponding LCD. As explained in paragraph 7.3.2, this equals the relation between LCD and electrical conductivity. Using the relation between both, it is possible to determine the limiting current density values for all EC values in the diluate cell. Higher electrical conductivity values have the ability to conduct a higher electrical current, therefore a higher EC lead to higher LCD values. Moreover, comparing both regression lines shows a quicker increase in LCD for higher cross-flow speeds.

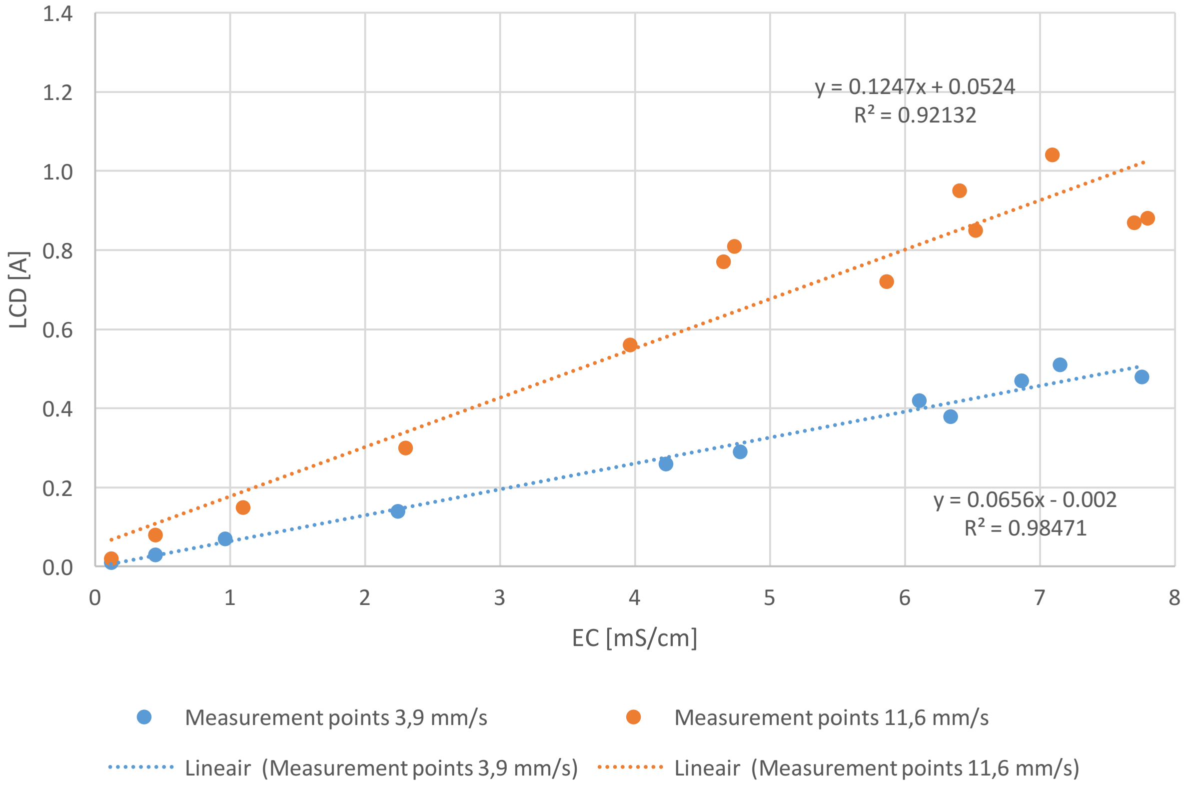

*Figure 45 – Relation between LCD and EC for constant cross-flow velocities*

### 7.3.4 Relation maximum concentration and electrical conductivity

Former experiments conducted with sodium chloride show the same trend in EC, and an equal electrical conductivity factor of four. In these experiments, an initial concentration of 34 g/L, with a corresponding electrical conductivity of 47 mS/cm and a final conductivity of 181 mS/cm is observed. Results from these experiments are shown in Figure 46.

