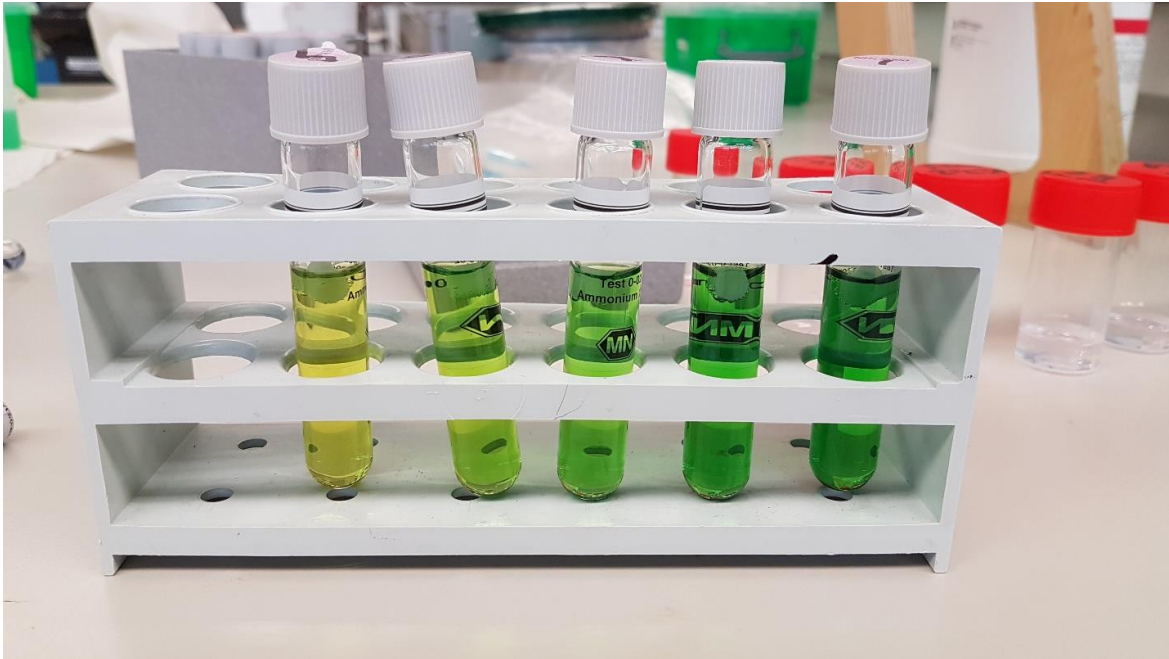


Concentrating Ammonium

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Delft University of Technology
Watermanagement
Sanitary Engineering

September 2017

Concentrating Ammonium

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in partial fulfillment of the requirements for the degree of

Master of Science
in Civil Engineering

at the Delft University of Technology,
to be defended publicly on Tuesday September 26, 2017 at 11:30 AM.

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This thesis is confidential and cannot be made public.

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Acknowledgements

During an excursion for the course “Industry Water”, I learned about the N2kWh project from Niels van Linden. The project took existing technologies and used them for a new purpose. To turn ammonium, that usually uses a lot of energy to process, into energy. The project looks at a waste product and sees a potential new energy source, something I expect will (need) to happen in a lot of other areas as well. So I was glad to be able to help with the project during my master thesis.

One part of the project focused on increasing the ammonium concentration in a solution. A literature research showed that it was hard to compare different technologies with regards to achievable concentrations and energy use. This thesis focused on comparing three technologies. The research called for quite some theoretical and experimental research to complete the thesis. The experiments were a lot of fun to do and provided a lot of insight into the technologies.

During my thesis, I thankfully had a lot of help, and I would like to thank a lot of people. Firstly Henri Spanjers, for being my supervisor and helping me shape my thesis. Niels van Linden, for the day to day help with the experimental research and the thesis itself. The periodic meetings between the three of us were also very helpful and educational. The other members of my thesis committee, Jules van Lier, Bas Heijman and Fokko Mulder. Thank you for taking time to be a part of my thesis committee. Your question and comments during the meetings and presentations were very beneficial to the quality of the final thesis.

Thank you, Franka Kramer, for allowing me to use the Reverse Osmosis (OSMO) set-up you were using for your PhD. Besides the experiments being useful for the thesis, it was a lot of fun working with a larger set-up (compared to the Electrodialysis and Ion Exchange set-up). Also, a big thank you to Ran Shang for your help with troubleshooting the Reverse Osmosis set-up when it was not working properly during the first experiments.

During the Electrodialysis experiments, I worked with Rob Deckers, who was using the same set-up for his thesis work. During the longer, and somewhat more tedious experiments, it was a lot of fun to have someone to work with. Discussions on what experiments should be done and how experiments were done helped me with further experiments and writing of the thesis. I would also like to thank the staff of the Waterlab. Armand and Mohammed were able to help with whatever I needed during the experiments and were very helpful in helping me find my way around the lab.

Christiaan Hordijk
Bodegraven, September 2017

Abstract

This thesis provided an overview of the achievable ammonium concentrations, and the energy used to achieve these concentrations, by ion exchange, electrodialysis and reverse osmosis. The need for this overview arose during research for the N2kWh project, where one step in the process focused on increasing the ammonium concentration of (anaerobic digestion) reject water. The research presented some knowledge gaps. As available reports focused on the ammonium removal from the solution, the concentration in the residual stream was barely mentioned. Even when concentrations were reported, the conditions between the discussed technologies made it hard to make a comparison between the three technologies. Even less was reported on the energy that was needed to achieve the various concentrations.

To compare the three technologies, a 1.5 g NH_4^+ /L solution was used as feed water for all three technologies. The technologies used different techniques to increase the ammonium concentration (using zeolites, electrical current over a membrane or high pressure through a membrane). This made comparing the technologies, very difficult. By using the same feed water for all experiments, the achieved concentrations and the energy that was used in the process could be used to compare the three technologies.

The highest ammonium concentration that was achieved during the experiments (7.1 g NH_4^+ /L) was produced by Electrodialysis. Ion exchange achieved a concentration of 6.0 g NH_4^+ /L, while a laboratory scale Reverse Osmosis achieved 4.5 g NH_4^+ /L. The amount of energy used by the three technologies to produce 6 g NH_4^+ /L was: ion exchange = 0.24 kWh, electrodialysis = 6 kWh, reverse osmosis = 4 kWh (per m^3 of produced concentrated NH_4^+ solution). ROSA software was used to estimate energy use for Reverse Osmosis to achieve 6 g NH_4^+ /L (as the laboratory scale Reverse Osmosis was unable to provide sufficient pressure to achieve this concentration). So ion exchange was the most energy efficient, but the maximum achievable ammonium concentration was the lowest of the three technologies. Electrodialysis was able to achieve the highest ammonium concentration but was less energy efficient and used more energy in the process.

Table of Contents

Acknowledgements.....	ii
Abstract.....	iii
List of Figures	vii
List of Tables	viii
1 Introduction	1
1.1 NH ₃ -cycle.....	1
1.2 N2kWh Project	1
1.3 Solid Oxide Fuel Cell.....	3
1.4 Anaerobic Digestion Reject water.....	4
1.5 Concentrating Ammonium.....	4
1.5.1 Suitable Technologies	4
1.5.2 Knowledge Gaps.....	5
1.6 Technologies	6
1.6.1 Ion exchange	6
1.6.2 Electrodialysis	6
1.6.3 Reverse Osmosis	7
1.7 Research Objective	9
1.8 Thesis Lay-Out.....	10
2 Theoretical Background	11
2.1 Anaerobic Digestion.....	11
2.2 NH ₄ HCO ₃	11
2.3 Ion Exchange	13
2.3.1 Bed Volume.....	13
2.3.2 Loading.....	13
2.3.3 Regeneration.....	14
2.3.4 Zeolite and Resin.....	14
2.4 Electrodialysis	14
2.4.1 Concentration Polarization	14
2.4.2 Limiting Current Density	14
2.4.3 Electro-Osmosis	15
2.4.4 Electrodialysis Reversal.....	15
2.5 Reverse Osmosis	15
2.5.1 Spiral Wound Membrane.....	15
2.5.2 Trans Membrane Pressure.....	16

2.5.3	Recovery.....	16
2.5.4	Limiting Factors.....	16
3	Materials and Methods.....	17
3.1	Feed Water.....	17
3.2	NH ₄ ⁺ Measurements	17
3.2.1	Electrical Conductivity.....	17
3.2.2	Analysis of NH ₄ ⁺	17
3.3	Comparing the Technologies	18
3.4	Set-Up IEX.....	18
3.4.1	Loading by Feed water	18
3.4.2	Regeneration.....	19
3.4.3	Zeolite	20
3.4.4	Full scale Set-Up.....	20
3.5	Set-Up ED	22
3.5.1	Full scale Set-Up.....	24
3.6	Set-Up RO.....	24
3.6.1	OSMO Inspector	24
3.6.2	TFC Membrane.....	27
3.6.3	Full scale Set-Up.....	27
4	Results.....	28
4.1	Results IEX.....	28
4.1.1	Loading.....	28
4.1.2	Regeneration.....	29
4.1.3	Total Energy Used	34
4.2	Results ED.....	38
4.2.1	Efficiency: Flow and Current	38
4.2.2	Maximum Concentration	40
4.2.3	Energy Used	41
4.3	Results RO	42
4.3.1	Experimental Results vs ROSA	42
4.3.2	Energy Used	44
5	Discussion.....	45
5.1	IEX	45
5.1.1	Short Loading/Regeneration Time	45
5.1.2	NaCl Concentration	45

5.1.3	K ⁺ Removal	45
5.2	ED	45
5.2.1	fouling	45
5.2.2	Alternative Staging Design	45
5.3	RO.....	46
5.3.1	Fouling.....	46
5.3.2	ROSA.....	46
5.4	Residual Streams.....	47
5.4.1	Feed Water Needed	47
5.4.2	Residual Stream Concentration	49
6	Conclusions	52
6.1	IEX	52
6.2	ED	52
6.3	RO.....	52
6.4	Overview	53
7	Recommendations	55
7.1	IEX	55
7.1.1	Loading, Regeneration, Reloading	55
7.1.2	Alternative Regeneration.....	55
7.2	RO.....	56
7.3	Reject Water	56
8	Appendix	57
8.1	Appendix A: ED.....	57
8.1.1	LCD calculation.....	57
8.1.2	Achieved NH ₄ ⁺ concentration.....	59
8.1.3	Energy Used - ED Pumps	60
8.2	Appendix B: NH ₄ ⁺ Measurements	62
8.2.1	Electrical Conductivity.....	62
8.2.2	Analysis of NH ₄ ⁺	63
8.3	Appendix C: IEX Energy Used Calculations.....	64
8.3.1	Regeneration NaOH – pH = 12.5	64
8.3.2	Regeneration Recirculation with Small Volume	65
8.4	Appendix D: ROSA Energy Used.....	67
9	Bibliography	68

List of Figures

Figure 1: NH ₃ -Cycle (van Linden et al., 2016).....	1
Figure 2: Research Track N2kWh (van Linden et al., 2016)	2
Figure 3: Schematization of SOFC workings (van Linden et al., 2016).....	3
Figure 4: Schematization of Ion Exchange Zeolite	6
Figure 5: ED Cell Schematization ("Electrodialysis Reversal," 2016)	7
Figure 6: Schematization of Osmosis and Reverse Osmosis (van Lier et al., 2011).....	8
Figure 7: Graph: NH ₃ - NH ₄ ⁺ Equilibrium, depending on pH and temperature (Capodaglio et al., 2015) ..	12
Figure 8: Graph: H ₂ CO ₃ - HCO ₃ ⁻ - CO ₃ ²⁻ Equilibrium, depending on pH and temperature (IAEA, 2016).....	12
Figure 9: IEX schematization; Loading (black line) and Regeneration (red line)	13
Figure 10: RO - Spiral Wound Membrane schematization ("Learning-Center," 2017).....	15
Figure 11: Photo of IEX Laboratory Set-Up	19
Figure 12: Schematization of IEX Laboratory Set-Up, regeneration with pH 12.5 solution	20
Figure 13: Photo of ED Laboratory Set-Up.....	22
Figure 14: Schematization of ED Laboratory Set-Up.....	23
Figure 15: Photo of RO Laboratory Set-Up.	25
Figure 16: Schematization of RO Laboratory Set-Up	26
Figure 17: RO ROSA Software: Input Wizard	26
Figure 18: IEX Laboratory Set-Up: Breakthrough Curve of 1.5 g NH ₄ ⁺ /L feed water	28
Figure 19: IEX Laboratory Set-Up: Regeneration of 100 % saturated IEX bed with 6.5 g NaCl/L	29
Figure 20: IEX Laboratory Set-Up: Regeneration of 100 % saturated IEX bed with 100 g NaCl/L	30
Figure 21: IEX Laboratory Set-Up: Regeneration with 100 g NaCl/L: maximum NH ₄ ⁺ concentration	31
Figure 22: IEX Laboratory Set-Up: Regeneration with a pH = 12.5 solution	32
Figure 23: IEX Laboratory Set-Up: Regeneration pH = 12.5 solution: maximum NH ₄ ⁺ concentration	33
Figure 24: IEX Laboratory Set-Up: Regeneration; Green: 100 g NaCl/L. Blue: 100 g NaCl/L pH = 12.5.	33
Figure 25: IEX Laboratory Set-Up: Regenerated by recirculating a small volume over the IEX bed.....	34
Figure 26: IEX Full Scale Set-Up: Achievable NH ₄ ⁺ Concentration + Energy Used by IEX,.....	37
Figure 27: ED Laboratory Set-Up: ED Efficiency Test: Cross flow velocity = 43 L/h, LCD.....	39
Figure 28: ED Laboratory Set-Up: Achievable NH ₄ ⁺ Concentration + Energy Used by ED	40
Figure 29: ED Full Scale Set-Up: Achievable NH ₄ ⁺ Concentration + Energy Used by ED (Full scale).....	41
Figure 30: RO Laboratory Set-Up: Syphoning Permeate; Sample Measurements	42
Figure 31: RO ROSA Software: Achievable NH ₄ ⁺ Concentration + Energy Used by RO (Full scale).....	44
Figure 32: Schematization of Alternative ED Set-Up	46
Figure 33: RO; Pyramid staging design (BV, 2001).....	47
Figure 34: All Technologies: Volume of feed water needed vs The Achievable CF	49
Figure 35: All Technologies: Percentage of Available NH ₄ ⁺ in the Residual Stream vs The Achievable CF. 51	
Figure 36: All Technologies: Energy Used by the Full scale Set-Ups vs the Achievable CF.....	53
Figure 37: IEX Laboratory Set-Up: Breakthrough Curve of 1.5 g NH ₄ ⁺ /L feed Water	55
Figure 38: Schematization of Alternative Regeneration Set-Up.....	56
Figure 39: ED Laboratory Set-Up: LCD and Cross flow velocity = 43 m/h.....	57
Figure 40: ED Laboratory Set-Up: LCD for Cross flow velocity = 43 m/h	58
Figure 41: Photo of Pressure Sensors: Calculating Power [W] Pumps ED Laboratory Experiments.	60
Figure 42: EC; Measured EC vs Known concentrations	62
Figure 43: Measured vs Known NH ₄ ⁺ concentration.....	63

List of Tables

Table 1: Characteristics of Reject Water (Solon, 2015)	4
Table 2: IEX Full Scale Set-Up: Estimated Vessel Size	21
Table 3: IEX Full Scale Set-Up: Pressure Drop during Loading	21
Table 4: IEX Full Scale Set-Up: Pressure Drop during Regeneration 100 g NaCl/L	22
Table 5: IEX Full Scale Set-Up: IEX Bed Capacity for NH_4^+	35
Table 6: IEX Full Scale Set-Up: IEX Bed Loading	35
Table 7: IEX Full Scale Set-Up: IEX Regeneration with 100 g NaCl/L.....	35
Table 8: IEX Full Scale Set-Up: Subsequent Loading (Regeneration with 100 g NaCl/L).....	36
Table 9: IEX Full Scale Set-Up: Energy Used by IEX (1 st loading)	36
Table 10: IEX Full Scale Set-Up: IEX Reloading	36
Table 11: IEX Full Scale Set-Up: Energy Used by IEX (subsequent loading)	37
Table 12: ED Laboratory Set-Up: ED Efficiency Test: Results of all Efficiency Tests	39
Table 13: RO ROSA Software Validation: ROSA Software Results	43
Table 14: RO ROSA Software Validation: Laboratory Set-Up Results and ROSA Software Results	43
Table 15: ED; Achievable NH_4^+ concentrations and Energy used, laboratory scale and full scale set-up ..	59
Table 16: ED Laboratory Set-Up: ED Efficiency Test: Calculating Pressure Drop over the ED Cell	60
Table 17: ED Laboratory Set-Up: ED Efficiency Test: Total Energy Used by ED and Pumps	61
Table 18: IEX Full Scale Set-Up: IEX Regeneration with pH = 12.5 Solution.....	64
Table 19: IEX Full Scale Set-Up: Subsequent Loading (Regeneration with pH = 12.5 Solution)	64
Table 20: IEX Full Scale Set-Up: IEX Regeneration by Recirculating Small volume (100 g NaCl/L)	65
Table 21: IEX Full Scale Set-Up: Subsequent Loading (Regeneration by Small Volume; 100 g NaCl/L).....	65
Table 22: IEX Full Scale Set-Up: IEX Regeneration by Recirculating Small volume (pH = 12.5)	66
Table 23: IEX Full Scale Set-Up: Subsequent Loading (Regeneration by Small Volume; pH = 12.5).....	66
Table 24: IEX Full Scale Set-Up: Achievable NH_4^+ Concentration + Energy Used by IEX).....	66
Table 25: RO ROSA Software Results	67

1 Introduction

This chapter introduces ammonium and in what context it is important to increase the concentration. The technologies which this thesis focused on are introduced and the research questions and objective are given.

1.1 NH₃-cycle

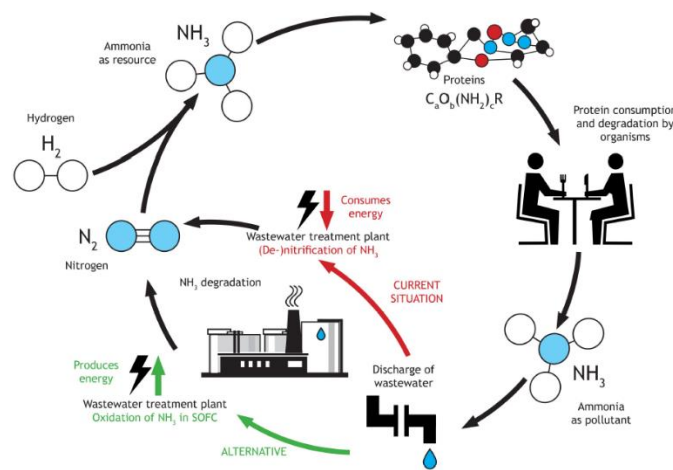


Figure 1: NH₃-Cycle (van Linden et al., 2016)

Ammonia is mainly used in artificial fertilizers and is produced by the Haber-Bosch process. The process, designed by Fritz Haber and Carl Bosch, converts nitrogen (N₂ from the atmosphere) and hydrogen (H₂ from sources like methane, natural gas and electrolysis of water) into ammonia (NH₃) under high pressure and temperatures (50 - 200 bar and 400 – 500 °C (Vojvodic et al., 2014)). Due to this high pressure/temperature process, about 2% of the world's energy is used in the production of ammonia (University of Toulouse, 2014). The ammonia component usually ends up, via our diet, in the wastewater streams. To prevent environmental pollution (i.e. eutrophication and toxicity for fish) this component (NH₄⁺)

need to be removed before wastewater can be discharged. Removing ammonium, usually via biological nitrification/denitrification, requires high amounts of energy (in the form of aeration). This increases the energy consumption for the global NH₃-cycle. After this last step, nitrogen ends up in the atmosphere (as N₂, closing the cycle). There is a process where ammonium together with phosphate is reused as struvite, which can be used as a fertilizer. However, farmers are hesitant in using struvite because of uncertainties in fertilizer consistency and possible pollutants found in struvite, and they have less experience with the slower release of phosphates compared to current (cheaper) fertilizers. So, struvite is not yet widely used in the Netherlands (De Graaff & Naber, 2016).

1.2 N2kWh Project

The N2kWh project seeks to find a solution for the energy demand of the final step in the N-cycle, where ammonia is converted back to nitrogen (N₂, to be discharged to the atmosphere), which uses a lot of energy. Rather than seeing the ammonia (NH₃) as a waste-product, it is seen as a resource for energy. A Solid Oxide Fuel Cell (SOFC, see 1.3), using ammonia gas as a fuel, produces energy (thermal and electrical), while exhausting water (vapor) and nitrogen (N₂ gas) as residual compounds. This process can reduce the total energy demand of the wastewater treatment plant (WWTP).

The project explores two options to valorize ammonia from waste streams; the first option focuses on a waste stream with both a high nitrogen concentration and a high organic content. This stream is processed using anaerobic digestion, producing biogas where the present methane (CH₄) can be used to fuel the SOFC. During the anaerobic digestion, the organically bound nitrogen is converted to ammonium (NH₄⁺). Under alkaline conditions the NH₄⁺/NH₃ equilibrium shifts towards NH₃ (gas), the formed CH₄ can then be used to strip the NH₃ from the solution. The difficulty of this set-up is getting the anaerobic digestion to

work under alkaline conditions. The proposed solution should be able to fit within standard set-ups, so it is easier to implement. This track is not discussed further in this thesis.

The second option focuses on a waste stream with high nitrogen contents but a low organic fraction, such as reject water from anaerobic digestion and urine. This research is divided into 4 separate parts, focusing on Pre-Treatment, Concentration Technologies, Gas Production Technologies and the SOFC (see Figure 2).

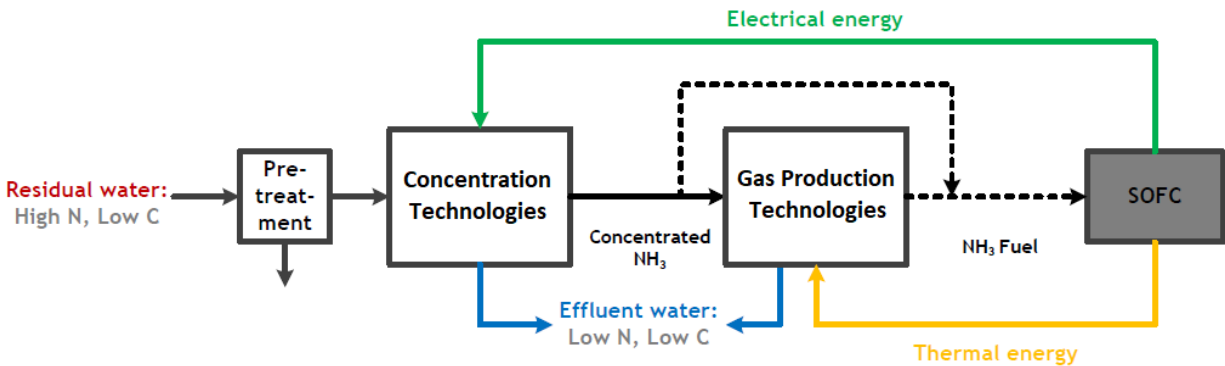


Figure 2: Research Track N2kWh (van Linden et al., 2016)

The first part focuses on any pre-treatment of the urine or reject water before concentration technologies can be implemented. The second part examines which technologies can be used to increase the concentration of NH_4^+ . The third part focuses on membrane distillation to produce NH_3 gas from the solution. The last part focuses on the SOFC itself.

A concentration step is added because it is expected that a solution with higher concentration of NH_4^+ can deliver a higher concentration of NH_3 gas in the third part. This is due to the fact that an increase in ammonium concentration, results in an increase of ammonia (by increasing the pH) and an increase in ammonia results in an increase of the vapor pressure of the solution. The difference in vapor pressure between the solution and the gas (divided by a membrane) is the driving force for ammonia to migrate through the membrane (Xie et al., 2009).

This Master thesis focuses on the concentration step, trying to find the technology best suited to increase the NH_4^+ concentration.

1.3 Solid Oxide Fuel Cell

A fuel cell converts chemical energy from a fuel (usually hydrogen, H₂) into electricity, via a chemical reaction of hydrogen ions and oxygen. Besides electricity, water and heat are formed. A Solid Oxide Fuel Cell (SOFC) is characterized by a solid oxide or ceramic electrolyte and high operating temperature (800 - 1000 °C).

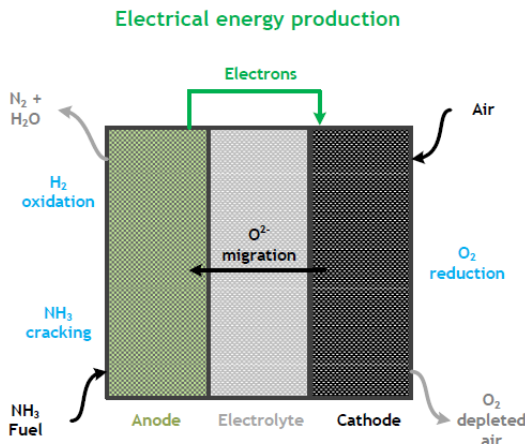


Figure 3: Schematization of SOFC workings (van Linden et al., 2016)

At these high temperatures, an oxidation reaction occurs at the anode side, forming H⁺ and electrons. Electrons from the hydrogen form an electric current (producing electricity) before forming oxygen ions at the cathode side. The electrolyte allows transportation of the negative oxygen ions from the cathode to the anode. Here water (H₂O) is formed from the two ions, producing the residual (gaseous) stream (see Figure 3).

The higher operating temperature does mean a longer start-up and a need for insulation. However, the advantages of this type of fuel cell include long-term stability, fuel flexibility, low emissions and high efficiency. The SOFC has an efficiency between 40 – 60 %, but if the produced heat is reused, efficiencies as high as 85% are possible (DOE, 2017).

When ammonia is used as fuel, at these high operating temperatures, a two-stage process appears to occur (Fuere et al., 2009). First, ammonia is cracked (at >450 °C, in the presence of a catalyst) into nitrogen and hydrogen ($2 \text{ NH}_3 \rightarrow \text{N}_2 + 3 \text{ H}_2$) and then the hydrogen reacts with the oxygen ions to form water ($\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2 \text{ e}^-$). So when ammonia is used as fuel, nitrogen (N₂) is produced as a (harmless) byproduct to the residual stream.

There are some advantages to using ammonia as a fuel: the energy density of liquefied ammonia is higher than that of liquid hydrogen (Fuere et al., 2009), ammonia is less flammable, and the byproducts are nitrogen and water (Cinti et al., 2016). While ammonia is toxic, leaks are easily detected by a human nose (under 1 ppm). It is estimated that ammonia can produce 3.7 kWh/kg-NH₃ (van Linden et al., 2016).

The N2kWh project focuses on recovering ammonia from (anaerobic digestion) reject water (see 1.4), to use the ammonia as a fuel for SOFC.

1.4 Anaerobic Digestion Reject water

This thesis focused on anaerobic digestion reject water only, not urine, as reject water is more readily available (centralized collection).

During biological wastewater treatment, sludge is formed. To reduce this sludge (and its processing costs) it can be anaerobically digested. During anaerobic digestion, microorganisms (in the absence of oxygen) convert the biodegradable fraction of biomass into biogas (CH_4 , CO_2). The organic nitrogen present in the sludge is released/transformed into dissolved NH_3 and NH_4^+ . Dewatering of the anaerobically digested sludge results in reject water, with a high concentration of NH_4^+ (Jenicek et al., 2007)). Usually, the reject water is returned to the nitrification/denitrification step to remove the NH_4^+ , as such the reject water is responsible for 10-25% of the NH_4^+ load in the wastewater treatment plant (Solon, 2015). The typical characteristics of reject water from a municipal wastewater treatment plant are given in Table 1.

Table 1: Characteristics of Reject Water (Solon, 2015)

	Value	Reference
N-Kj	690 – 1700 mg/L	(Wett et al., 1998)
NH_4^+	950 – 2000 mg/L	(Berends et al., 2005)
P_{tot}	< 130 mg/L	(Pitman et al. 1991)
COD	700 – 1400 mg/L	(Thorndahl, 1993)
Temperature	25 – 40 °C	
pH	7-13	(Wett et al., 1998)
Alkalinity	53 – 150 mmol/L	(Wett et al., 1998)
Mg^{2+}	13 – 18 mg/L	(Suschka & Popławski, 2013)
K^+	152 – 195 mg/L	(Suschka & Popławski, 2013)
Ca^{2+}	62 – 89 mg/L	(Suschka & Popławski, 2013)

1.5 Concentrating Ammonium

1.5.1 Suitable Technologies

A literature research presented three technologies to increase the NH_4^+ concentration: Ion Exchange (IEX), Electrodialysis (ED) and Reverse Osmosis (RO).

IEX zeolites are often used for their ability to remove ammonium, due to their selectivity for this ion (Lahav & Green, 1998). There are reports on removing ammonium from sources like digested sludge liquors (Thornton et al., 2007), anaerobic digestion reject water (Guo et al., 2013; Wirthensohn et al., 2009) and landfill leachate (Ye et al., 2015). While IEX is very efficient at removing ammonia from solution (>95% removal was observed (Thornton et al., 2007)). The maximum concentration that can be achieved with IEX is not reported in the found reports because the focus is put on regenerating the IEX zeolite so it can be used again.

ED is usually used for desalination and production of table salt, but novel applications are found in environmental and biotechnological industries (Lee et al., 2003). Applications include removing ammonium sulfate from fermentation waste, recovering and concentrating of ammonia from swine manure (Mondor et al., 2008) and treatment of steam condensate from ammonium nitrate production (Melnikov et al., 2016). Reported maximum concentrations range from 1.7 to 14 g NH_4^+ /L depending on feed concentration, applied current and feed flow (Melnikov et al., 2016; Mondor et al., 2008). Other reports focus on removal (72% removal (Lee et al., 2003)) and “clean” water ammonium concentration (lowest found ammonium concentration is 27 mg NH_4^+ /L (Siminiceanu & Cotet, 2005)).

RO has been researched to remove ammonium from different sources, like mine effluent water (Awadalla et al., 1994; Hayrynen et al., 2009), anaerobic digesters (Carter et al., 2015), landfill leachate (Kosutic et al., 2015; Linde et al., 1995) and manure (Masse et al., 2008). With reported maximum rejection (percentage of concentration removed) varying from 82% to 99% resulting in concentrations in the concentrate varying from 0.1 to 13 g NH_4^+ /L. The large variation in results are caused by the difference in the feed concentration, the pressure applied, permeate flow, the membrane used and what counter-ion was present in the solution (for example SO_4^{2-} , NO_3^- or HCO_3^-). However, the reports did show that RO is suitable to increase the concentration of ammonium.

1.5.2 Knowledge Gaps

In choosing the technology for a project like N2kWh it is important to remember that the concentration step is a part of a larger process to produce energy from ammonium. Increasing the concentration of NH_4^+ can have a positive effect in the next step, where NH_3 gas is extracted. An increase in gas extraction would mean higher fuel production and ultimately higher energy production, but the concentration step also uses energy. So the energy used for a certain ammonium concentration, achieved by one of the technologies, has to be known to see if the concentration step has a positive effect on the overall energy efficiency of the process as a whole.

In order to make a choice on which technology is best suited for a particular process, a comparison should be made on the basis of what concentration can be achieved and the energy that is needed for that concentration. While the different reports in paragraph 1.5 show that the different technologies are suitable for ammonium removal/concentration, making a comparison is difficult because of two factors:

1. The concentrations found in the various reports were produced using different feed concentrations and chemical compositions.
2. Very little is reported on the energy that is needed in the process.

This thesis sought to fill these knowledge gaps by performing experiments with these technologies, using the same feed water, while also focusing on used energy during the experiments.

1.6 Technologies

As this thesis focused on IEX, ED and RO, this paragraph gives an overview of these three technologies. Explaining the basic workings of each technology.

1.6.1 Ion exchange

An ion exchanger is (usually) a resin or zeolite in which an ion is bound to this zeolite or resin. This ion (Na^+) can be released to allow the ion exchanger to bind with another ion (NH_4^+). This process results in a solution without the targeted ion (NH_4^+), called the permeate (see Figure 4; top). Ion exchangers are divided into cation exchangers (which exchange cations) and anion exchangers (exchanging anions).

The ion exchanger can then be regenerated. Releasing the second ions (NH_4^+) to allow the ion exchanger to bind with the ions in the regeneration solution (Na^+), the released ions end up in the regenerant (see Figure 4; bottom). Essentially, the targeted ion (NH_4^+ in Figure 4) is removed from one solution (feed water) and released in another (the regenerant).

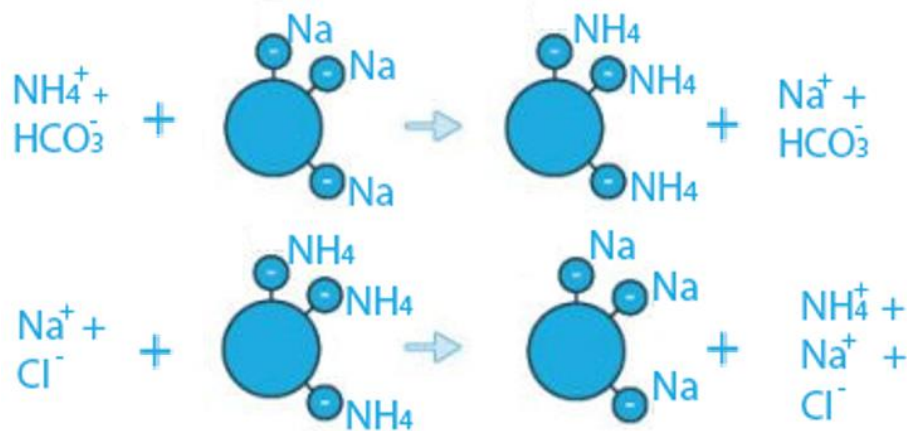


Figure 4: Schematization of Ion Exchange Zeolite; Top: Loading with NH_4^+ ; Bottom: Regeneration with (high) NaCl /L concentration (Merck BV, 2017)

1.6.2 Electrodialysis

Electrodialysis uses an electrical current and ion exchange membranes to separate ions into a diluate (low concentration) and concentrate (high concentration) stream. Two streams pass through the electrodialysis cell (ED cell) divided into smaller streams, separated by cation- and anion-exchange membranes, alternating the two streams, while an electrical potential is applied perpendicular to the flow. In the solutions, the cations are attracted by the cathode and migrate from one stream to the next towards the cathode. Similarly, anions are attracted by the anode and migrate in the opposite direction from one stream to the next towards the anode (see Figure 5). Ion flux is dependent on the cross flow velocity (of the concentrate and diluate) through the ED-cell and the applied current on the ED-cell. The electrolyte flow passes the cathode and anode (not shown in Figure 5), the NaNO_3 solution provides electrons which pass the power supply to form a closed circuit.

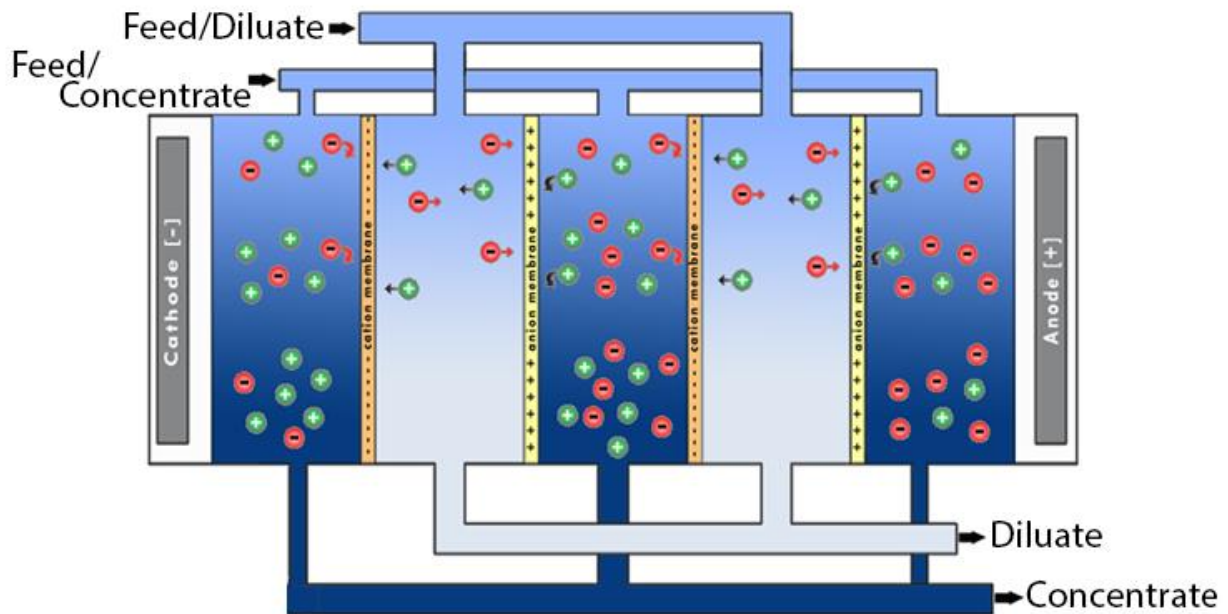


Figure 5: ED Cell Schematization ("Electrodialysis Reversal," 2016)

While cations migrate toward the cathode and the anions migrate towards the anode, the cation- and anion-exchange membranes (separating the diluate and concentrate streams) reject anions and cations, respectively. Cation-exchange membranes ("ion exchange resin in film form" (Strathmann, 2010)) contain negatively charged ions fixed with its polymer (negatively charged membranes in Figure 5). These ions form an equilibrium with the cations which cross the membrane, while anions are rejected. So cation-exchange membrane only allows cations to cross while anions are rejected, while similarly, anion-exchange membrane only allows anions to cross while cations are rejected.

The ED cell has an anode on the left and a cathode on the right (see Figure 5); while negative ions are attracted to the left they pass an anion-exchange membrane and are stopped by the next membrane, a cation-exchange membrane, and the opposite happens with cations. So streams with a cation-exchange membrane on the left and an anion-exchange membrane on the right "hold" ions while the other streams "lose" ions, resulting in a concentrate and diluate stream respectively (see Figure 5).

1.6.3 Reverse Osmosis

Reverse Osmosis uses high pressure to feed water through a semipermeable membrane that blocks certain ions, molecules and larger particles, resulting in a permeate with a low concentration of solvents.

1.6.3.1 Osmosis

When two containers of water, with different concentrations of ions, are connected via a semipermeable membrane, water will cross from one container to the other, from low concentration to high. This increases the volume (and decreases the concentration) in one container while decreasing the volume (and increasing the concentration) in the other until an equilibrium between the concentrations (of the two containers) is formed. This is called osmosis. The driving force behind this process is called osmotic pressure, an increase in the concentration of ions results in an increase of osmotic pressure (see Figure 6).

1.6.3.2 Reverse Osmosis

In reverse osmosis the flow of water is reversed, i.e. from high concentration to low, resulting in a permeate flow with a low concentration of ions and other contaminants. The membrane is semipermeable, meaning it will allow water to pass but will reject ions, molecules and larger particles. A pressure is applied to the feed flow to compensate for the osmotic pressure difference (between the permeate and feed flow) (see Figure 6).

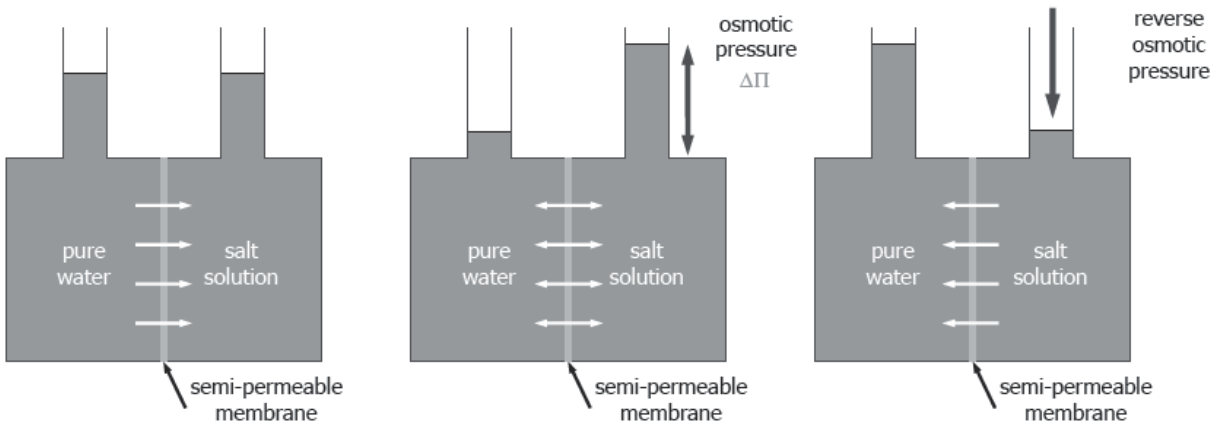


Figure 6: Schematization of Osmosis and Reverse Osmosis (van Lier et al., 2011)

1.6.3.3 ROSA

IEX and ED are easily applied in a laboratory scale set-up to be used for experiments, but the high pressures needed for an RO (to reach the similar NH_4^+ concentrations as with IEX and ED) cannot be safely provided in laboratory scale set-up (within the TU Delft laboratory).

ROSA (Reverse Osmosis System Analysis) software is able to model pressures needed to produce various concentrate NH_4^+ concentrations. ROSA is a design tool made by DOW chemicals (DOW Software, 2016). With input on feed concentration and RO set-up, it gives a report on water quality, flow rates and pressures. It acts as a first design tool, giving information on required vessels (membranes) and energy used by the set-up for the desired permeate concentration. However, the model is not usually used for scientific research. So experimental measurements were compared to the results of the model to validate the model. When validated, ROSA was then used to estimate the achievable NH_4^+ concentrations and energy used by RO.

1.7 Research Objective

This thesis focused on choosing a technology to increase the ammonium concentration. The three technologies operate very differently from each other: IEX removes NH_4^+ from a solution by binding it to the zeolites, ED uses a current to migrate NH_4^+ ions from one stream to the next and RO uses high pressure to feed water through a membrane resulting in a concentrate with a high NH_4^+ concentration.

This means it is difficult to compare the three technologies with each other. But by using the same feed water for all three technologies, the achieved NH_4^+ concentrations can be compared. A 1.5 g NH_4^+ /L solution was used as this feed water (see 3.1). And while the three technologies use different methods to increase the NH_4^+ concentration, all three use energy: pumping the solution through the RO membrane, over the IEX bed and pass the ED (which also applies a current). The used energy can also be used to compare the three technologies.

By focusing on the achievable NH_4^+ concentration and the energy that was used during the experiments, the knowledge gaps introduced in 1.5 would be filled.

The research objective was:

Find the achievable ammonium concentrations and the energy used, produced from a 1.5 g NH_4^+ /L feed water, by Ion Exchange, Reverse Osmosis and Electrodialysis.

To reach this objective there were several research questions:

Because IEX consists of two steps (i.e. loading and regeneration) the research questions focused on these steps separately. The research questions with regards to IEX were:

1. What is the NH_4^+ concentration in the permeate after loading of IEX bed, compared to the 1.5 g NH_4^+ /L feed solution. This indicates the removal efficiency of the IEX zeolite
2. What concentrations can be achieved by regenerating a saturated IEX bed
3. What is the energy used by pumping the solution during loading and regeneration, to achieving these NH_4^+ concentrations

Before achievable NH_4^+ concentration using ED could be found, first the most energy-efficient set-up regarding the flows over the ED-cell and current applied to the ED-cell had to be found. The research questions with regards to ED were:

1. What is the most energy efficient set-up regarding flows through and current density applied to the ED-cell
2. What concentrations can be achieved with ED, using the 1.5 g NH_4^+ /L feed solution
3. How much energy is used by the current that is applied to ED cell, to achieve these NH_4^+ concentrations

Pressures needed to achieve high NH_4^+ concentrations were not able to be produced with a laboratory set-up. ROSA model was used to simulate these pressures. Because the model is not usually used for experiments, experimental measurements were used to validate the model. If the model was validated for the low pressures, the model was used to estimate the achievable NH_4^+ concentrations and the energy used by RO. The research questions with regards to RO were:

1. Is the ROSA model validated by the experimental measurements
2. What concentrations can be achieved with RO, according to the ROSA model with 1.5 g NH_4^+ /L feed solution
3. What is the energy used by RO to achieve these concentrations, according to the ROSA model

1.8 Thesis Lay-Out

This thesis holds nine chapters:

- Chapter 1 Introduction: the need for new research was introduced, an overview was given of the technologies that are the focus of the thesis. The research objectives and research questions were also presented.
- Chapter 2 Theoretical Background: Relevant theoretical background information was given on anaerobic digestion, ammonium bicarbonate and the three technologies: IEX, ED and RO.
- Chapter 3 Materials and Methods: The set-up of the experiments performed to answer the research questions were presented. The feed water, used during the experiments was introduced as well.
- Chapter 4 Results: The results of the experiments were presented; The achievable NH_4^+ concentrations and the energy used per m^3 of produced concentrated NH_4^+ solution were reported for each technology.
- Chapter 5 Discussion: Effects of using real reject water as feed water was discussed, expected negative effects differ between the three technologies.
- Chapter 6 Conclusions: The conclusion of the research questions and objective were discussed using the results and discussion. Before an overview of the three technologies was given, the research questions on each technology were answered separately.
- Chapter 7 Recommendations: Research topics that arose over the course of the thesis were presented here for future research.
- Chapter 8 Appendix: Elaboration on calculations presented in the thesis.
- Chapter 9 Bibliography

2 Theoretical Background

2.1 Anaerobic Digestion

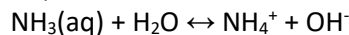
Anaerobic digestion is a fermentation process in which organic material is degraded and biogas (mainly CH₄ and CO₂) is produced. In a wastewater treatment plant activated sludge, produced during aerobic treatment, is treated with anaerobic digestion. Anaerobic digestion removes the biodegradable organic compounds from the sludge while producing biogas as well as mineralized compounds like NH₄⁺. The produced sludge is stabilized and reduces the amount of activated sludge up to 90% (van Lier et al., 2011).