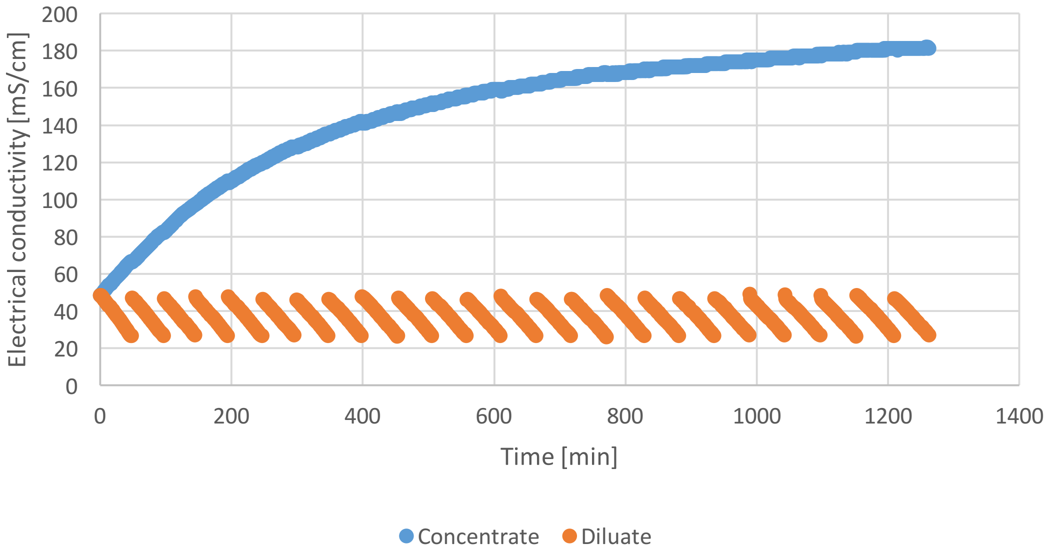

*Figure 46 - Sodium chloride time versus EC*

## 7.4 Data

### 7.4.1 Water transport

| Run | EC Conc | EC Dil | Delta EC | Water transfer |
|---|---|---|---|---|
| | [mS/cm] | [mS/cm] | [mS/cm] | [L] |
| 1 | 13.99 | .93 | 13.06 | .04 |
| 2 | 18.29 | 0.83 | 17.47 | 0.038 |
| 3 | 21.70 | 0.97 | 20.73 | 0.045 |
| 4 | 24.40 | 0.99 | 23.41 | 0.057 |
| 5 | 26.50 | 1.04 | 25.46 | 0.068 |
| 6 | 28.20 | 0.98 | 27.22 | 0.064 |
| 7 | 29.40 | 0.82 | 28.58 | 0.086 |
| 8 | 30.40 | 1.00 | 29.40 | 0.088 |
| 9 | 30.90 | 1.00 | 29.90 | 0.096 |
| 10 | 31.50 | 0.99 | 30.51 | 0.12 |
| 11 | 31.70 | 0.24 | 31.46 | 0.12 |
| 12 | 31.80 | 1.00 | 30.80 | 0.103 |
| 13 | 31.90 | 0.96 | 30.94 | 0.11 |
| 14 | 32.10 | 0.99 | 31.11 | 0.118 |
| 15 | 32.30 | 1.02 | 31.28 | 0.125 |
| 16 | 32.70 | 1.01 | 31.69 | 0.123 |
| 17 | 32.80 | 1.01 | 31.79 | 0.125 |
| 18 | 32.70 | 0.80 | 31.91 | 0.136 |
| 19 | 32.90 | 1.00 | 31.90 | 0.136 |
| 20 | 32.80 | 0.99 | 31.82 | 0.138 |

### 7.4.2 Volume ratio tests

| VR | 1 | 0.65 | 0.5 | 0.33 | 0.25 | 0.20 |
|---|---|---|---|---|---|---|
| Energy efficiency [$Wh^{-1}$] | 1.86 | 2.01 | 2.23 | 2.63 | 2.86 | 2.94 |
| $NH_4^+$ mig. Per energy [mg/Wh] | 1.48 | 1.27 | 1.33 | 1.36 | 1.24 | 1.20 |
| Volume treated/energy [L/Wh] | 2.36 | 2.12 | 2.11 | 2.10 | 1.98 | 1.79 |

*Table 9 – Test results for different volume ratio, one liter diluate and STM*

| VR | 1 | 0.5 | 0.33 | 0.1 |
|---|---|---|---|---|
| Energy efficiency [$Wh^{-1}$] | 0.90 | 1.26 | 1.43 | 1.95 |
| $NH_4^+$ mig. Per energy [mg/Wh] | 1.56 | 1.63 | 1.55 | 1.29 |
| Volume treated/energy [L/Wh] | 2.23 | 1.63 | 1.37 | 0.95 |

*Table 10 – Test results for different volume ratios, two liter diluate and STM*

| VR | 1 | 0.5 | 0.25 | 0.05 |
|---|---|---|---|---|
| Energy efficiency [$Wh^{-1}$] | 1.11 | 1.47 | 1.81 | 2.69 |
| $NH_4^+$ mig. Per energy [mg/Wh] | 1.92 | 2.00 | 1.78 | 1.50 |
| Volume treated/energy [L/Wh] | 2.79 | 1.99 | 1.51 | 1.11 |

*Table 11 – Test results for different volume ratios, two liter diluate and MVM*