The process can be divided into four phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Since bacteria are unable to take up the large polymeric particles (making up the organic matter of the sludge), during hydrolysis they are degraded into smaller molecules. During hydrolysis amino acids, simple sugars and long chain fatty acids are produced. In the acidogenesis step, these products are fermented or anaerobically oxidized into mainly volatile fatty acids, (i.e. acetate, propionate and butyrate), H₂, CO₂ ethanol, NH₃ and carbonic acid (H₂HCO₃). Fatty acids (other than acetate; produced during acidogenesis) are converted into acetate, H₂ and CO₂ during the acetogenesis step. In the methanogenesis step acetate, with water, is converted to CH₄ and HCO₃⁻ by bacteria. During the same step, other bacteria use CO₂ and H₂ to produce CH₄ (van Lier et al., 2011).

The organic nitrogen present in the sludge is released/transformed into dissolved NH₃ and NH₄⁺ during acidogenesis. While ammonia is an essential nutrient for bacterial growth, high concentrations may inhibit methanogenesis (Yenigun & Demirel, 2013). Controlling the feedstock C:N ratio, pH and operating at a low temperature are feasible options to reduce ammonia toxicity during anaerobic digestion (Rajagopal et al., 2013). So, during stable/normal operation of anaerobic digestion, ammonium concentration is found inside a range, i.e. 950 – 2000 mg/L (Berends et al., 2005), see Table 1.

2.2 NH₄HCO₃

Since the NH₄HCO₃ solution was used to make the feed water (see 3.1), it is important to know how NH₄HCO₃ behaves in solution. Both NH₄⁺ and HCO₃⁻ are in an equilibrium depending on the pH and temperature of the solution. NH₄⁺ is in equilibrium with NH₃:



Whether a solution holds NH₃ or NH₄⁺ depends on the pH and temperature of that solution, as shown in Figure 7. The lines show the percentage of the ion or gas in solution, as a function of pH and temperature.

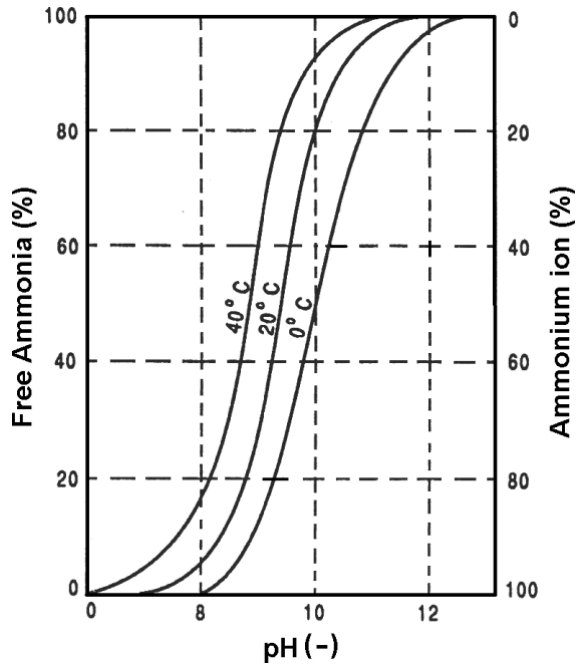


Figure 7: Graph: $\text{NH}_3 - \text{NH}_4^+$ Equilibrium, depending on pH and temperature (Capodaglio et al., 2015)

HCO_3^- is in equilibrium with CO_2 and CO_3^{2-} :

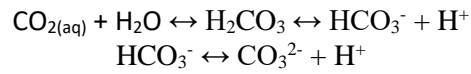


Figure 8 describes the equilibrium between H_2CO_3 , HCO_3^- and CO_3^{2-} as a function of pH and temperature.

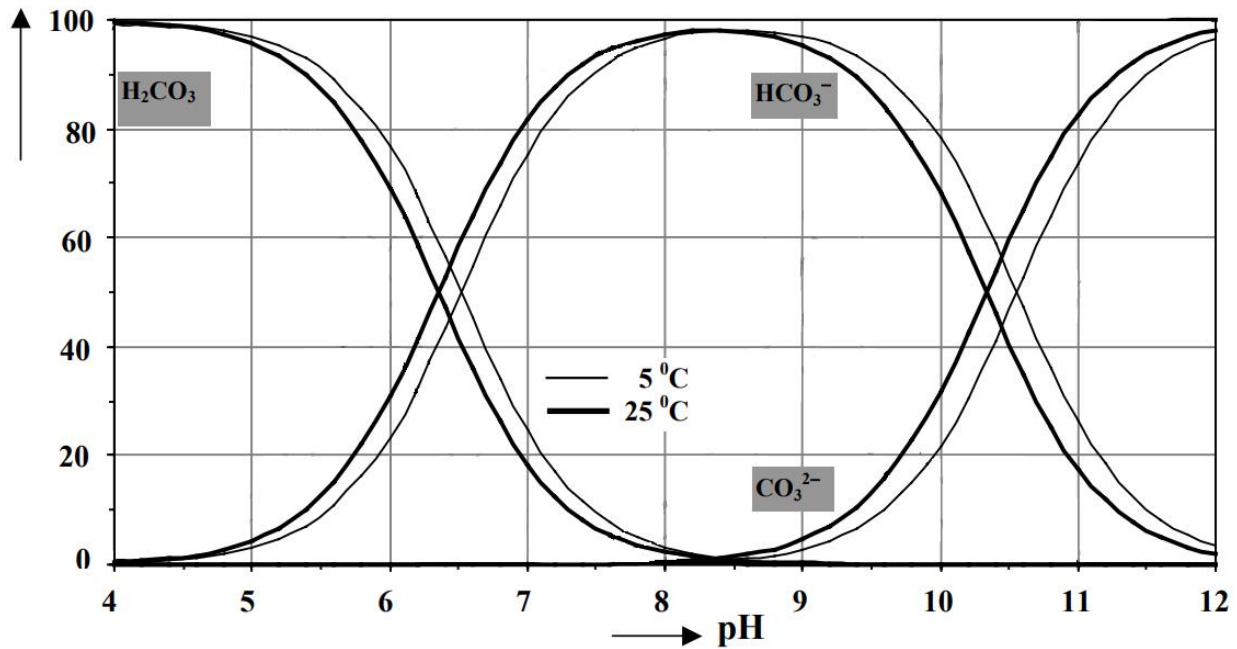


Figure 8: Graph: $\text{H}_2\text{CO}_3 - \text{HCO}_3^- - \text{CO}_3^{2-}$ Equilibrium, depending on pH and temperature (IAEA, 2016)

The pH of the 1.5 g NH_4^+ /L solution was about 8 (within the range found in Table 1) and temperatures varied between 18 and 25 °C, resulting in a solution of mainly NH_4^+ and HCO_3^- . This means that it is not necessary to alter the pH or alter the temperature in the experiments as all the technologies operate with these ions:

- The RO rejects the HCO_3^- ions, and by electro-neutrality the NH_4^+ ions.
- IEX zeolites exchanges NH_4^+ for Na^+ .
- ED transports only ions from the diluate to the concentrate stream.

2.3 Ion Exchange

2.3.1 Bed Volume

Bed volume (BV) is a normalized unit, used to denote the flow over an IEX bed, given in BV/h. BV is also used to show what amount of volume has passed the IEX bed, before breakthrough occurs or when regeneration is complete. This means that results from a small (laboratory scale) set-up can be used for a larger (full scale) set-up when using the same flow (in BV/h). While the absolute flow is bigger in a full scale set-up, when BV/h is the same as in the laboratory scale set-up, breakthrough occurs after the same time period. Regeneration time is also the same for both set-ups.

2.3.2 Loading

During loading of the IEX bed a solution is fed through a column with a bed of ion exchanger, here the targeted ion (NH_4^+) is bounded with the ion exchanger and another ion is released (Na^+), resulting in a flow without NH_4^+ . At some point, when most of the ion exchanger holds NH_4^+ , NH_4^+ is again found in the solution, this is called breakthrough. The ion exchanger is then regenerated. See Figure 9 for a schematization of the IEX process.

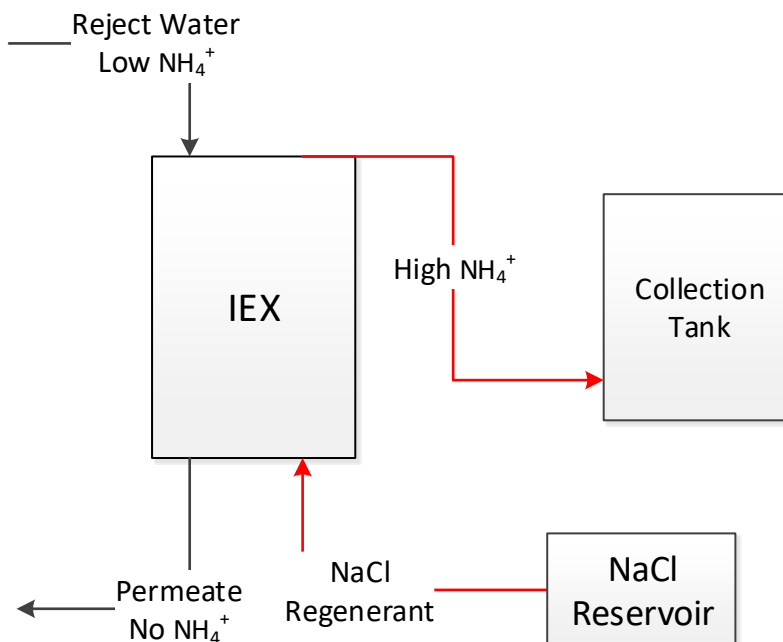


Figure 9: IEX schematization; Loading (black line) and Regeneration (red line)

2.3.3 Regeneration

During regeneration the bed is “flushed” via a countercurrent flow with a solution with a high concentration of Na^+ (this solution is called the regenerant), resulting in another ion exchange. The regenerant now holds the NH_4^+ , with a high concentration of NaCl (not all Na^+ is used during regeneration). After regeneration, the bed is ready for reuse.

2.3.4 Zeolite and Resin

Zeolites are microporous minerals that are naturally occurring and mined in open-pit mining. The porous structure of the zeolites can hold a variety of ions, but these can easily be exchanged.

Ion exchange resin is synthetically produced porous beads that provide a large surface area. The resin is made out of a polymer that holds an ion (which is part of the polymer), this ion can hold and exchange another ion. Zeolites can also be synthetically produced/alterd to have a higher capacity for ions, i.e. $\text{g}_{\text{ion}}/\text{g}_{\text{zeolite}}$.

While resin and synthetic zeolite have a higher capacity and efficiency for ion exchange, natural zeolites have a higher selectivity for NH_4^+ (Dyer, 2007). A higher selectivity for NH_4^+ , means zeolites have a higher affinity to bond with NH_4^+ .

2.4 Electrodialysis

2.4.1 Concentration Polarization

Concentration polarization takes place at the membrane surface. Directly at the surface of the concentrate side of the membrane, the concentration is highest with ions coming through the membrane, before being mixed with the solution. At the diluate side, the concentration is lowest directly on the surface, where ions go through the membrane. There are various parameters that influence the concentration polarization; the applied current, the velocity parallel to the membrane and the concentration in the diluate (Lee et al., 2006).

2.4.2 Limiting Current Density

The ion flux is the speed at which ions flow from the diluate to the concentrate, divide by the area of the membrane. The ion flux depends on the concentration in the diluate stream, the cross flow velocity through the ED cell and the current density applied to the ED cell. The current density is the current applied to an ED cell, divided by the area of the membrane.

A higher current density means more energy available to move ions (ammonium) from diluate to concentrate, but there is a limit to the current density which can be efficiently applied. At a certain point, the concentration in the diluate is so low that the concentration directly at the membrane (due to concentration polarization see 2.4.1) reaches zero. At this point, the membrane/solution is no longer conductive. The current density at which this occurs is called the limiting current density (LCD). Applying a current above the LCD results in energy being used to split water into H^+ and OH^- , which is wasted energy. So the current density should be kept below the LCD. The value of the LCD is dependent on the concentration in the diluate stream and the cross flow velocity of the diluate stream. The LCD is calculated in 8.1, Appendix A.

2.4.3 Electro-Osmosis

ED is designed to migrate ions from a low concentration stream (diluate) to high concentration stream (concentrate) while leaving water in its original stream. However, the ion migration always includes a co-migration of water. When there is an ion flux as a result of a current, a kinetic coupling occurs. This coupling is called electro-osmosis (Han et al., 2015). The electro-osmosis decreases the efficiency of the ED, as adding water to the concentrate decreases its concentration. The amount of water that co-migrates with the ion is linked to the hydration number of that ion, however, it is difficult to determine theoretically (Han et al., 2015) (so it is not determined beforehand during this thesis).

2.4.4 Electrodialysis Reversal

As in most membrane separation processes, fouling can be a problem during electrodialysis (Strathmann, 2010). Ions or suspended solids (SS) with an electrical charge (such as humic acids and biological materials) can be deposited on the membrane surface (scaling), increasing the resistance of the membranes (Strathmann, 2010). By reversing the polarity of the current applied to the ED cell (in a certain time interval), the negative effect can be largely reversed (Strathmann, 2010). This technique is called electrodialysis reversal (EDR).

A negatively charged SS migrates towards the anode until it is rejected by a cation-exchange membrane. Over time this can cause fouling at the membrane. By reversing the polarity, the negatively charged SS migrates towards the cation (which is now the anode), effectively removing the SS from the membrane.

2.5 Reverse Osmosis

2.5.1 Spiral Wound Membrane

A commonly used configuration is the spiral wound, shown in Figure 10. It maximizes the surface area within the tube and is a cheaper configuration (Li & Yan, 2016). A spiral wound membrane is operated in cross-flow, meaning the feed solution is fed past the membrane. Through a pressure difference over the membrane, the water passes through the membrane to the permeate collection material. From there it flows to the center of the permeate collection holes and out through permeate output. The concentrate (or 'Retentate') with an increased NH_4^+ concentration ends up at the other end of the membrane.

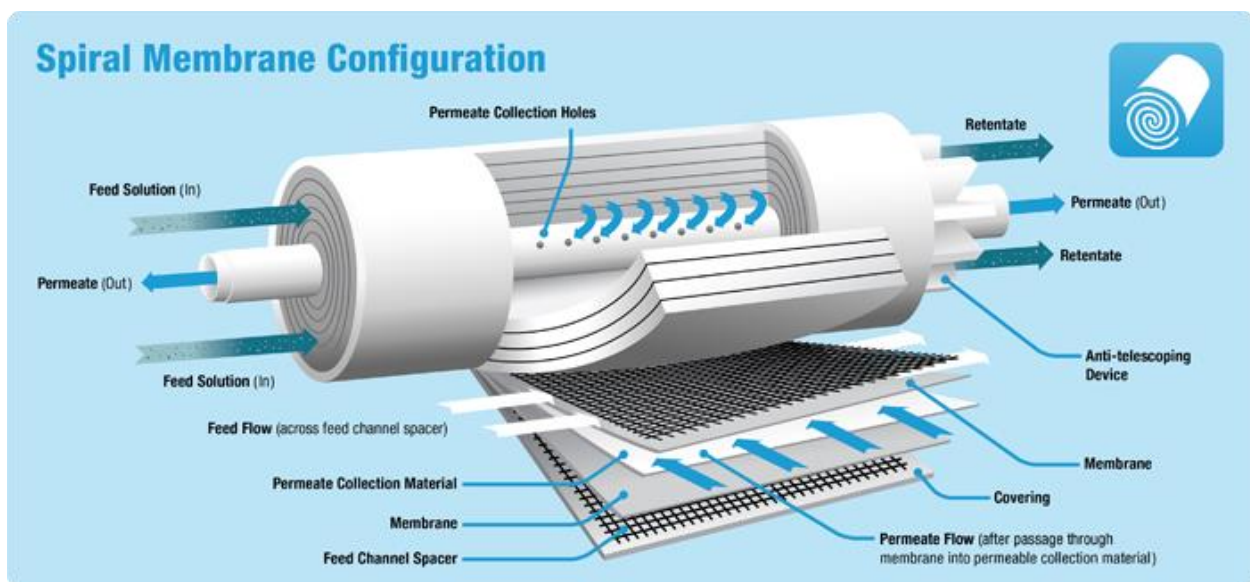


Figure 10: RO - Spiral Wound Membrane schematization ("Learning-Center," 2017)

Due to the way the membranes are produced the membrane is negatively charged (at pH>3), which helps to reject negative ions and, by electro-neutrality, the positive ions (in this case the NH₄⁺) as well (Childress & Deshmukh, 1998).

2.5.2 Trans Membrane Pressure

To push the water through the membrane a pressure is needed to overcome the osmotic pressure, preventing osmosis. This pressure is called the trans membrane pressure (TMP). The TMP is calculated by “the average pressure over the membrane” minus the permeate pressure or:

$$(P_{\text{feed}} + P_{\text{concentrate}})/2 - P_{\text{permeate}} = \text{TMP}$$

Where the feed pressure (P_{feed}) is the pressure applied to the feed flow because the spiral wound configuration is operated in cross-flow the concentrate flow still holds a high pressure ($P_{\text{concentrate}}$). The pressure in the permeate flow (P_{permeate}) is usually low (or atmospheric).

2.5.3 Recovery

The percentage of feed water that ends up as permeate is called the recovery. A higher recovery means more permeate, also less concentrate but with an increased NH₄⁺ concentration. Of course, an increase of the recovery also means an increase in energy use. Usually, multiple membranes are placed after each other (called stages), so the concentrate passes multiple membranes, to increase the overall recovery.

2.5.4 Limiting Factors

The performance of the RO process is negatively influenced by different phenomena: concentration polarization, fouling, scaling and biofouling. They are explained in this paragraph.

2.5.4.1 Concentration Polarization

Rejection of dissolved matter by the RO membrane results in an accumulation of these substances. The highest concentration occurs directly at the membrane, this is called concentration polarization (Macedonio & Drioli, 2010). The increase concentration results in an increase in osmotic pressure, which increases the pressure needed in the feed flow as well as the leakage of solute through the membrane (Macedonio & Drioli, 2010).

2.5.4.2 Fouling

One form of fouling is chemical fouling, or scaling. Scaling is where concentration polarization or (due to high recovery) increases the concentration of an ion, until their solubility is exceeded, resulting in precipitation (most likely to cause scaling are Ca²⁺, Mg²⁺ and CO₃²⁻ ions (Macedonio & Drioli, 2010)). Lowering of the pH or adding anti-scaling agents can reduce the effects of scaling (Macedonio & Drioli, 2010).

Another form is biological fouling. Microorganisms present in the feed water can, under favorable conditions, form a biofilm by reproducing on the membrane. The concentration of nutrients available in the feed water is increased as well, creating an ideal environment for the microorganisms. Due to the biofouling, the permeability of the membrane is reduced, so feed pressure has to be increased. Biodegradation is also possible, where acidic by-products of the microorganisms damage the membrane (Macedonio & Drioli, 2010).

Physical fouling is caused by SS, colloidal, and microorganism matter on the membrane. Membrane (microfiltration (MF) and/or nanofiltration (NF)) pretreatment can usually remove these, colloidal particle sometimes require coagulation or flocculation (Macedonio & Drioli, 2010).

3 Materials and Methods

3.1 Feed Water

This thesis focused on the concentration step, trying to find the technology best suited to increase the NH_4^+ concentration. To compare the concentrations achievable with the three technologies the reject water was simulated by a solution of ammonium bicarbonate. Bicarbonate was chosen as a counter-ion because bicarbonate is produced during anaerobic digestion (carbonic acid (H_2HCO_3) produced during acidogenesis (see 2.1) dissolves into bicarbonate (van Lier et al., 2011)). Other compounds were left out to isolate the effect of the NH_4HCO_3 solution. When later experiments add other compound found in reject water, results from this thesis can be used as a benchmark to evaluate the effects of these compounds. Because this thesis focuses on NH_4^+ , a 1.5 g NH_4^+ /L (= 1.17 g $\text{NH}_4^+\text{-N/L}$) solution was used as feed water in all the experiments (this falls in the middle of the range found in Table 1). To produce this concentration, a 6.6 g NH_4HCO_3 /L solution is made with Honeywell Ammonium bicarbonate (A6141, >99% reagent grade).

3.2 NH_4^+ Measurements

Because this thesis focuses on the NH_4^+ concentration it is important to be able to measure this concentration. This is done in two ways: in situ, by measuring the electrical conductivity and relating this to the concentration through calibration, and by taking a sample and using a Macherey-Nagel Nanocolor Photometric Water Analysis.

3.2.1 Electrical Conductivity

Electrical Conductivity (EC) is a measure of the ability of a solution to conduct an electrical current. An increase in the concentration of ions comes with an increase in EC. Since the solution in the experiments only holds NH_4HCO_3 , a higher EC means a higher NH_4HCO_3 concentration. By measuring the EC of various solutions with known concentrations, an EC- NH_4^+ relationship can be calculated. The found relationship was given in 8.2, Appendix B.

Because the EC is measured continuously, the increase and decrease of the concentrations could be followed in real time. Giving a good indication of how the experiment was going. However, for the IEX experiments, EC could not be applied because the Na^+ ions influenced the EC. So to compare all three technologies, with more precise measurements, a Photometric Water Analysis test kit was used.

3.2.2 Analysis of NH_4^+

The photometric water analysis that was used, was Macherey-Nagel Nanocolor Ammonium 200/2000 test kits (MN test kits). The test kit contains two test tubes. A 500 μL sample is added to the first test tube, where an acidic solution ensures that all NH_4^+ and dissolved $\text{NH}_3(\text{aq})$ is turned to NH_4^+ (see 2.2). 200 μL of this solution is then added to a second test tube, where the ammonium reacts with the present hypochlorite and salicylate, in the presence of sodium nitroprussiate as a catalyst, to form a green indophenol. The test tube is then read by a Macherey-Nagel Nanocolor VIS II spectrophotometer. The spectrophotometer measures the color intensity in the test tube. A high intensity means more hypochlorite reacted, which means a high concentration NH_4^+ (see cover page). Because of the solution in the first test tube, this analysis actually measures both NH_4^+ and $\text{NH}_3(\text{aq})$. But only a small fraction is present as $\text{NH}_3(\text{aq})$ (see 2.2). The deviation between known and measured NH_4^+ concentrations (giving an indication of the precision of the MN test kits) are given in 8.2, Appendix B.

3.3 Comparing the Technologies

The technologies that were compared, differ in how NH_4^+ concentrations were increased (using zeolites, electrical current over- or high pressure through a membrane). Because all the experiments used the same 1.5 g NH_4^+ /L feed water, the achieved concentrations could be used to compare the three technologies.

The following paragraphs show the set-ups that were used during the experiments of the three technologies. The experiments focused on finding the achievable concentrations and the amount of energy that was used in the process.

The experiments that were performed produced different amounts of concentrated NH_4^+ solutions for the different technologies, so comparing the energy used was difficult. Results found with laboratory scale set-ups, during experiments, were then used to calculate the energy used in a full scale set-up to produce 1 m³ of concentrated NH_4^+ solution. This was done for all technologies, so these results could be used to compare the three technologies.

3.4 Set-Up IEX

3.4.1 Loading by Feed water

The IEX experiments were executed with a laboratory scale IEX column with an approximate height of 24 cm and a diameter of 1.5 cm, resulting in a bed volume of approximately 42 mL. Loading was supplied from a 1 L reservoir with a 1.5 g NH_4^+ /L feed solution. It was pumped through the column by a Watson Marlow 120U pump, connected by 4.5 mm flexible plastic tubing (see Figure 9 and Figure 11).

3.4.2 Regeneration



Figure 11: Photo of IEX Laboratory Set-Up; Regenerant (right reservoir) was pumped up through the IEX bed and collected in clean reservoir (left).

Regeneration is carried out in a counter-current flow, where the regeneration solution flows up through the IEX bed. Counter-current regeneration has a higher efficiency and lower leakage of ammonium in the permeate stream (compared to co-current, (DOW Chemical, 2013). Regeneration with a high concentration NaCl causes the ammonium to release from the zeolite, increasing the concentration of ammonium in the regenerant. During regeneration, the same tubing used during loading was rearranged to allow the counter-current flow, seen in Figure 11.

Two solutions were used to regenerate the ion exchange zeolite. A 100 g/L NaCl (DOW Chemicals, 2013) solution and a NaOH solution with pH=12.5 (Guo et al., 2013).

While Na^+ is used to replace the ammonium on the zeolite the Cl^- (in the NaCl solution) has no function, and ends up in the regenerant flow (with NH_4^+). The hydroxide (in the NaOH solution) had the possibility of reacting with the ammonium. This reaction results in the formation of ammonia ($\text{NH}_4^+ + \text{OH}^- \rightarrow \text{NH}_3 + \text{H}_2\text{O}$). This could be beneficial for two reasons; ammonia cannot react with the ion exchange zeolite anymore, which could increase regeneration efficiency. And the ammonia is already in the form needed for the SOFC. If the ammonia is also converted from $\text{NH}_3(\text{aq})$ to $\text{NH}_3(\text{gas})$ fewer process steps are needed. A schematization is given in Figure 12.

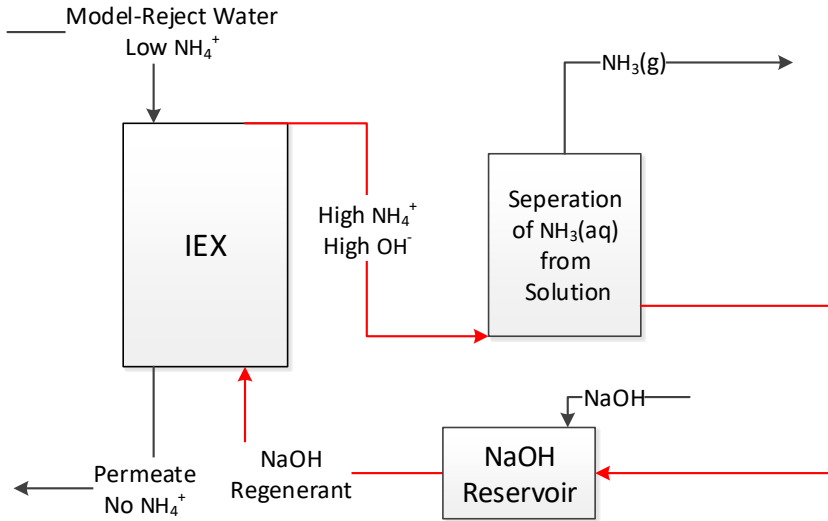


Figure 12: Schematization of IEX Laboratory Set-Up, regeneration with pH 12.5 solution; Loading (black line) and Regeneration (red line)

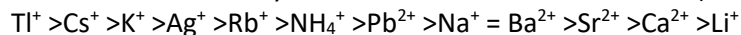
The experiment was executed at 2 flows for loading and regeneration flows; 6 and 13 BV/h, which was suggested in previous research (Ye et al., 2015).

3.4.3 Zeolite

Natural zeolites were used during the IEX experiments. Due to the high selectivity for NH_4^+ , a purer NH_4^+ concentration (after regeneration) can be produced, because fewer other ions are exchanged.

The IEX zeolite used for the experiments was St. Cloud mining Bowie Chabazite (AZLB-Na). Also available was Ash Meadows Clinoptilolite, but this had a lower capacity, which would result in a faster breakthrough (Leyva-Ramos et al., 2010; "St Cloud Data Sheets," 2016).

The order of selectivity for the Bowie Chabazite zeolite is (St.Cloud, 2013):



The zeolite has the highest "affinity" for thallium and lowest for lithium.

3.4.4 Full scale Set-Up

For IEX, only the used energy for pumping the feed and regenerant through the IEX bed was considered. The used energy for pumping during the laboratory experiment could not be measured directly and scaled to full scale set-up because deviations in flow patterns can exist (i.e. small air bubbles have a larger effect in laboratory scale set-ups) (Verbeek et al., 2011). So assumptions had to be made about the size of a full scale set-up. Then Kozeny-Carman was used to calculate the pressure drop over the (full scale) IEX bed.

In a full scale set-up, it is assumed that two IEX beds would be placed behind the first. This allows the saturated bed to be regenerated while still processing the reject water. This also means the first bed could be fully loaded while not allowing ammonium to end up in the outflow. Because the bed is fully loaded (holds more NH_4^+ ions) a higher concentration can be achieved during regeneration.

3.4.4.1 IEX Vessel Size

To calculate the energy used by IEX, some assumptions about the size of the IEX vessel (or bed) were made. A typical depth of 2m is chosen and a diameter of 2m to keep the ration of height to diameter between 2/3 – 3/2 [-], this gives a good distribution over the bed and limits the pressure drop over the bed (DOW Chemical, 2017). An overview of the estimated vessel size was given in Table 2.

Table 2: IEX Full Scale Set-Up: Estimated Vessel Size

Diameter [D]	2.0	m
Area	3.1	m ²
Height [H]	2.0	m
H/D	1.0	-
BV	6.3	m ³

3.4.4.2 Kozeny-Carman

To calculate the energy needed to pump the feed water and regenerant through the IEX bed, Kozeny-Carman equation was used to calculate the pressure drop over an IEX bed. The Kozeny-Carman equation is given by:

$$\Delta p = \frac{150\mu}{\Phi^2 D^2} * \frac{(1-\varepsilon)^2}{\varepsilon^3} * v * L.$$

With Δp = pressure difference [Pa], μ = dynamic viscosity [Pa*s], Φ = sphericity [-], D = IEX zeolite diameter [m], ε = porosity [-], v = empty bed velocity [m/s], L = bed length [m](McCabe et al., 1993).

The assumed values for the parameters (Heijman, 2017) and calculated pressure drop over the (full scale) IEX bed during loading and regeneration were given in Table 3 and Table 4.

Table 3: IEX Full Scale Set-Up: Pressure Drop during Loading

D	0.001	m
μ	0.001	Pa.s
ε	0.4	-
Φ	0.8	-
v	0.003	m/s
L (3 IEX beds)	6	m
Δp	26	kPa
Δp	2.7	m

Table 4: IEX Full Scale Set-Up: Pressure Drop during Regeneration 100 g NaCl/L

D	0.001	m
μ	0.001	Pa.s
ε	0.4	-
Φ	0.8	-
v	0.007	m/s
L (1 IEX beds)	2	m
Δp	18	kPa
Δp	1.9	m

Results from the laboratory experiments on loading and regeneration time can then be used together with these pressure drops to calculate the energy used by a full scale set-up.

3.5 Set-Up ED

An ED three streams; the concentrate, diluate and electrolyte. In the laboratory scale set-up, the three streams were recirculated through the ED cell and the three separate 1 L reservoirs until the required diluate NH_4^+ concentration is achieved. Recirculated was done by a Watson Marlow 520S pump with three separate heads (operating at the same speed). A 1 cm compressible malprene tube was used in the pump heads and connected, by 8 mm plastic tubing, to the ED cell and reservoirs. The current was provided by a Tenma 72-2535 programmable DC Power Supply. Tenma software was used to log the current and potential on a laptop (see Figure 13 and Figure 14)



Figure 13: Photo of ED Laboratory Set-Up; Concentrate, diluate and electrolyte were recirculated in the three reservoirs (right), pumped by (green) pumps. The current was provided by Tenma DC Power Supply (left), a laptop was used to log measurements.

From the parameters mentioned in 2.4.2, the parameters that could be varied were, the cross flow velocity of the three streams through the cell and the current set over the cell, while the concentration in the diluate decreased during the experiments. The experiment focused on the applied current density (not potential) because the current density had a maximum (LCD, see 2.4.2).

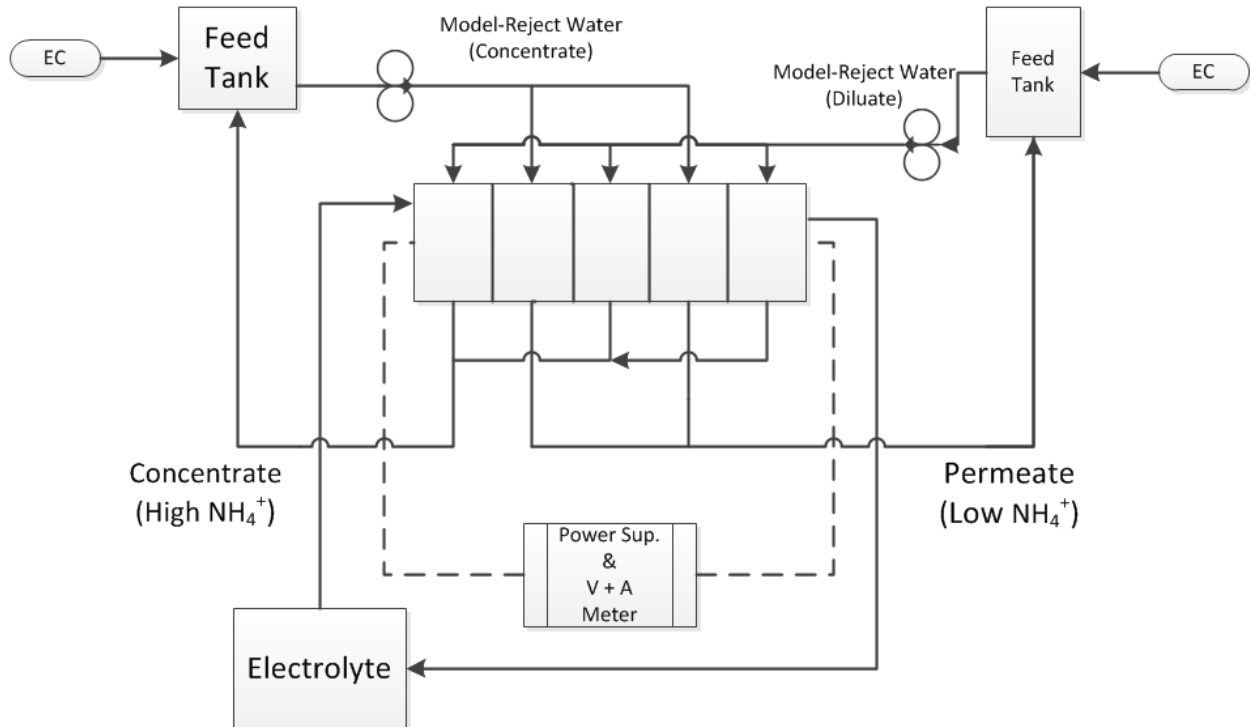


Figure 14: Schematization of ED Laboratory Set-Up

The maximum flow the system (i.e. ED cell + pump + reservoirs + tubes connecting the three) could handle without connections leaking, was found to be 17 L/h or (a cross flow velocity of 43 m/h). Just as with the current, an increase in cross flow velocity results in an increase of ion flux but uses more energy.

So an optimum between the cross flow velocity of the three streams and the applied current had to be found. To see which combination of cross flow velocity/current was the most efficient, the three reservoirs were recirculated (until most of the ammonium had been transported from the diluate reservoir to the concentrate reservoir) under different circumstances with every new run. The cross flow velocities applied were 43 (maximum cross flow velocity for the laboratory set-up) or 14 m/h. The value of 14 m/h was chosen somewhat arbitrarily (if the experiment was found to be more efficient with a lower cross flow velocity, other velocities, between 43 and 15 m/h, would have had to be investigated). The current density that was applied was either at LCD (or maximum current density, see 572.4.2), half of the LCD or at 15.6 A/m². The experiment was repeated six times to see which combination of cross flow velocity and current density was the most energy efficient. During initial test runs, it was decided to apply a minimum of 15.6 A/m² and to stop when the concentration in the diluate reservoir was about 100 - 150 mg NH₄⁺/L (from the initial 1.5 g NH₄⁺/L), to keep the experimental runtime at a reasonable limit.

The most energy efficient combination between applied cross flow velocity and the current density was used to find the maximum concentration. Both concentrate and diluate started with the 1.5 g NH₄⁺/L feed water when the diluate reached an NH₄⁺ concentration of 100 - 150 mg NH₄⁺/L, the experiments were paused to take samples and to replace the diluate reservoir with a new 1 L reservoir of 1.5 g NH₄⁺/L feed water. The concentrate (with increased NH₄⁺) was used again. So with each new reservoir, the concentration of the concentrate increased until a maximum was reached.

3.5.1 Full scale Set-Up

A full scale set-up can be executed in a batch system or a continuous system. In the batch system, the permeate and concentrate flow are recirculated until the desired concentration is reached. The continuous ED system consists of multiple stacks of large ED-cells where the diluate stream makes a single pass (the concentrate stream can be recirculated to minimize concentrate volume) (Valero et al., 2011).

It was assumed that the energy used by the laboratory set-up could be scaled to a full-size set-up. To find the energy used by the full scale set-up. The energy used by the laboratory scale is multiplied by 1000/X (where X = volume of concentrate volume [L]). This results in the energy needed to produce 1 m³ of concentrated NH₄⁺ solution.

3.6 Set-Up RO

To increase NH₄⁺ concentration, a solution with an increased osmotic pressure had to pass the RO membrane, which means that an increased pressure was needed. At some point, high pressures could not be safely provided with the laboratory set-up. To still be able to compare RO with ED and IEX a software program (ROSA) was used to estimate the achievable NH₄⁺ concentrations of a full scale set-up. Results found with the lower pressures and concentrations (that were possible to run with the laboratory scale set-up) were used to validate some of the results found with ROSA.

3.6.1 OSMO Inspector

The laboratory set-up consisted of a pump to pressurize the feed flow, an OSMO inspector, a pressure vessel and a feed and permeate tank. Water from the feed tank was pumped through the OSMO inspector, which measured the pressure and temperature (see Figure 16). From the OSMO, the feed water flows into the pressure vessel. In the pressure vessel, housing one spiral wound membrane element, water was separated in a high concentration flow (concentrate) and a low concentration flow (permeate). These two flows were again fed through the OSMO inspector, that again measures the pressures before the two flows were recirculated to the feed tank (see Figure 15 and Figure 16). These pressure measurements allowed the TMP to be calculated. It was also possible to siphon off the permeate flow in a separate (permeate) tank, which resulted in an increase of concentration in the feed tank (as “low concentration” water was siphoned off and “high concentration” water was recirculated).

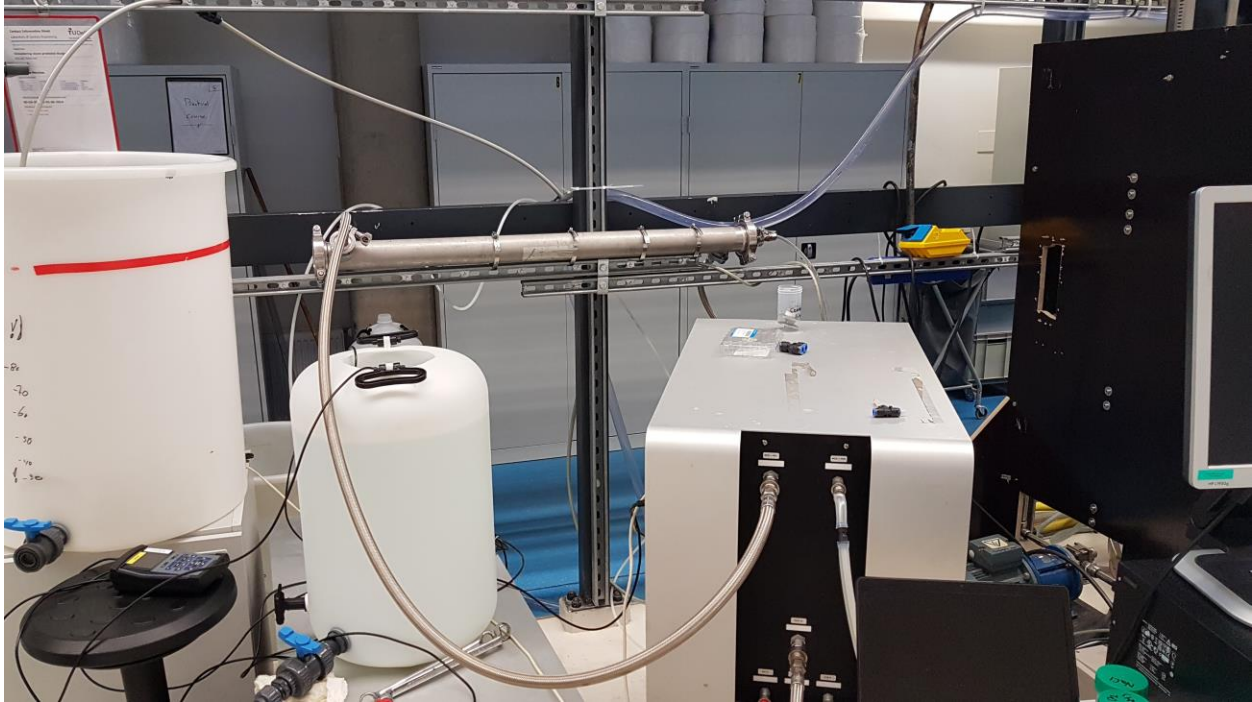


Figure 15: Photo of RO Laboratory Set-Up. Feed water tanks (Feed Water left or clean/flush water right), water is pumped through the OSMO-inspector (right) to measure pressure, then into a pressure vessel (center, holding the membrane) and back (via OSMO-inspector to measure pressure) to the feed tank. Measurements are logged by a laptop.

For the laboratory experiment, using one RO element, a recovery of 15% was used (a number used by DOW in their product data sheet) but for the ROSA simulations, other recoveries were used to get more data points. A flux of 20 L/h/m^2 was used, this resulted in a turbulent flow within the membrane. This helps to mix the water, to minimize the effects of concentration polarization (see 2.5.4.1). The XLE membrane had an area of 2.6 m^2 , so a permeate flow of 52 L/h was used to reach the desired flux. A feed flow of 350 L/h resulted in a recovery of 15%.

First, the permeate and concentrate were both recirculated to the feed tank until the system was stable at the feed and permeate flow discussed above (red line in Figure 16). Next, the permeate was siphoned off and collected in the permeate tank (see Figure 16). This caused the concentration in the feed tank to increase from the original $1.5 \text{ g NH}_4^+/\text{L}$ until the maximum pressure of the set-up was reached (15 bar). During the experiment, at different time intervals samples were taken to measure the NH_4^+ concentrations in the feed tank, permeate flow and concentrate flow. These values, together with the TMP calculated with the OSMO read-outs were used to validate the values found with the ROSA simulation.

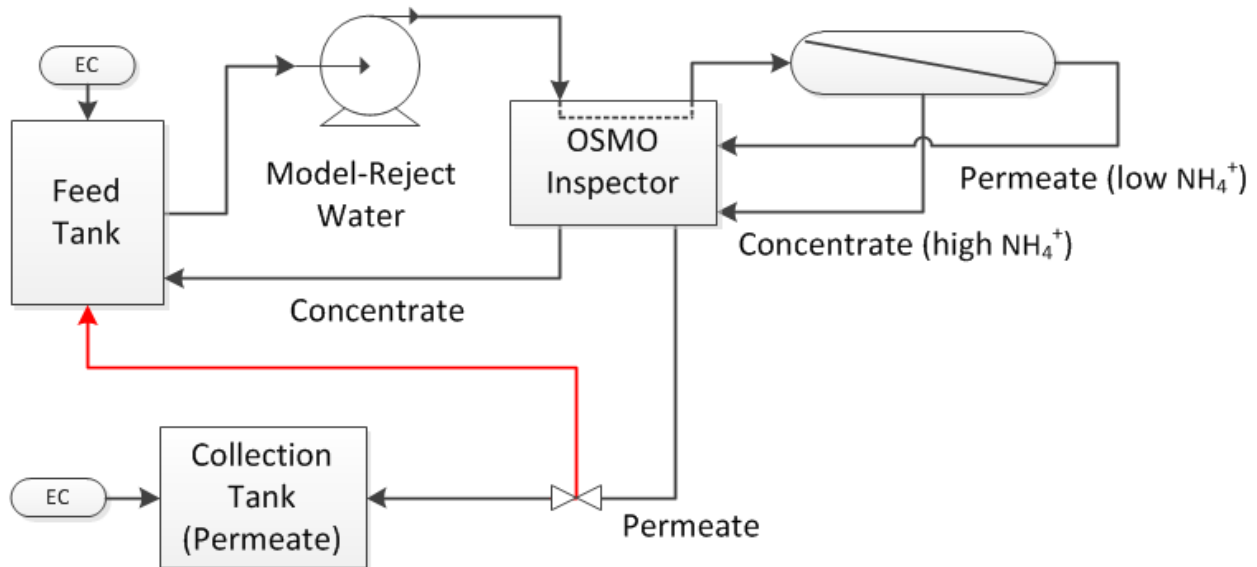


Figure 16: Schematization of RO Laboratory Set-Up

Unfortunately, the energy used could not be checked with the laboratory set-up because the OSMO installation released the pressure after the concentrate and permeate pressures were measured. However, a full scale set-up would have used the pressure still present in the concentrate to feed the flow through subsequent membranes, so a set-up with more stages (individual membranes) was more efficient. The software could model up to 9 stages. After inputting the desired feed flow and recovery (see Figure 17) the software reported on the pressure, flow and concentrations after each stage and the overall energy used by the entire set-up.

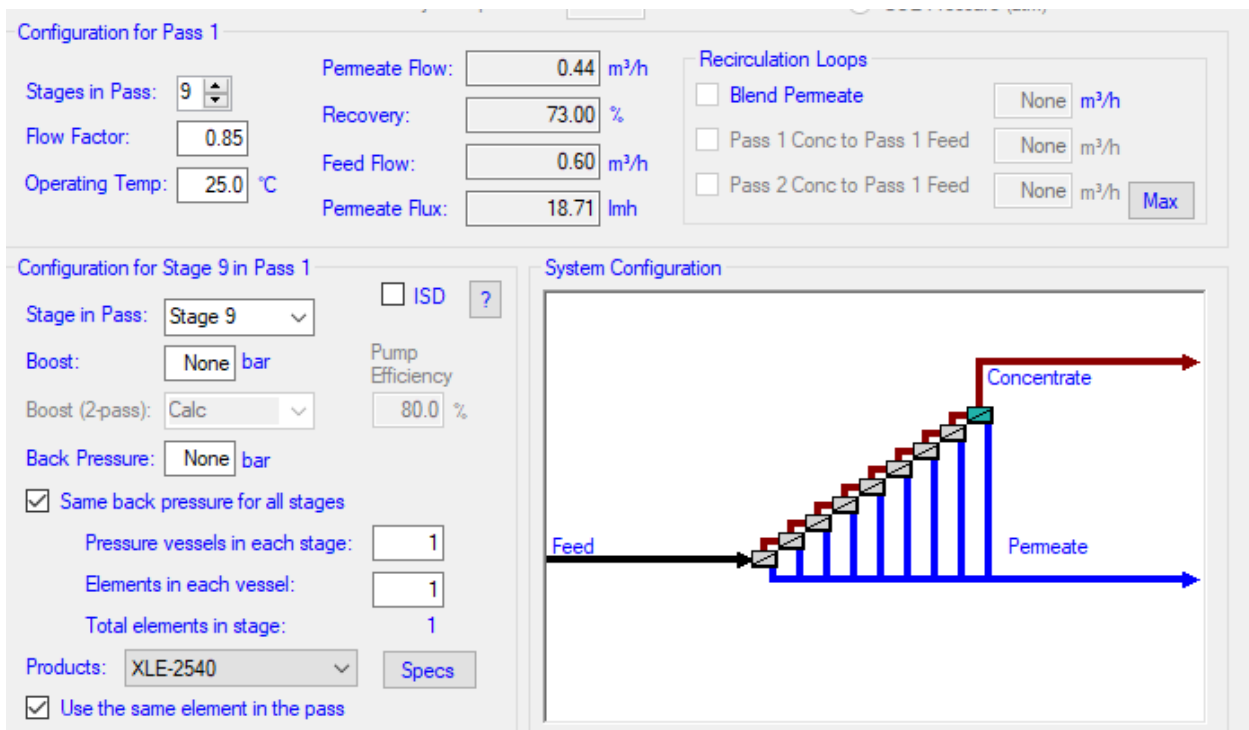


Figure 17: RO ROSA Software: Input Wizard

3.6.2 TFC Membrane

For the membrane itself, an XLE 2540 DOW Filmtec membrane was used. The XLE (“Extra Low Energy”) is a thin film composite (TFC) RO membrane. TFC membranes are the most commonly used membrane today and allow a higher water flux and salt rejection compared to other membranes (Duarte & Bordado, 2016). A TFC membrane is composed of two layers, a thicker support layer that supports the thinner skin, that determines the separation properties of the membrane (Duarte & Bordado, 2016). The XLE membrane can be operated at lower pressures (compared to other membranes (DOW FILMTEC, 2016)) so energy use can be kept low. The XLE 2540 is also produced by the same company that developed the ROSA software. So, measurements made during the experiments (with the laboratory scale set-up) can be used to compare with ROSA results.

3.6.3 Full scale Set-Up

If experimental results were able to validate the ROSA model, the ROSA model could be used to estimate the energy used during a full scale set-up.

4 Results

4.1 Results IEX

The IEX process was divided into two parts, the loading and regeneration. The first experiments focused on loading, to assess the NH_4^+ removal efficiency of the IEX zeolites. The rest of the experiments focused on different methods of regeneration to maximize the NH_4^+ concentration in the regenerant. Finally, the results were used to estimate the total energy used by a full scale set-up.

4.1.1 Loading

The IEX bed was loaded with 1 L of 1.5 g NH_4^+ /L feed water at two flows; 6 and 13 BV/h. This not only showed which flows (previously found in literature) worked best but also gave a chance to check the NH_4^+ removal efficiency and the capacity of the chosen zeolite. To investigate how an IEX bed reacted, the permeate was sampled every few minutes and the concentration was measured with the MN test kits (see 3.2.2).

The results were presented in Figure 18, called a breakthrough curve. The graph showed the NH_4^+ concentration of the permeate (compared to the 1.5 g NH_4^+ /L feed water) against the volume of feed water processed (in BV, see 2.3.1)

When the feed water flowed through the IEX bed, at first all NH_4^+ was removed. After some time the IEX bed became saturated and NH_4^+ was found in the permeate. When the IEX bed was completely saturated (filled with only NH_4^+ rather than Na^+) the concentration of the permeate was the same as the original (feed) concentration.

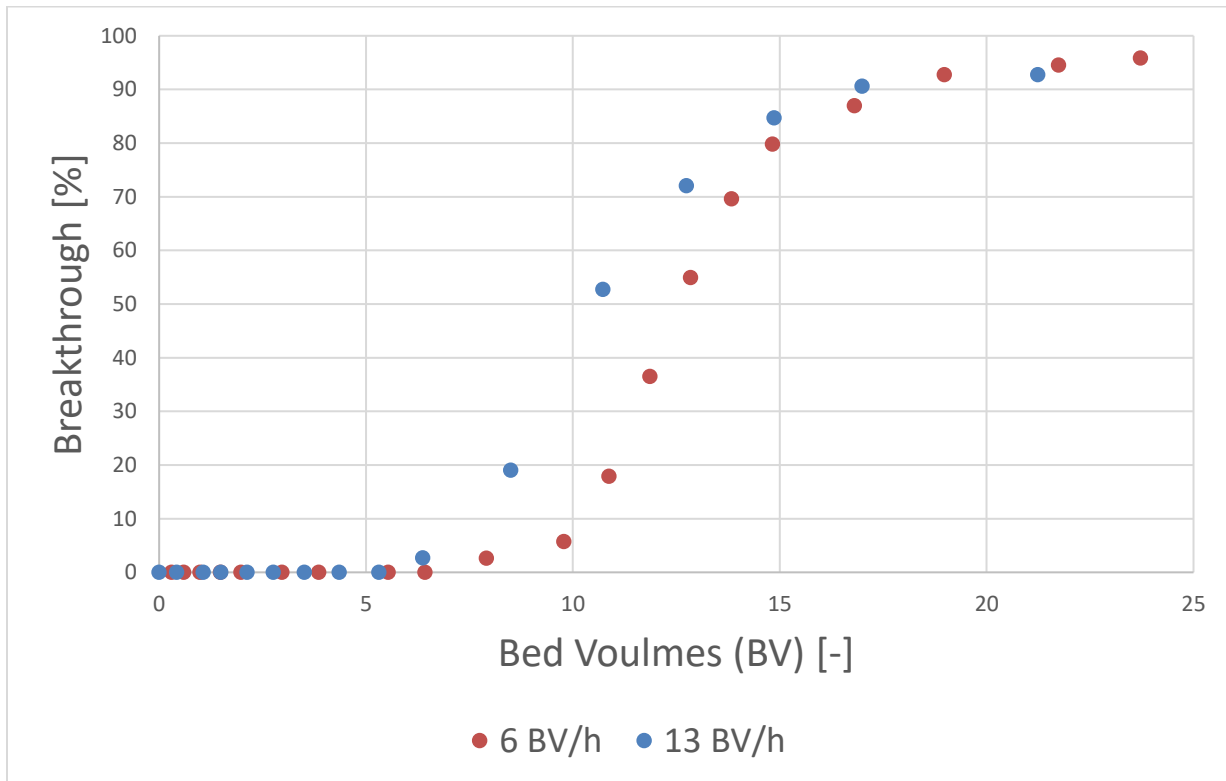


Figure 18: IEX Laboratory Set-Up: Breakthrough Curve of 1.5 g NH_4^+ /L feed water; Feed flow of 6 and 13 BV/h. Sample points after IEX bed measure percentage of original (feed) concentration in effluent at different intervals.

The graph showed that breakthrough occurs after 6 and 8 BV for the high and low feed flow respectively. Because three IEX beds are placed after each other, the first bed would be fully loaded. So, before running a regeneration experiment, the IEX bed was fully (100%) loaded with NH_4^+ .

4.1.2 Regeneration

It was assumed that a full scale set-up would use three IEX beds, placed in series, to fully saturate the IEX bed (to maximize the concentration of the regenerant). The regeneration of this fully saturated bed is discussed here. Again, the purpose is to produce a solution with a high ammonium concentration, which is not necessarily the most efficient means of regenerating an IEX bed.

A concentration of NaCl (6.5 g/L) was used to see if the regeneration should be carried out at low (6 BV/h) or high (13 BV/h) flow, both discussed in a report (Ye et al., 2015). The results of the NH_4^+ concentration measured in the samples taken from permeate, given in Figure 19, showed no discernable difference in efficiency between the two flows. So in the interest of time, the faster flow, i.e. 13 BV/h, was chosen for the rest of the experiments.

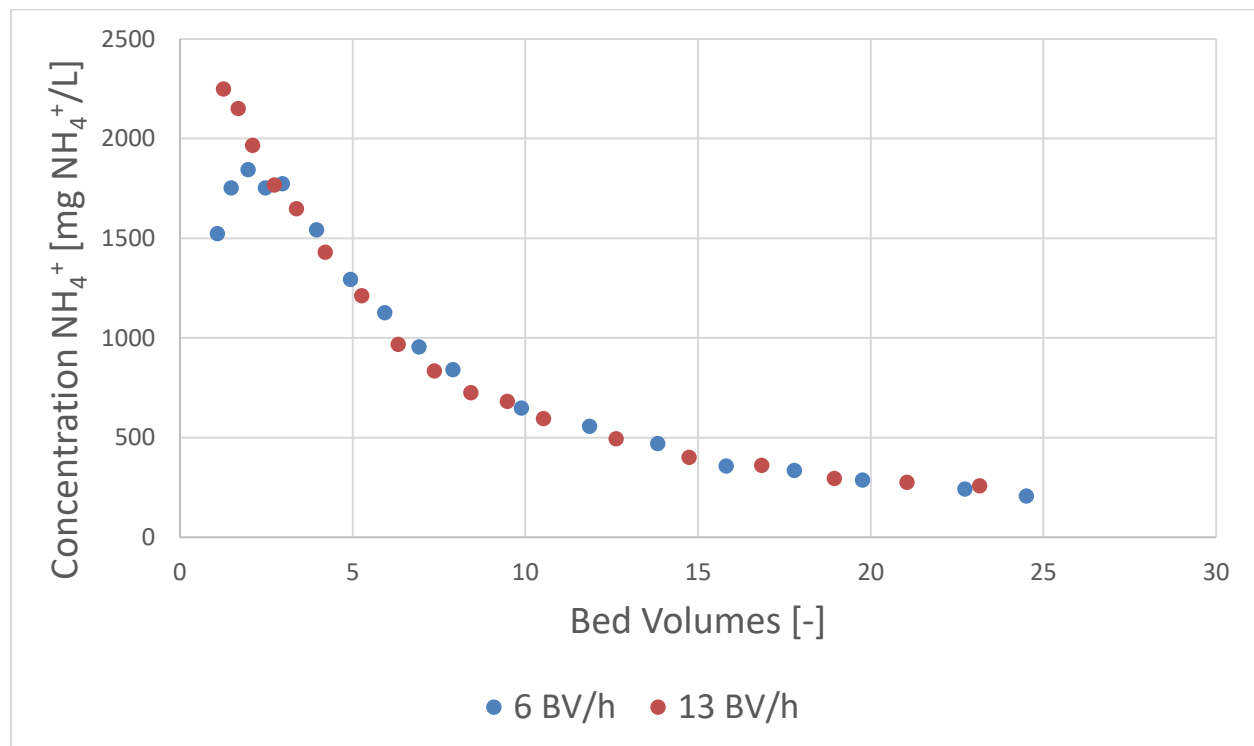


Figure 19: IEX Laboratory Set-Up: Regeneration of 100 % saturated IEX bed with 6.5 g NaCl/L; Feed flow of 6 and 13 BV/h; Sample points after the IEX bed measure the concentration of the regenerant exiting the IEX tube at different intervals.

4.1.2.1 Regeneration: 100 g NaCl/L

The previous experiment also showed that the regeneration with a concentration of 6.5 g NaCl/L did not yield a high NH_4^+ concentration. The regenerant (1 L) had a concentration of about 700 mg NH_4^+ /L after fully regenerating the IEX bed. To get higher concentration from regeneration, a concentration of 100 g NaCl/L was needed (DOW Chemical, 2013). In Figure 20 the results from three regeneration experiments were given. The results showed that higher regenerant NH_4^+ concentrations of up to 9000 mg NH_4^+ /L were reached after 1 BV. However, the concentration of the regenerant (1 L) after fully regenerating the IEX bed was only 900 mg NH_4^+ /L. So 100% regeneration of the IEX bed did not seem beneficial for creating solutions with high NH_4^+ concentration.

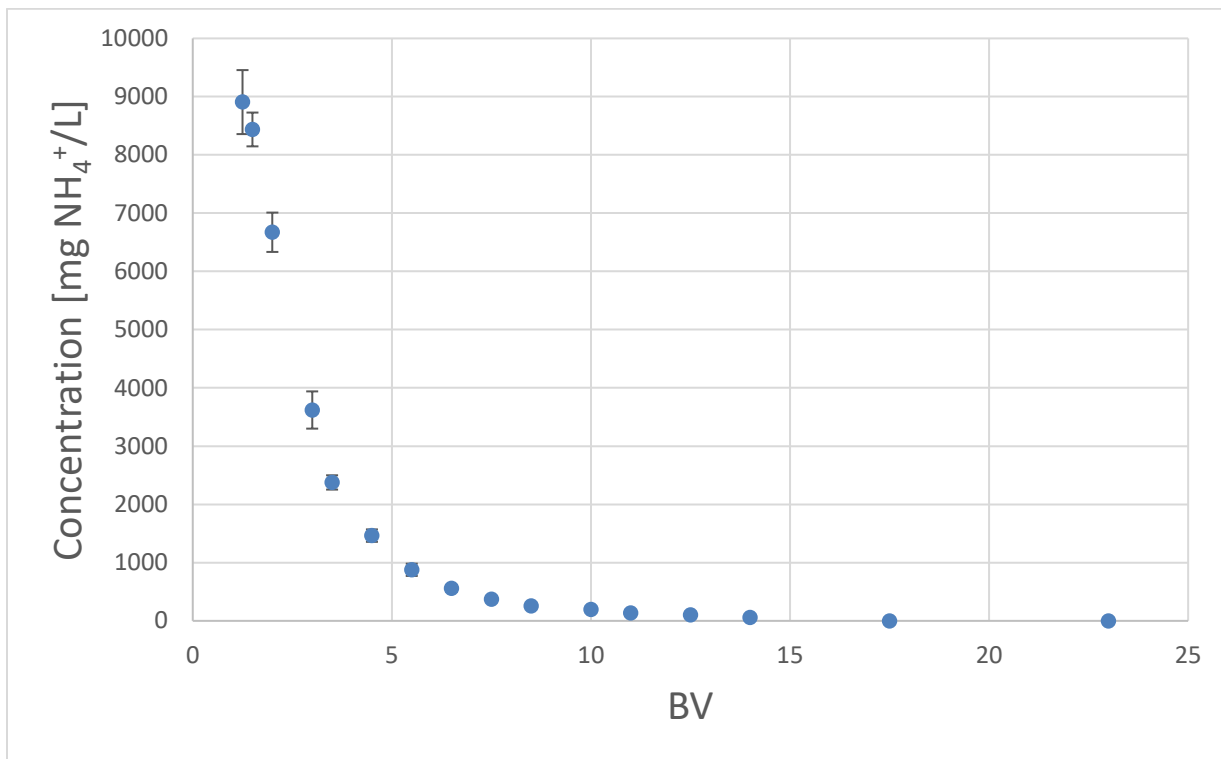


Figure 20: IEX Laboratory Set-Up: Regeneration of 100 % saturated IEX bed with 100 g NaCl/L; Feed flow of 13 BV/h; Sample points after the IEX bed measure the concentration of the regenerant exiting the IEX tube at different intervals.

The NH_4^+ concentration of the regenerant is calculated by dividing the amount of NH_4^+ [mg] removed by the volume of the regenerant [L]. The amount of NH_4^+ removed is given by the area below the graph (in Figure 20) and the volume is given by the BVs. So for each sample point (in the graph) the concentration of the regenerant (assuming regeneration is stopped after that sample point) can be calculated. Figure 21 gave the concentrations of the regenerant (if regeneration were stopped after different sample points). The maximum concentration in the regenerant occurred after 2.1 BV.



Figure 21: IEX Laboratory Set-Up: Regeneration with 100 g NaCl/L: Calculation of the maximum NH_4^+ concentration of the Regnerant after processed BV. Maximum concentration after 2.1 BV (6.0 g NH_4^+ /L)

4.1.2.2 Regeneration: NaOH pH = 12.5

The second experiment was to assess the regeneration efficiency with NaOH instead of NaCl. Because the concentration of sodium was lower in the case of NaOH, the NH_4^+ concentration in the regnerant will likely be less, but if the majority (or even all) of the NH_4^+ was released in the form of $\text{NH}_3(\text{g})$, this solution could be very beneficial. To check if this was the case the experiment was performed six times, three times while collecting the regnerant in an acid (1 L, pH = 1), to make sure that all $\text{NH}_3/\text{NH}_4^+$ that was present would be in the NH_4^+ form and no NH_3 would evaporate from the solution. During the other three experiments, there was no acid to collect the regnerant, and any NH_3 that was formed was free to evaporate. It was assumed that the difference in NH_4^+ concentrations between these two experiments was the amount of $\text{NH}_3(\text{g})$ that escaped. The results were given in Figure 22.

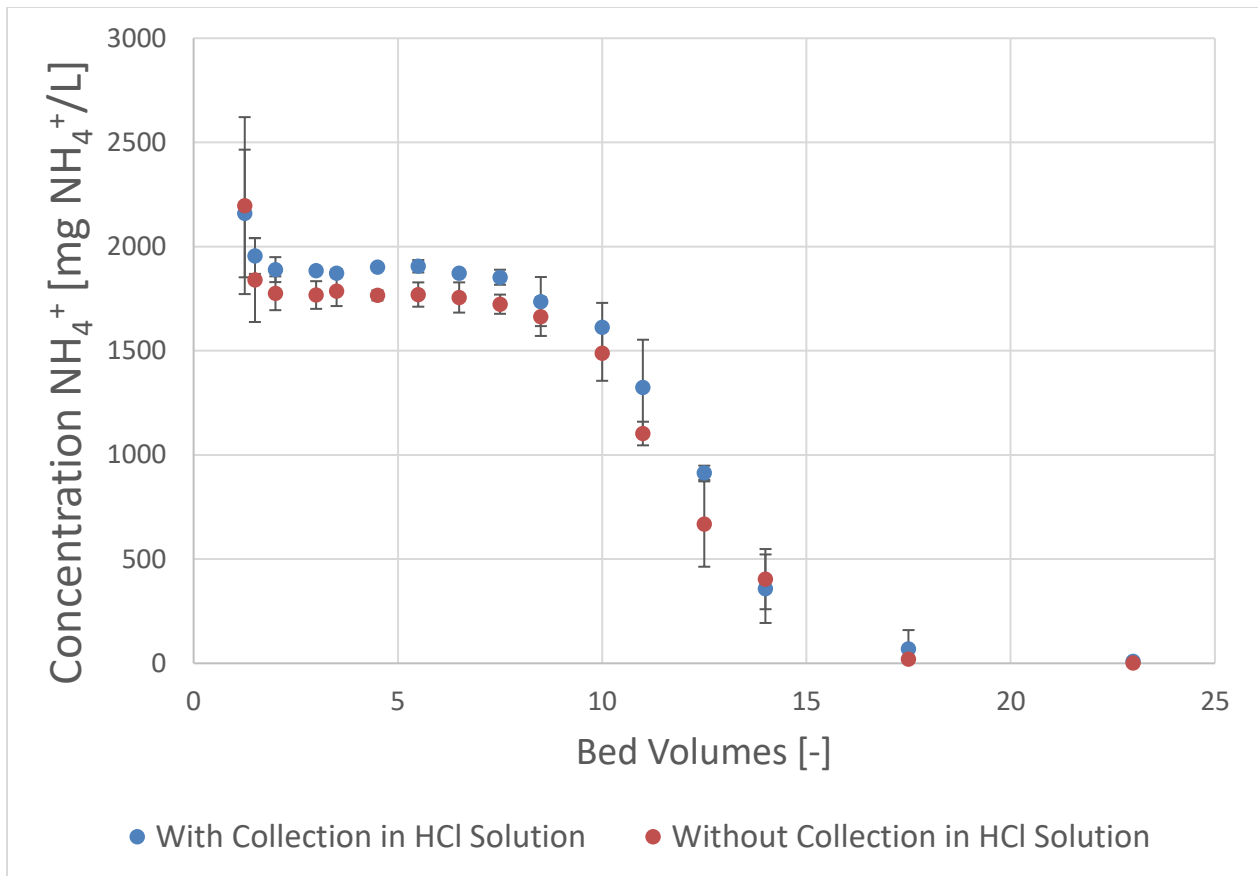


Figure 22: IEX Laboratory Set-Up: Regeneration with a pH = 12.5 solution; Feed flow of 13 BV/h; Sample points after the IEX bed measure the concentration of the regenerant exiting the IEX tube at different intervals; Blue: The Regenerant is collected in a pH=1 solution, Red: The Regenerant is collected in an empty reservoir.

The result showed that there was a difference between the two experiments, but it did not seem to be a big difference. While no negative effects were observed, the long-term effect on the zeolite of regenerating at such a high pH would have to be investigated.

As in 4.1.2.1, Figure 23Figure 21 gave the concentrations of the regenerant (if regeneration were stopped after different sample points). The maximum concentration in the regenerant occurred after 8.3 BV with a concentration of 1.7 g NH₄⁺/L.

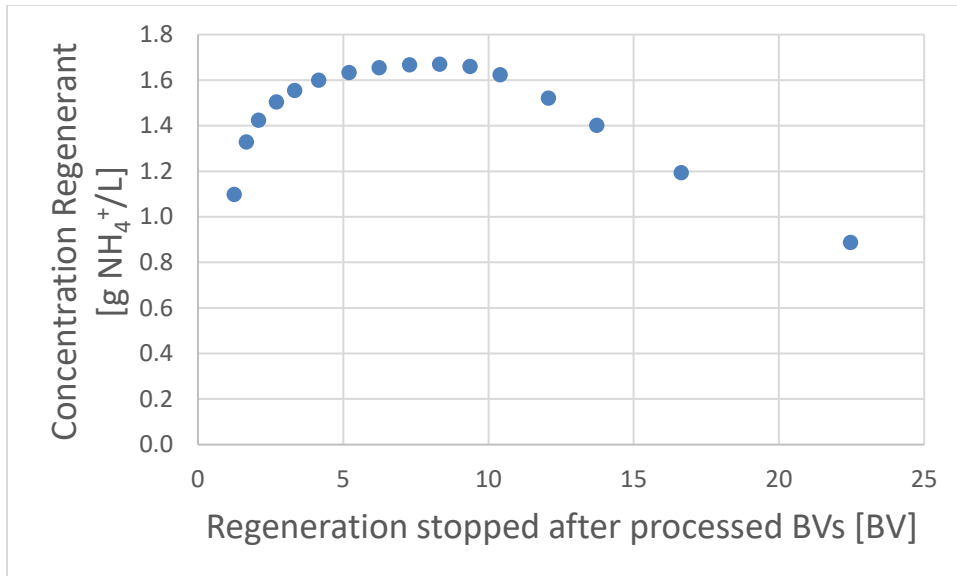


Figure 23: IEX Laboratory Set-Up: Regeneration with a pH = 12.5 solution: Calculation of the maximum NH₄⁺ concentration of the Regenerant after processed BV. Maximum concentration after 2.1 BV (6.0 g NH₄⁺/L)

Also, the combination of a high NaCl concentration and high pH did not seem to have a big effect on the efficiency (compared to regeneration with 100 g NaCl/L only), the results were given in Figure 24.

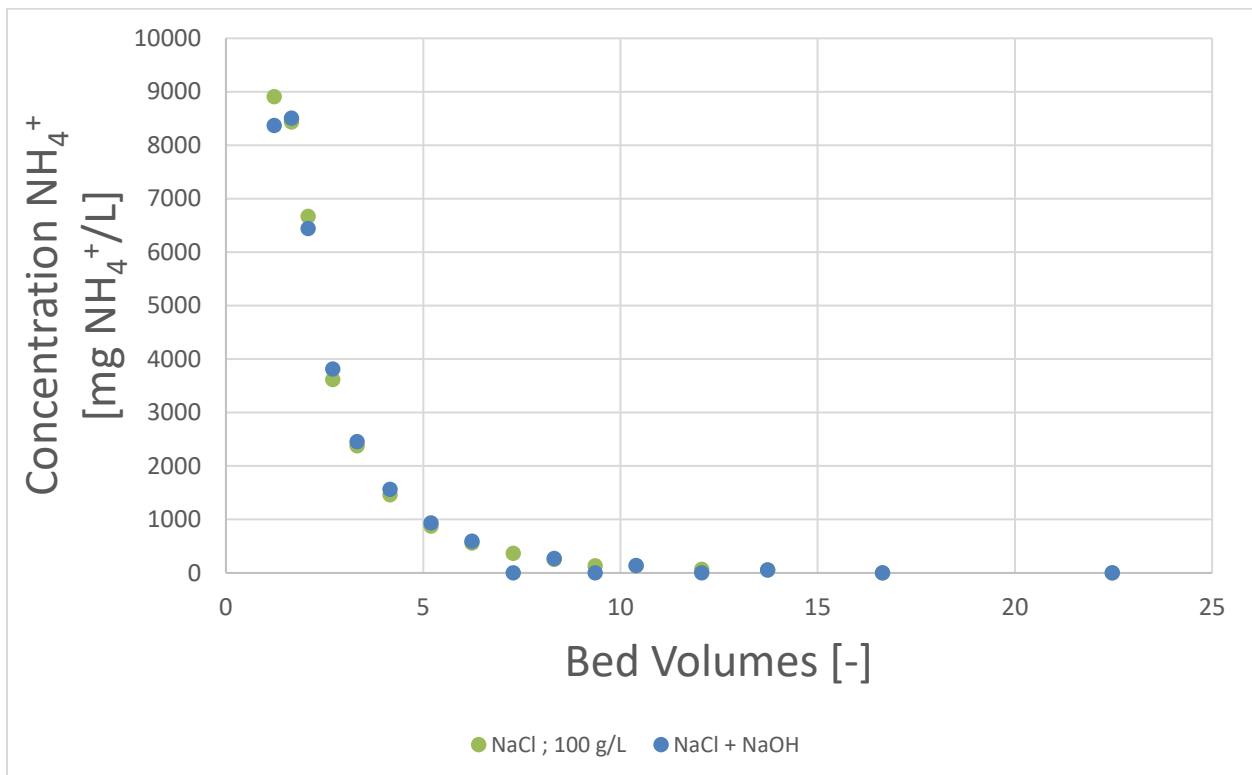


Figure 24: IEX Laboratory Set-Up: Regeneration of 100 % saturated IEX bed; Feed flow of 13 BV/h; Sample points after the IEX bed measure the concentration of the regenerant exiting the IEX tube at different intervals. Green: Regeneration with 100 g NaCl/L. Blue: Regeneration with 100 g NaCl/L with pH = 12.5.

4.1.2.3 Regeneration: Recirculating smaller regenerant volumes

The final experiment tried to increase the concentration of NH_4^+ in the regenerant by recirculating a smaller volume (Heijman, 2017). To recirculate a smaller volume, a second column of about 80 mL was used. It was filled with a 70 mL (1.65 BV) 100 gr NaCl/L solution and (later) with a NaOH (pH = 12.5) solution. The choice of 70 mL was a practical one, as the column holding the IEX zeolites was 55 mL, this left enough volume to take samples while ensuring the column stayed submerged (preventing air to enter the bed). The results were given in Figure 25.

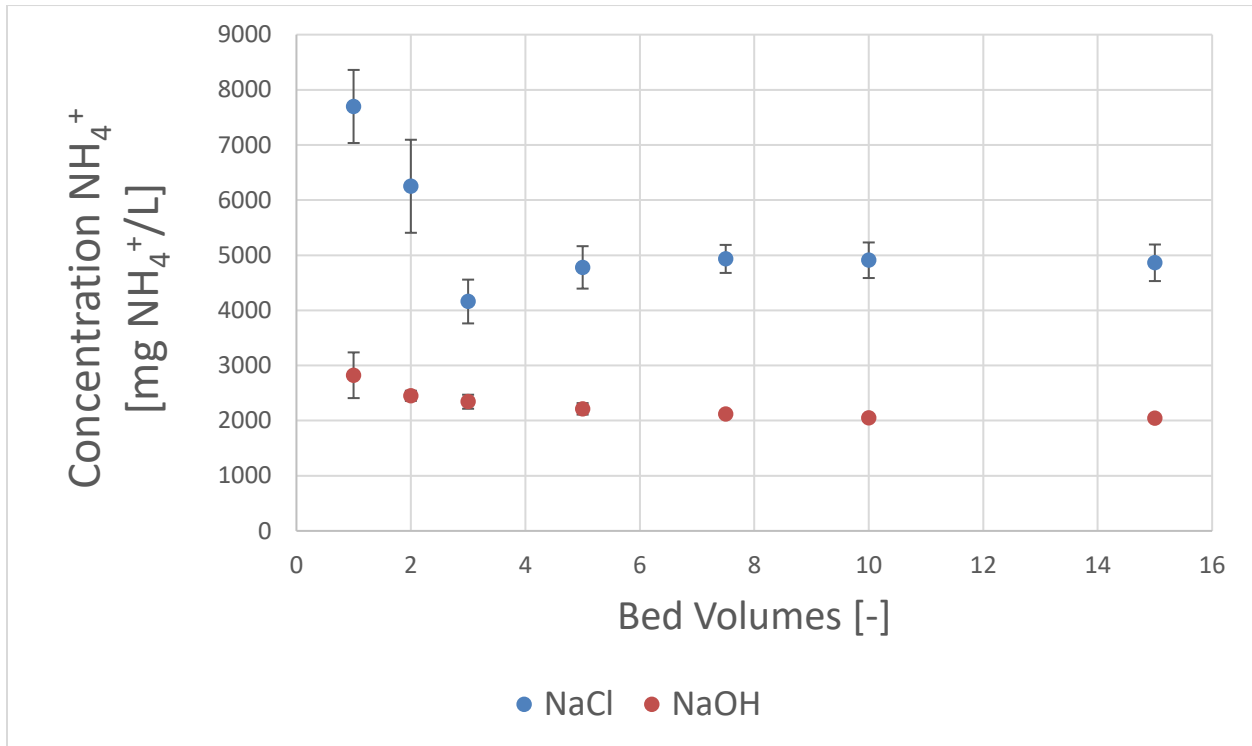


Figure 25: IEX Laboratory Set-Up: Regeneration of 100 % saturated IEX bed; Feed flow of 13 BV/h; Regenerated by recirculating a small volume over the IEX bed. Sample points after the IEX bed measure the concentration of the regenerant exiting the IEX tube at different intervals. Blue: 100 g NaCl/L Solution. Red: Solution with pH = 12.5.

Figure 25 showed that the NH_4^+ concentration was higher after 1-2 BV, this is because the sampling point is just after the first column (which holds the IEX bed; to prevent air entering the bed) so the column had just been filled, and only a small volume had a chance to pass the IEX bed and had not been mixed with the rest of the regenerant yet. After some time an equilibrium was reached (5000 mg NH_4^+ /L for NaCl solution and about 2000 mg NH_4^+ /L for the NaOH solution).

4.1.3 Total Energy Used

4.1.3.1 Full scale: Loading and Regeneration

The parameters found during the laboratory experiments could be applied to the vessel discussed in 3.4.4.1. The total capacity of the IEX for holding NH_4^+ was calculated in Table 5. An overview of the loading and regeneration step applied to the vessel discussed in 3.4.4.1 was given in Table 6 and Table 7. (The “breakthrough” and “fully loaded after” was taken from Figure 18). Here regeneration with 100 g NaCl/L is given as an example, calculations of the other forms of regeneration are given in 8.3, Appendix C.

The IEX was not fully regenerated, to maximize the concentration of the regenerant. Regeneration stopped after 2.1 BV to achieve a 5.96 g NH₄⁺/L concentration in the regenerant. A regenerant volume of 2.1 BV (13 m³) with a concentration of 5.96 g NH₄⁺/L holds 78 kg of NH₄⁺. Only 78 of the 132 kg in the IEX bed was released during regeneration, this means that when the bed was loaded a second time the IEX bed was already 41% loaded. During this second (and subsequent) loading the IEX bed was fully loaded after 1.7 h (see Table 8). (It is assumed that Figure 18 can be used to estimate how many BV are needed to get the saturation back to 100% again.)

Table 5: IEX Full Scale Set-Up: IEX Bed Capacity for NH₄⁺

BV Density (from Experiments)	465	g/L
IEX Capacity Zeolite	2.5	eq/kg
M Weight NH ₄ ⁺	18.04	g/mol
IEX bed	$465 \text{ [kg/m}^3\text{]} * 6.3 \text{ [m}^3\text{]} = 2922$	kg
Capacity IEX Bed	$2.5 \text{ [eq/kg]} * 2922 \text{ [kg]} = 7306$	eq/BV
Capacity IEX Bed	$18.04 \text{ [g/mol]} * 2.5 \text{ [eq/kg]} = 132$	kg NH ₄ ⁺ /BV

Table 6: IEX Full Scale Set-Up: IEX Bed Loading

Feed Flow	5.9	BV/h
Feed Flow	37	m ³ /h
Feed Flow	0.01	m ³ /s
Velocity	12	m/h
Velocity	0.003	m/s
Breakthrough	8	BV
Breakthrough	1.3	h
Fully Loaded after	22	BV
Fully Loaded after	3.7	h
Total Volume Exchanged	138	m ³

Table 7: IEX Full Scale Set-Up: IEX Regeneration with 100 g NaCl/L

Feed Flow	12.5	BV/h
Feed Flow	78	m ³ /h
Feed Flow	0.02	m ³ /s
Velocity	25	m/h
Velocity	0.007	m/s
Max Concentration Regenerant after	2.08	BV
Volume Regenerant	13.1	m ³
Run Time	0.17	h
Concentration	6.0	g/L
Total NH ₄ Removed	78	kg

Table 8: IEX Full Scale Set-Up: Subsequent Loading (Regeneration with 100 g NaCl/L)

NH ₄ ⁺ in IEX bed	54	kg
Saturation	41	%
Fully Loaded after	10	BV
Fully Loaded after	1.7	h
Total Volume Exchanged	63	m ³

4.1.3.2 Energy Used

With this pressure drop over the IEX bed discussed in 3.4.4.2, the energy use could be calculated. With a known pressure drop, flow and density (1000 kg/m³) and assumed pump-efficiency of 60% the energy used by loading and regeneration, per m³ of produced concentrated NH₄⁺ solution, could be calculated (see Table 9).

Table 9: IEX Full Scale Set-Up: Energy Used by IEX (1st loading)

Loading			Regeneration		
pressure drop	2.7	m	pressure drop	1.9	m
Flow	0.01	m ³ /s	Flow	0.02	m ³ /s
Power Pump	0.8	W	Power Pump	1.4	kW
Energy used	2.9	Wh	Energy used	0.2	kWh
			Total Energy	3.2	kWh
			Energy/m ³	0.2	kWh

The energy used by the subsequent loading and regeneration was given in Table 10 and Table 11. Because the regeneration was stopped after 2.08 BV there was still NH₄⁺ within the IEX bed.

Table 10: IEX Full Scale Set-Up: IEX Reloading

NH ₄ ⁺ in IEX bed	54	kg
Saturation	41	%
Fully Loaded after	10	BV
Fully Loaded after	1.7	h
Total Volume Exchanged	63	m ³

The regeneration step is the same as before.

Table 11: IEX Full Scale Set-Up: Energy Used by IEX (subsequent loading)

Loading			Regeneration		
pressure drop	2.7	m	pressure drop	1.9	m
Flow	0.01	m ³ /s	Flow	0.02	m ³ /s
Power Pump	0.8	W	Power Pump	1.4	kW
Energy used	1.3	Wh	Energy used	0.2	kWh
			Total Energy	1.6	kWh
			Energy/m ³	0.1	kWh

Figure 26 gave an overview of the results of the different regeneration methods. The maximum concentration of regenerating with NaCl and NaOH occurred after 2 and 8 BV respectively, so while the first regenerant had a higher concentration the volume was less (see 4.1.2.1 and 4.1.2.2). Because the IEX bed was not fully regenerated, less feed water was needed during the reloading, to again saturate the IEX bed. So less energy was used during these subsequent runs. The achievable NH₄⁺ concentration and the energy used by the four methods of regeneration (per m³ of produced concentrated NH₄⁺ solution) are given in Figure 26. Full calculations are given in 8.3, Appendix C.

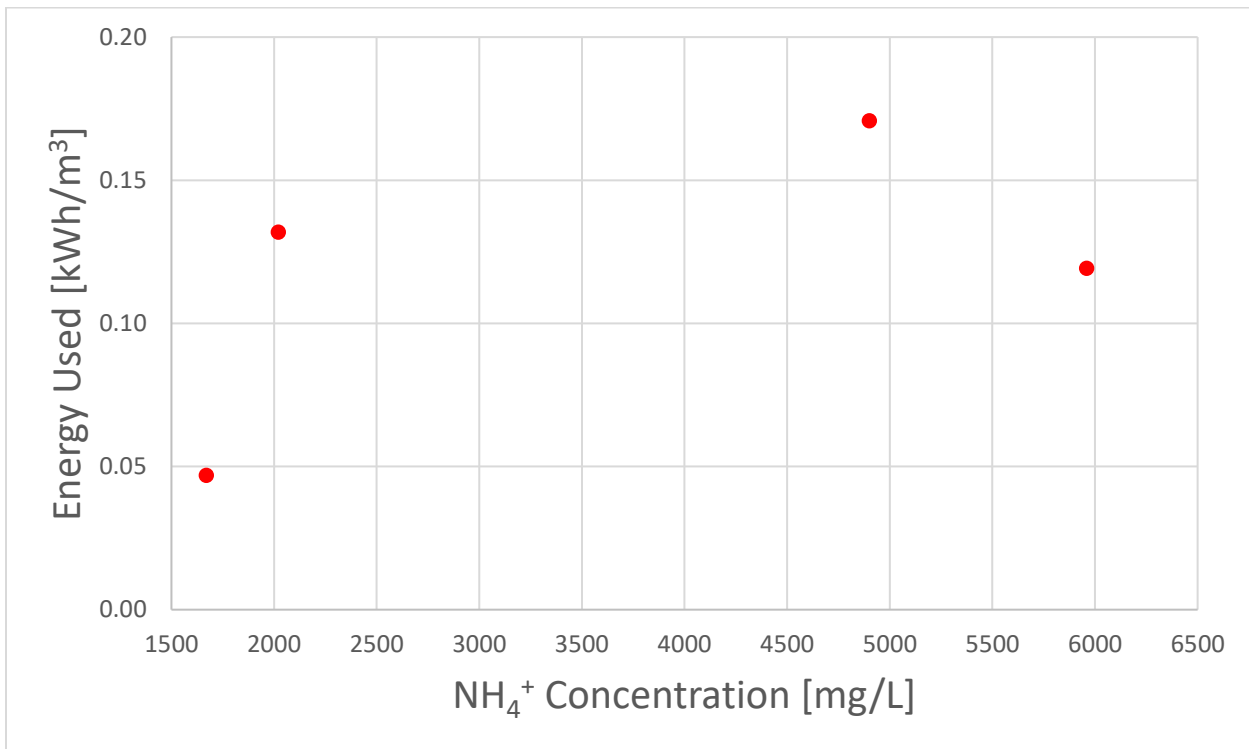


Figure 26: IEX Full Scale Set-Up: Achievable NH₄⁺ Concentration + Energy Used by IEX, using various Regeneration Methods (per m³ of produced concentrated NH₄⁺ solution)

4.2 Results ED

First, the most energy efficient combination of cross flow velocity and current density was found in 4.2.1. Then the maximum concentration achievable with ED could be found. The maximum concentration was found by replacing the diluate solution each time the concentration reached 100 - 150 mg NH_4^+ /L while using the same concentrate solution. The energy used during the experiment could later be scaled-up to a full scale set-up.

4.2.1 Efficiency: Flow and Current

First, the most efficient combination of current and flow was found by running multiple combinations to see which used the least amount of energy. The combinations were a cross flow velocity of 43 m/h, with a current density of 15.6 A/m², 50% of LCD and at LCD (maximum current density) and with a flow of 14 m/h, with the same three current densities. Three (1 l) reservoirs (the concentrate and the diluate, both with a concentration of 1.5 g NH_4^+ /L and the electrolyte, with a concentration of 85 g NaNO_3 /L) were fed through the ED cells and recirculated to their original reservoirs until the EC read about 400 $\mu\text{S}/\text{cm}$ (about 75 mg/L). Figure 27 showed the results of one such experiment (cross flow velocity = 43 L/h; current density = maximum, i.e. on LCD). As the NH_4^+ concentration of the diluate decreased, the NH_4^+ concentration of the concentrate increased. As the concentration difference between the two reservoirs increased, the ion flux from the diluate to the concentrate decreased. This is due to the fact that as the concentration of the diluate decreased so did the maximum current density that was applied. Decreased current density resulted in a decrease of ion flux from one stream to the next. Because of the drop in current density, with lower diluate concentration, the power used by the ED cell decreased as well, resulting in a flattening of the energy used, shown in Figure 27.

During the runs, the concentration in the diluate streams dropped, causing the LCD to drop as well, so the current was adjusted accordingly throughout the run. As the diluate concentration dropped, (because only a very low current is applied) the ion flux from the concentrate to the diluate streams dropped as well.

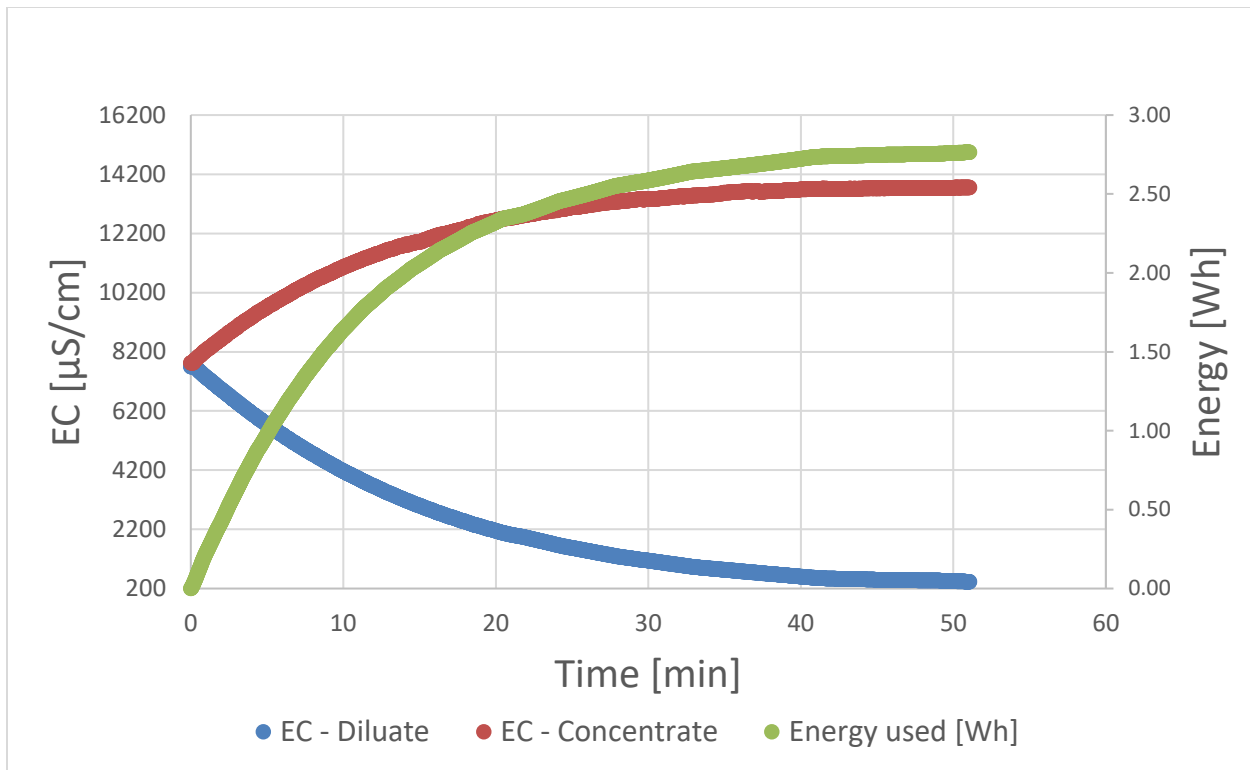


Figure 27: ED Laboratory Set-Up: ED Efficiency Test: Result of Combination: Cross flow velocity = 43 L/h, Maximum Current Density (LCD)

The results of the rest of the experiments were shown in Table 12. Pressure drop over the cell was so low that energy used by the pumps did not have an influence on the overall energy used by the process, so the difference in time was not an issue in these experiments (see 8.1.3, Appendix A).

Table 12: ED Laboratory Set-Up: ED Efficiency Test: Results of all Efficiency Tests

Set Up	Diluate final EC [µS/cm]	Concentrate final EC [µS/cm]	Total Time [h]	Energy Used ED [Wh]
43 m/h LCD	430	13750	0.9	2.76
43 m/h 0,5 LCD	476	14040	1.4	1.58
43 m/h 15.6 A/m ²	324	13950	2.7	0.93
14 m/h LCD	325	13970	1.9	1.67
14 m/h 0,5 LCD	526	13660	3.8	1.10
14 m/h 15.6 A/m ²	420	13880	2.7	1.34

4.2.2 Maximum Concentration

Now, these current density and flow are applied to find the maximum concentration that can be achieved with this ED set-up. To achieve this, one reservoir of concentrate was used, while the diluate reservoir was replaced when the EC reached 1000 $\mu\text{S}/\text{cm}$ (100 – 150 $\text{mg NH}_4^+/\text{L}$), with a new reservoir of 1L feed water (i.e. 1.5 $\text{g NH}_4^+/\text{L}$ solution). The results were presented in Figure 28.

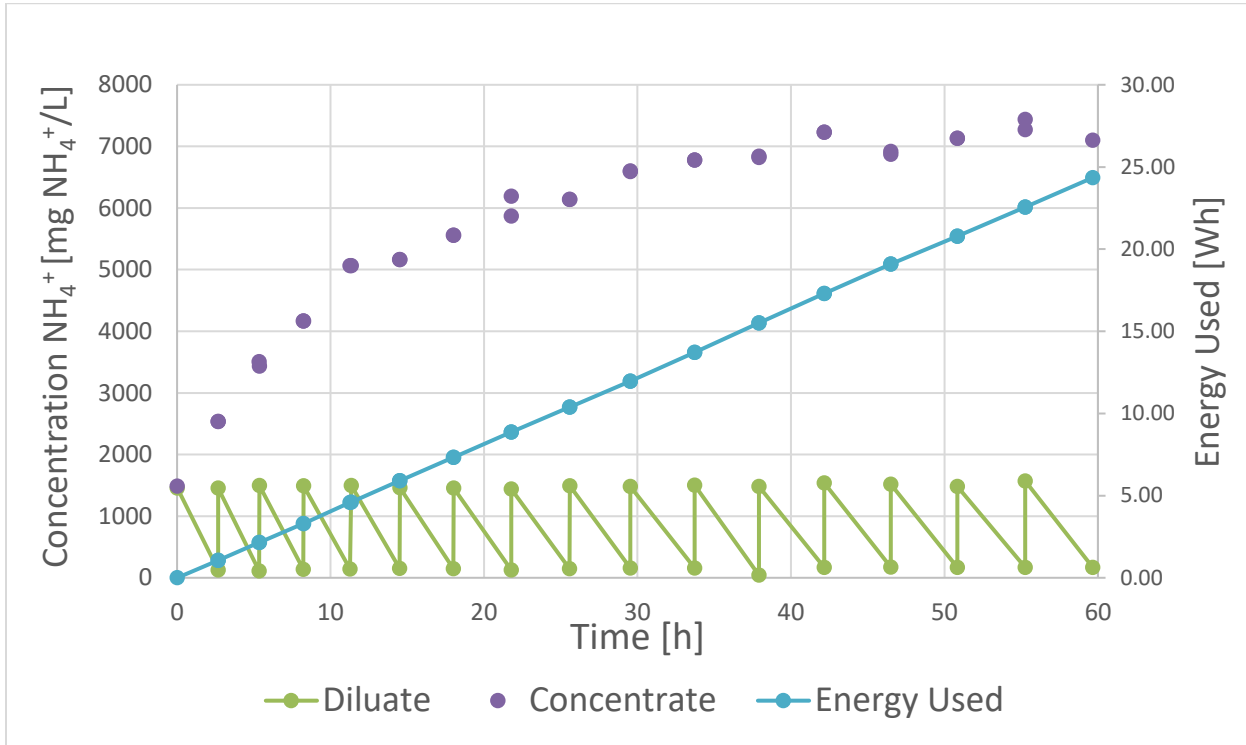


Figure 28: ED Laboratory Set-Up: Achievable NH_4^+ Concentration + Energy Used by ED (Diluate solution replaced 16 times)

The jumps in the diluate EC showed that the diluate solution was replaced and “emptied” 16 times, resulting in an increase of the concentration in the concentrate. The concentrate NH_4^+ concentration leveled off, this signaled that each new diluate solution (while the same amount of NH_4^+ was removed from each diluate solution) contributed less to the rise of the NH_4^+ concentration in the concentrate reservoir. So the efficiency of the ED decreased as the NH_4^+ concentration of the concentrate increased.

While electro-osmosis (see 2.4.3) does decrease the efficiency of the ED, this effect is constant (dependant on the hydration number of ammonium) and is not influenced by the concentrate concentration (Han et al., 2015). The leveling off is probably caused by osmosis (see 1.6.3.1) where extra water migrated from the diluate stream to the concentrate stream (diluting the concentration).

Because extra water migrates from the diluate stream to the concentrate stream, when the difference in concentration between the two streams increases, it takes longer for the diluate to reach 150 $\text{mg NH}_4^+/\text{L}$. When extra water migrates out of the diluate stream, the concentration is increased (increasing the runtime). This effect is confirmed by the fact that the end volume in each consecutive diluate reservoir decreases.

The amount of water, that migrated from concentrate to diluate, increased with each reservoir of diluate (i.e. an increase in concentration difference, resulted in an increase of water migration). While this is consistent with osmosis, further research will have to conclude whether this was because of osmosis, had another cause or had a combination of causes. However, it is obvious that the maximum achievable NH_4^+ concentration was $7.2 \text{ g NH}_4^+/\text{L}$.

4.2.3 Energy Used

During the experiment, the volume of the concentrate increased with every solution of diluate (see 8.1.2). So when calculating the energy used per m^3 of produced concentrate, this has to be taken into account (see 3.5.1). To find the energy used by the full scale set-up, the energy used by the laboratory scale is multiplied by $1000/X$ (where X = volume of concentrate solution [L]). The achievable NH_4^+ concentration and the energy used by ED (per m^3 of produced concentrated NH_4^+ solution) are given in Figure 29. End NH_4^+ concentration of the diluate and concentrate and energy used during the experiment were given in 8.1.2, Appendix A

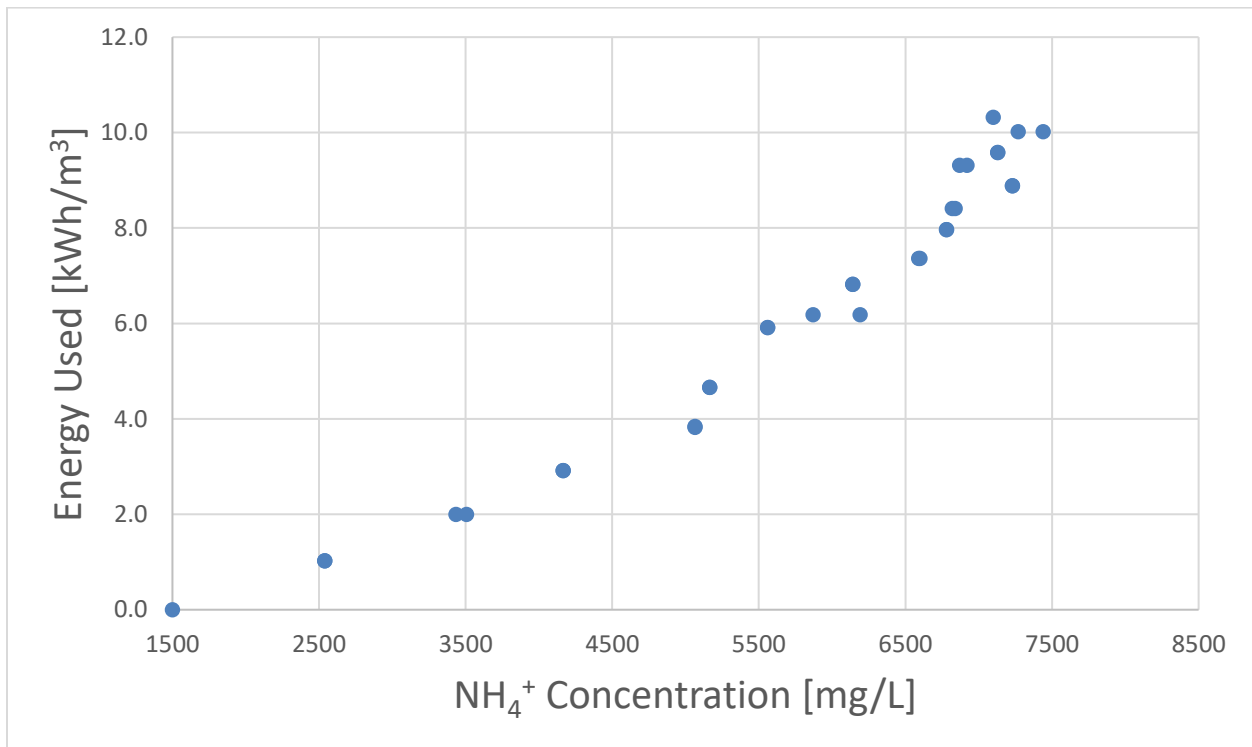


Figure 29: ED Full Scale Set-Up: Achievable NH_4^+ Concentration + Energy Used by ED (per m^3 of produced concentrated NH_4^+ solution)

4.3 Results RO

After the experiments with the laboratory set-up, the results were used to validate the ROSA software. The ROSA software was then used to estimate the achievable NH_4^+ concentrations and the energy used by the full scale set-up.

4.3.1 Experimental Results vs ROSA

Before the ROSA software was used to estimate the achievable concentrations and the energy used by a full scale set-up, the ROSA model was validated by comparing ROSA results with results from the laboratory scale experiment.

4.3.1.1 Experiment Results

During this experiment the permeate was siphoned off in a separate tank, this caused the concentration in the feed tank to increase. Seven times during the experiment samples were taken from the feed tank, permeate and concentrate flow as well as continuous measuring of the feed, concentrate and permeate pressures (which together were used to calculate the TMP).

Figure 30 showed how the concentration of the concentrate keeps increasing while the increase in the permeate was less significant.

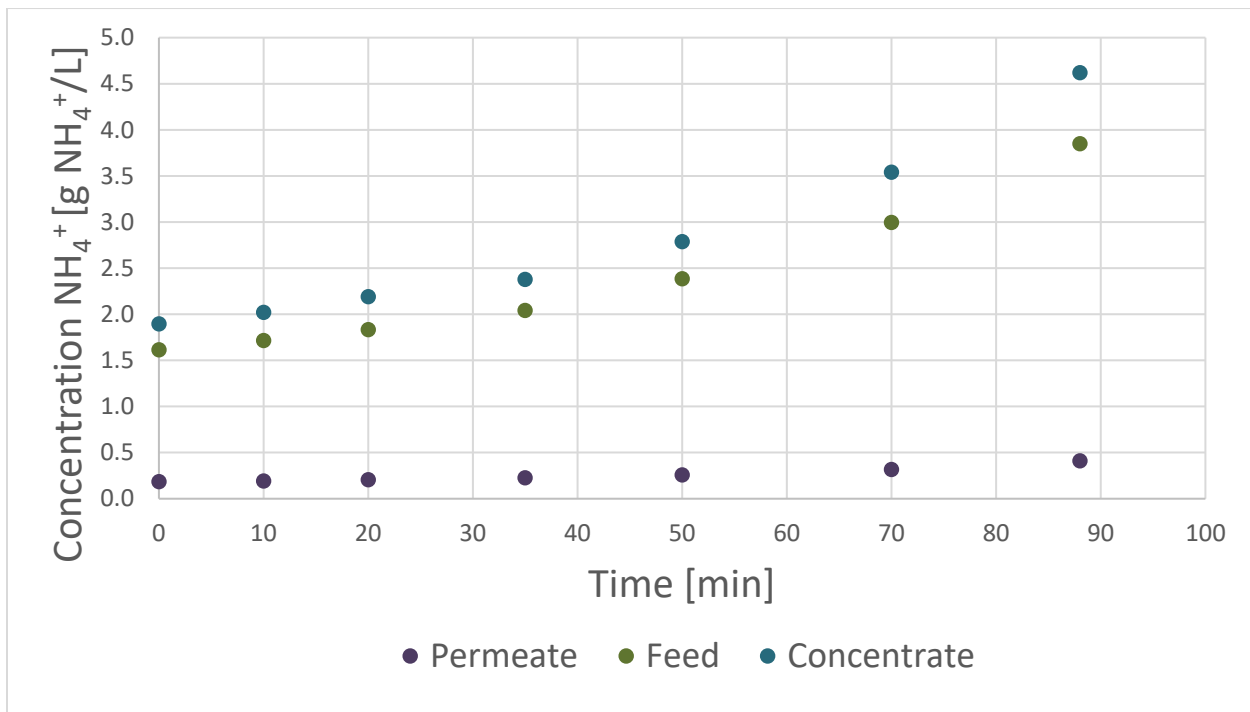


Figure 30: RO Laboratory Set-Up: Syphoning Permeate; Sample Measurements

4.3.1.2 ROSA Results

To validate the ROSA software, the same variable from the experiment were used as input for the software. The results were then compared with the results of the experiment.

In Table 13 the results of the ROSA simulations were given. The NH_4^+ concentrations of the feed tank were used as the input for the software, as well as temperature and pH (see 3.6.1). The results were the TMP and the NH_4^+ concentrations of permeate and concentrate.

Table 13: RO ROSA Software Validation: ROSA Software Results

ROSA Time	Feed [g NH ₄ ⁺ /L]	Feed [g HCO ₃ ⁻ /L]	Parameters		Permeate [g NH ₄ ⁺ /L]	Concentrate [g NH ₄ ⁺ /L]	TMP [bar]
			pH [-]	Temp [°C]			
0	1.62	5.46	8.3	24.1	0.28	2.03	7.7
10	1.72	5.81	8.2	24.3	0.27	2.13	8.0
20	1.84	6.21	8.2	24.5	0.29	2.28	8.4
35	2.04	6.91	8.1	24.9	0.30	2.51	9.0
50	2.39	8.07	8.1	25.3	0.36	2.93	10.1
70	3.00	10.13	8.0	25.8	0.46	3.64	11.8
88	3.85	13.02	7.9	26.5	0.60	4.63	14.4

To see how the simulation compared to the laboratory set-up, the differences between the experiment and the simulation were given in

Table 14. The differences were calculated with respect to the experimental value.

Table 14: RO ROSA Software Validation: Comparing Laboratory Set-Up Results and ROSA Software Results

Permeate Experiment [g NH ₄ ⁺ /L]	Permeate ROSA [g NH ₄ ⁺ /L]	Difference [%]	Concentrate Experiment [g NH ₄ ⁺ /L]	Concentrate ROSA [g NH ₄ ⁺ /L]	Difference [%]	TMP Experiment [bar]	TMP ROSA [bar]	Difference [%]
0.19	0.28	49	1.90	2.03	7	7.40	7.7	4
0.19	0.27	38	2.02	2.13	5	7.68	8.0	4
0.21	0.29	39	2.19	2.28	4	8.03	8.4	4
0.23	0.30	33	2.38	2.51	5	8.69	9.0	3
0.26	0.36	39	2.79	2.93	5	9.52	10.1	6
0.32	0.46	47	3.54	3.64	3	11.13	11.8	6
0.41	0.60	46	4.62	4.63	0	13.67	14.4	6

The differences are relatively large for the permeate concentration but relatively small for the concentrate concentration and the TMP. This is overall a very good simulation because the two values that matter the most: Concentrate concentration; this represented the produced concentrated NH₄⁺ solution. The TMP; this was very important because this was where the calculation of the energy used by RO was based on.

The concentration of the permeate would, of course, be important when designing a plant, the permeate concentration would dictate if further treatment was necessary. However, for this thesis, this was less important because the focus lies on the achievable concentration of the concentrate (and the permeate can be recycled to WWTP). Also smaller (absolute) deviations have a higher percentage deviation in lower values (which the permeate concentration is).

While the ROSA model was not validated for higher pressures than 15 bar, the model was still used to estimate the achievable NH₄⁺ concentration (up to 8.2 g NH₄⁺/L, to compare the results against the ED results) and the used energy by RO. Because the range of pressures that could be compared (with experiments), showed only a small deviation.

4.3.2 Energy Used

Now that the software was validated for lower pressures, it was assumed that the software could be used to estimate the energy used by the membrane to get to a certain (increased) concentration. With different feed and recovery choices, different ammonium concentrations and energy used by the set-up could be found. By using the concentrate from one simulation run and using it as an input for the next simulation run, even higher concentrations could be achieved, until the maximum pressure of the membrane was reached. However, only NH_4^+ concentrations up to $8.2 \text{ g NH}_4^+/\text{L}$ were estimated. This allowed the results of RO and ED to be compared with each other. The results were given in Figure 31. In 8.4 (Appendix D), a more extensive overview of the simulations was given.

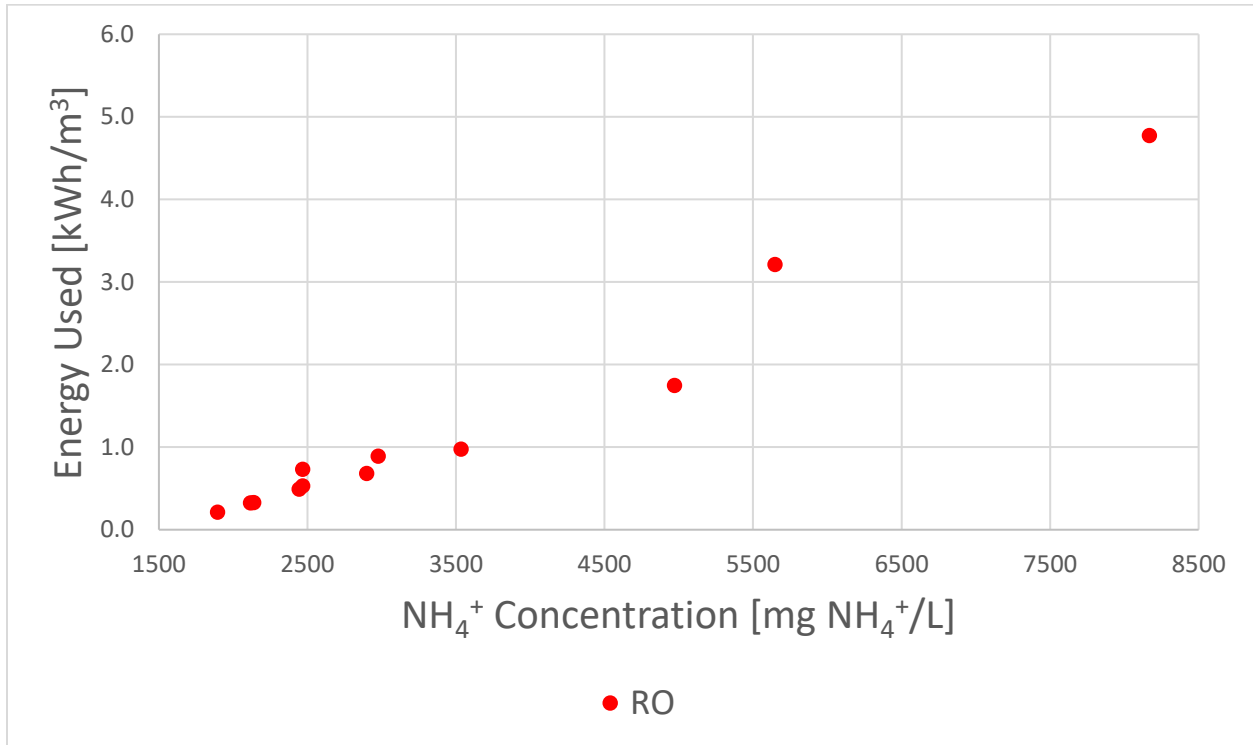


Figure 31: RO ROSA Software: Achievable NH_4^+ Concentration + Energy Used by RO (per m^3 of produced concentrated NH_4^+ solution)

5 Discussion

5.1 IEX

5.1.1 Short Loading/Regeneration Time

To produce a high NH_4^+ concentration with IEX, the IEX bed was not fully regenerated. Depending on the method of regeneration, the IEX bed was still 35 - 85 % saturated after regeneration. Continuing the regeneration would result in a higher total mass of NH_4^+ in the regenerant, but at a lower concentration (due to the higher volume). The combination of high concentration of NH_4^+ in the feed water and the focus on maximizing the concentration in the regenerant resulted in a short loading and regeneration period. Reloading the IEX beds would take, depending on the method of regeneration, 1.0 - 1.8 hours (compared to already short 3.7 hours of the first loading).

5.1.2 NaCl Concentration

To maximize the NH_4^+ concentration in the regenerant the IEX bed was regenerated with 100 g NaCl/L. This meant the high amount of NaCl had to be brought in, resulting in extra costs. This also meant a high concentration of NaCl was in the regenerant, which is processed in the gas production step of the overall N2kWh process (i.e. gas production, see Figure 2) further research will be needed to see if there are any negative effects of this NaCl concentration. The regeneration solution can then be reused (after gas production), however, sodium is still lost in the permeate (during loading).

5.1.3 K⁺ Removal

The zeolite has a high selectivity for NH_4^+ but has a higher selectivity for K^+ (potassium) (see 3.4.3). Because K^+ is present in (real) reject water (see Table 1) this could reduce the amount a 100% saturated IEX bed holds, which can negatively influence the achievable NH_4^+ concentration in the regenerant.

5.2 ED

5.2.1 fouling

When using ED to increase the NH_4^+ concentration of (real) reject water, scaling can be expected. Concentration polarization (see 2.4.1) can lead to inorganic scaling of phosphate, magnesium and calcium (Thompson Brewster et al., 2017). Possible pre-treatments include struvite recovery before ED to remove phosphates (however, this would also remove NH_4^+) and acid dosing (pH=5 to control calcium carbonate scaling) (Thompson Brewster et al., 2017). As an alternative, EDR (see 2.4.4) can be implemented to mitigate the scaling problem to a large extent (Strathmann, 2010) without the need of adding chemicals or removing NH_4^+ .

5.2.2 Alternative Staging Design

The efficiency of ED dropped as the difference in concentration between concentrate and diluate increased. A way to counter this could be to split the produced concentrate into a new concentrate and diluate stream, potentially increasing the concentration with each step without the drop in efficiency.

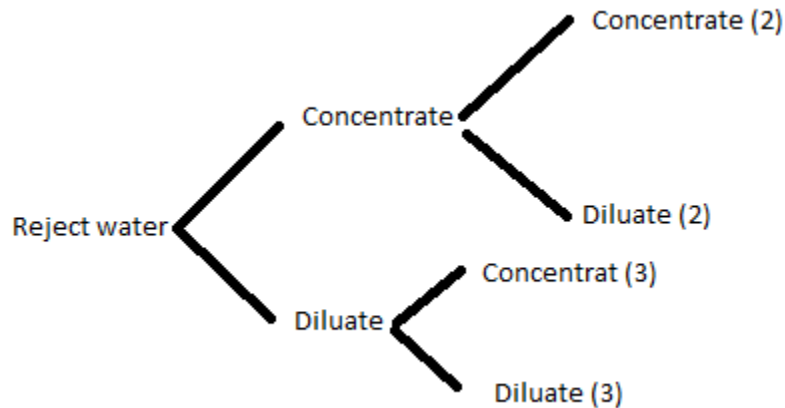


Figure 32: Schematization of Alternative ED Set-Up

Figure 32 gave a (simple) scheme of how this would work, the first concentrate is concentrated again, but now there is no concentration difference at the beginning of the second run. The same could be done with diluate, potentially extracting, even more, ammonium from the diluate. Further study will have to conclude if this results in an increase of achievable NH_4^+ concentration, and what energy efficiency of this staging design is.

5.3 RO

5.3.1 Fouling

Similar to ED, scaling can be expected while increasing the NH_4^+ concentration of (real) reject water. With RO, water (rather than ions) is passed through the membrane, so also SS (without a charge) present in the solution can cause problems. So next to scaling, physical fouling (see 2.5.4.2) can occur as well. Possible pre-treatments include anti-scaling, acid dosing or MF and NF. All these potential solutions would need extra energy or add chemicals.

5.3.2 ROSA

The ROSA software simulated multiple stages to increase the NH_4^+ concentration (see 3.6.1), however, in real RO set-ups, a pyramid staging design is applied. Here the concentrate flow of multiple vessels is used as feed flow for the next stage, which holds fewer pressure vessels (see Figure 33). Because of this staging design, an optimum feed/concentrate flow is maintained over all the vessels. When pyramid staging is not implemented, there is a maximum flow at the first vessel. This results in high pressure drops and possible structural damage to the membrane (however no warnings were given by the software, indicating that maximum pressure was not reached). Furthermore, the last vessel has a lower flow, which lowers the turbulence past the membrane (increasing salt concentrations at the membrane) (Lenntech BV, 2001). Applying a pyramid staging design would result in an increase in energy efficiency.

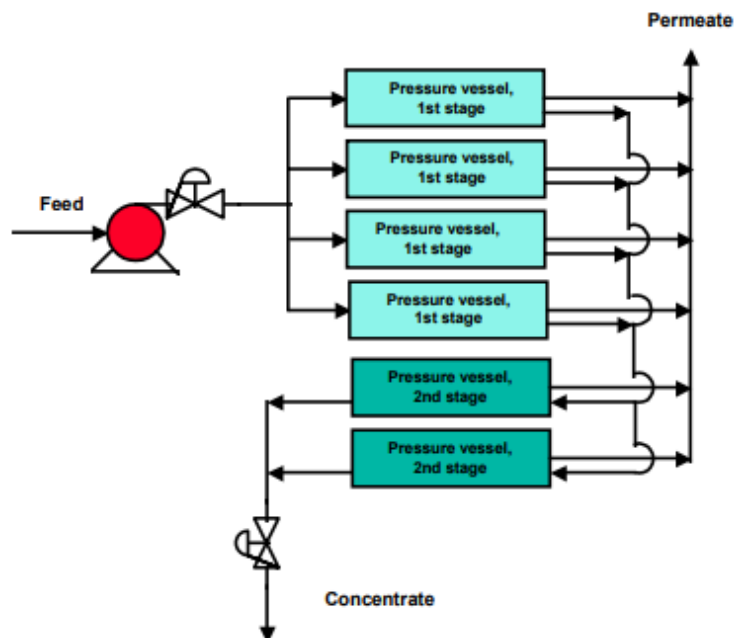


Figure 33: RO; Pyramid staging design (Lenntech BV, 2001)

5.4 Residual Streams

While this thesis focused on the achievable NH_4^+ concentration of the concentrated stream, it is also important to see what happens with the residual stream (i.e. diluate and permeate) of each of the three technologies. This paragraph looks at these streams. First by calculating how much of the processed feed water ends up in the residual stream. Secondly, the results of the experiments are used to calculate the NH_4^+ concentration of residual stream. These results together showed what percentage of available NH_4^+ in the feed water is not used (i.e. ends up in residual streams). A high concentration of NH_4^+ in the residual stream would still need energy to be processed.

5.4.1 Feed Water Needed

While the presented results focused on achievable concentrations of NH_4^+ and the energy that is needed, another aspect to consider is how much concentrated solution is produced from 1 m^3 of feed water (i.e. if 1 m^3 of feed water can produce 100 L with a $5 \text{ g NH}_4^+/\text{L}$ concentration, this is better than 50 L with a $5 \text{ g NH}_4^+/\text{L}$). Alternatively, how much feed water is needed (by the three technologies) to produce 1 m^3 of concentrated NH_4^+ solution (in a full scale set-up).

5.4.1.1 IEX

The feed water needed to produce 1 m^3 of concentrated NH_4^+ solution is calculated for regeneration with $100 \text{ g NaCl}/\text{L}$.

When focusing on second or subsequent loadings; during this loading, NH_4^+ was removed from 63 m^3 feed water. And regeneration produced 13 m^3 of regenerant (see Table 7). So for every 63 m^3 of reject water, 13 m^3 of a $5.96 \text{ g NH}_4^+/\text{L}$ solution was produced. Or 4.8 m^3 feed water is needed to produce 1 m^3 of regenerant.

An overview of the feed water needed for different regeneration methods was given in Figure 34.

5.4.1.2 ED

During the ED experiment, multiple 1 L reservoirs were used to increase the NH_4^+ concentration in the concentrate. So as the concentration increased so did the feed water used. During the experiment, water migrated from the diluate to the concentrate, increasing the volume of the concentrate with every diluate solution. The amount of feed water needed per m^3 of concentrate was calculated by

$$\text{Volume of diluate used [L]} * \frac{\frac{1000}{x}}{1000}$$

where X = volume of concentrate solution [L]

An overview was given in Figure 34.

5.4.1.3 RO [ROSA]

The ROSA software was used to simulate passing the feed water through multiple stages (up to 9 per simulated run). Different concentrations were reached by different feed flows and recoveries, where high recoveries (higher percentage of feed ends up as permeate) resulted in high concentrations in the concentrate, while simultaneously using more energy. For higher concentrations (i.e. $>5 \text{ g NH}_4^+/\text{L}$) the solution will have to pass the membrane multiple times. This was simulated by taking the concentrate flow from one simulation and using it as input for a second simulation. Every simulation step used a high feed and high recovery to maximize the concentration of the concentrate. In order to provide the second pass with enough feed, multiple streams would be needed in the first simulation. Resulting in an increase in feed water uses per produced concentrate. An overview of the different achievable concentrations with their energy used by the RO set-up and feed water used was given in Figure 34.

5.4.1.4 Overview

Since all technologies take the same 1.5 g NH₄⁺/L feed water, the achieved concentration can also be presented as a concentration factor (CF) from 1.5 g NH₄⁺/L. The CF was used to compare the three technologies in one graph. An overview of the amount feed water uses by the three technologies was given in Figure 34. In the graph, the feed water needed per m³ of produced concentrated NH₄⁺ solution was set against the achieved CF. The results showed a relationship between the achieved concentration and needed feed water; an increase in desired concentrations means more feed water is needed. IEX (using the method of regeneration which recirculated a small volume), had the biggest deviation from RO and ED. Where RO and ED had similar relationships (between the achieved concentration factor and amount of feed water needed).

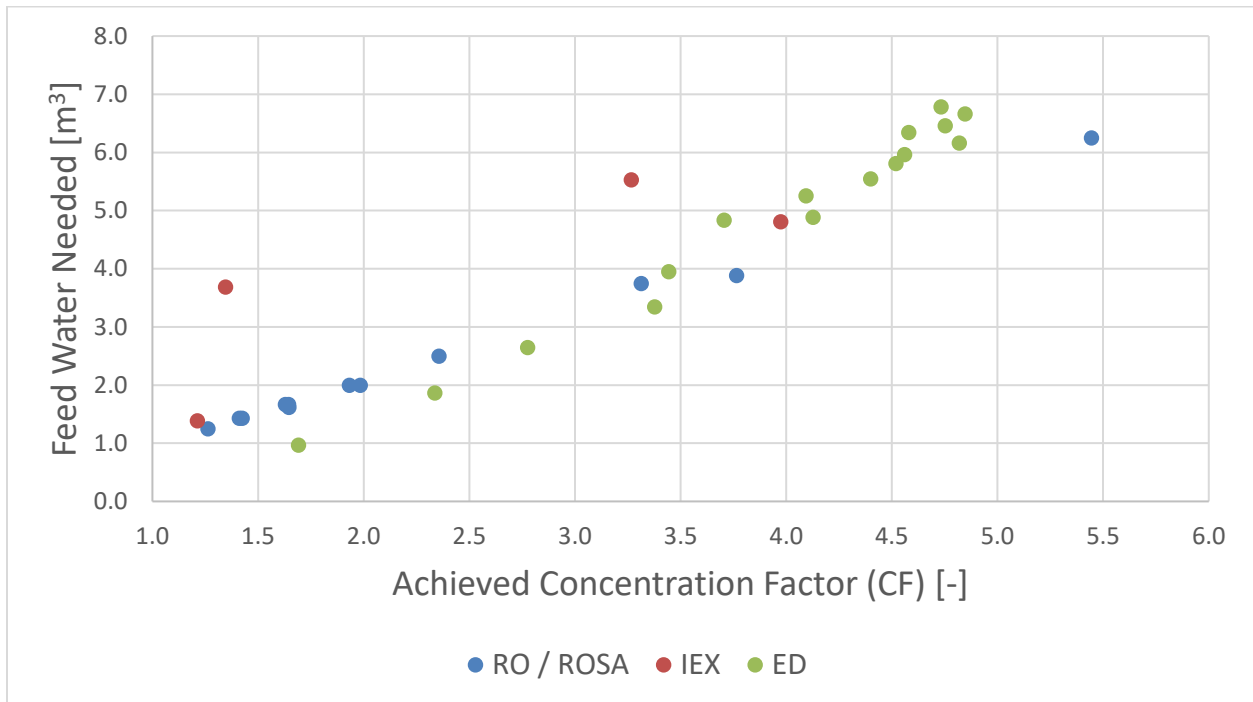


Figure 34: All Technologies: Volume of feed water needed (per m³ of produced concentrated NH₄⁺ solution) vs The Achievable CF

5.4.2 Residual Stream Concentration

When the amount of feed water needed and the amount of produced solution was known, so was the amount of residual solution. Together with the concentration of this residual the total amount of NH₄⁺ in the residual stream could be calculated. While this residual stream could be recycled to the WWTP, high NH₄⁺ concentrations still required high amounts of energy to remove via biological nitrification/denitrification.

5.4.2.1 IEX

The IEX zeolite removed all NH₄⁺ from the feed water until breakthrough occurs. However, because three beds were placed in series, the next IEX bed removed the residual NH₄⁺, while the first IEX bed was saturated to 100%. So the residual stream (permeate) held no NH₄⁺ and needed no further treatment (with respect to NH₄⁺).

5.4.2.2 ED

The end concentrations of the diluate solutions were previously mentioned in 4.2.3. With these concentrations and the calculated feed water needed, the total amount of NH_4^+ in the diluate could be calculated.

This amount divided by the total amount of NH_4^+ in the used feed water (i.e. the amount of NH_4^+ [g] in the feed flow = "volume of diluate used" x 1.5 g NH_4^+ /L), was the percentage of available NH_4^+ that ends up in the residual stream (i.e. diluate). This percentage was not used. This residual stream will need further treatment. The percentage of NH_4^+ that was not used (or that ended up in the residual stream) was given in Figure 35.

5.4.2.3 RO [ROSA]

The ROSA software not only reported the concentrate concentration and flow, but also the permeate concentration and flow. The results were reported in Figure 35.

Again, the percentage of available NH_4^+ that ends up in the residual stream (i.e. permeate) is reported. Compared to ED a higher percentage of the available NH_4^+ is not used. This residual stream will need further treatment.

5.4.2.4 Overview

The graph in Figure 34 showed no real difference in feed water needed by the different technologies. As the CF increases, so did the feed water needed per m³ of produced concentrated NH₄⁺ solution (i.e. concentrate and regenerant), as can be expected.

The percentage of NH₄⁺ that ended up in the residual stream, i.e. the percentage of NH₄⁺ that was not used, does differ between technologies. The graph in Figure 35 showed the percentage of available NH₄⁺ that ended up in the residual stream against the CF achieved in the concentrated NH₄⁺ solution. This showed that with RO a higher percentage of the available NH₄⁺ was wasted (especially with higher CF). The concentration of this residual stream could be concentrated again, but further research will need to determine the energy that is needed. With ED, 10% ends up in the residual stream, because the diluate solution is replaced when a concentration of 150 mg (=10% of 1.5 g NH₄⁺/L) is reached. By choosing at what point the diluate solution is replaced, the percentage NH₄⁺ that ends up in the residual stream can be altered.

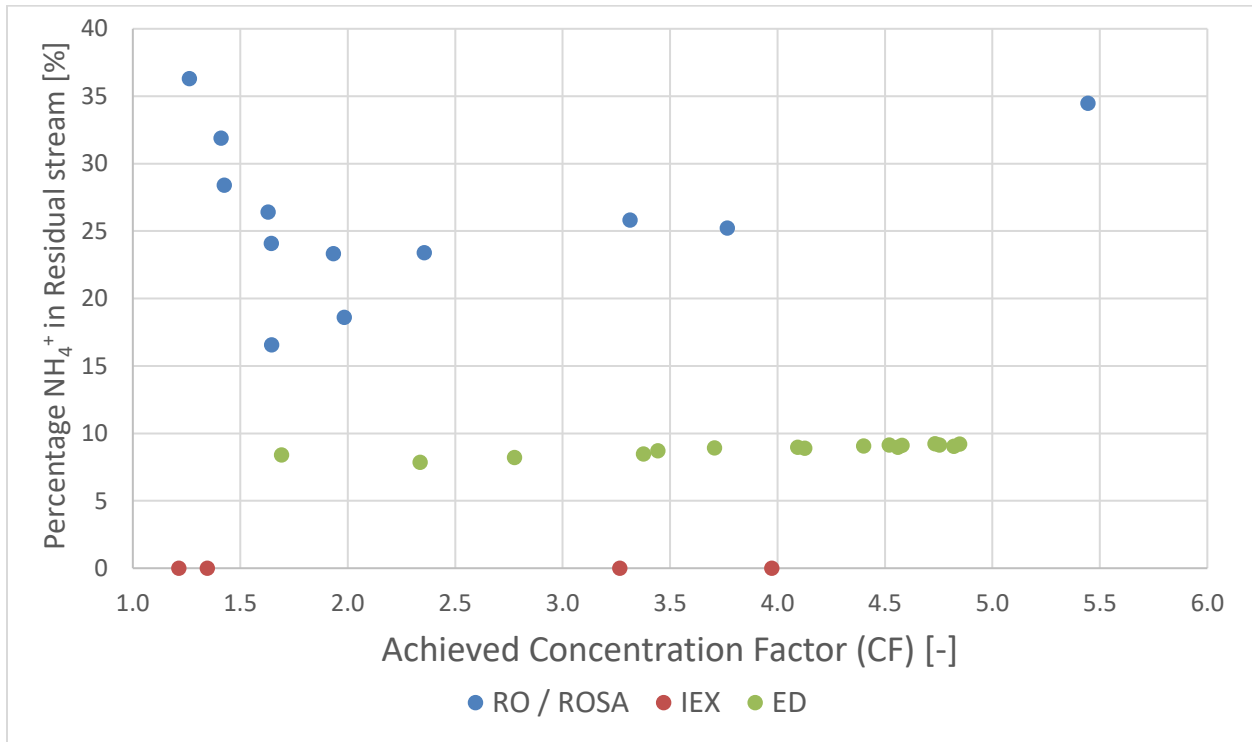


Figure 35: All Technologies: Percentage of Available NH₄⁺ in the Residual Stream vs The Achievable CF

6 Conclusions

6.1 IEX

The IEX was able to remove 100% of the NH_4^+ in the 1.5 g NH_4^+ /L feed water. Because the full scale set-up was assumed to have three IEX beds in series, to prevent the breakthrough of NH_4^+ , when the first bed became saturated. This also ensured a 100% saturation of the IEX before regeneration, which in turn maximized the achievable concentration with IEX. The maximum concentration that could be achieved by IEX was produced by regenerating with a 100 g NaCl/L solution. Resulting in a 6.0 g NH_4^+ /L solution.

The energy used by the IEX process (loading and regeneration), was calculated for full scale set-up using Kozeny-Carman and assumptions made about the IEX bed and measurements of the IEX vessel (discussed in 4.1.3). To achieve the maximum concentration, 0.12 kWh was used.

The results of the achievable concentrations and energy used per m^3 of produced concentrated NH_4^+ solution by IEX was given in Figure 36.

6.2 ED

The most energy efficient set-up was applying a current density of 15.6 A/ m^2 and a cross flow velocity of 43 m/h. The maximum achievable NH_4^+ concentration was achieved by replacing the diluate solution 16 times, resulting in an NH_4^+ concentration of 7.2 g NH_4^+ /L. energy used by a full scale set-up was calculated by scaling the results of the laboratory experiment. The maximum achievable concentration was 7.2 g NH_4^+ /L, using 8.9 kWh.

The achieved concentration in the concentrate (from the 1.5 g NH_4^+ /L feed water) and the energy used per m^3 of produced concentrated NH_4^+ solution were given in Figure 36.

6.3 RO

The experimental results validated the ROSA Software. There was a small difference (<7%) for the two values that mattered the most: Concentrate concentration and the TMP. The ROSA Software was then used to estimate the achievable NH_4^+ concentrations by a full-size set-up, while simultaneously reporting on the used energy.

The achievable concentrations with 1.5 g NH_4^+ /L feed water and their energy used per m^3 of produced concentrated NH_4^+ solution were given in Figure 36.

6.4 Overview

With the results of the three technologies, a comparison could be made between them. Since all technologies used the same 1.5 g NH₄⁺/L feed water, the achieved concentration could also be presented as a concentration factor (CF) from 1.5 g NH₄⁺/L. In Figure 36 the energy used per m³ of produced concentrated NH₄⁺ solution was set against the CF achieved, for all three technologies.

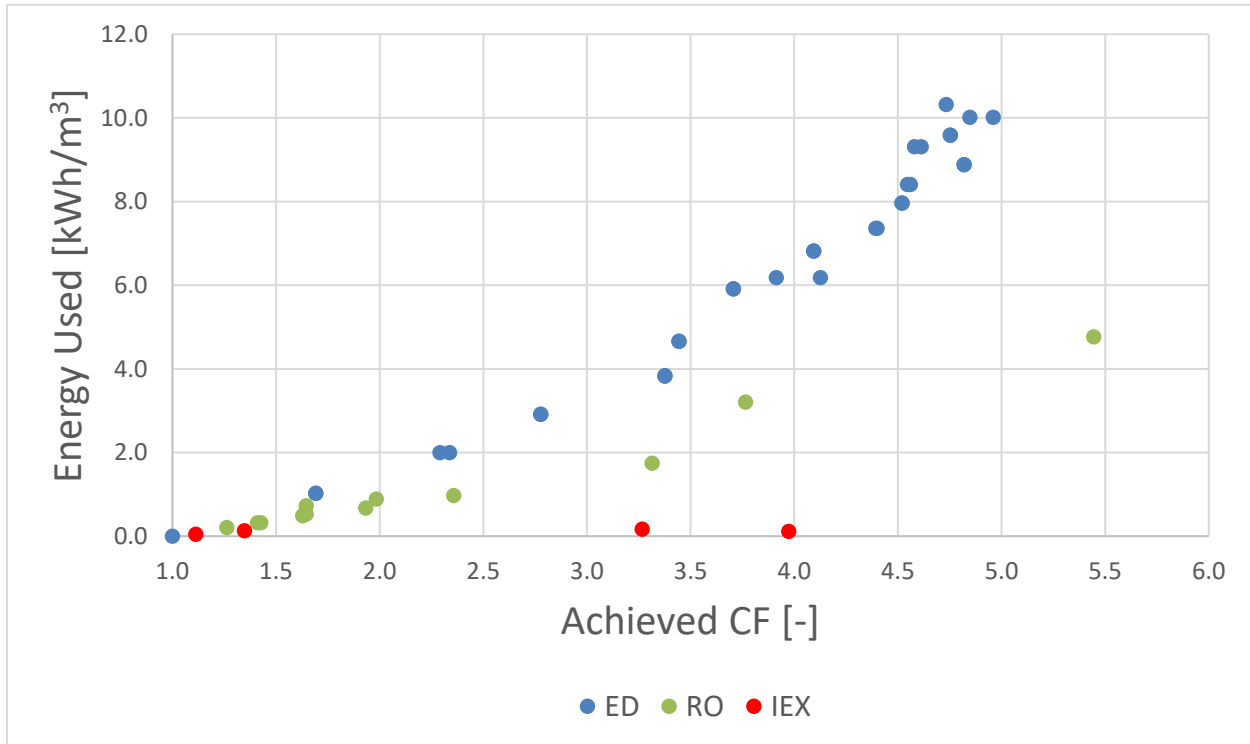


Figure 36: All Technologies: Energy Used by the Full scale Set-Ups (per m³ of produced concentrated NH₄⁺ solution) vs the Achievable CF (1.5 g NH₄⁺/L Feed concentration for all technologies)

Up to a CF of 4, the IEX used the least amount of energy per m³ produced, but there were some drawbacks. To get to a CF of 4, the IEX bed was regenerated with 100 g NaCl/L. This meant this high amount of NaCl had to be brought in, resulting in extra costs. This also meant a high concentration of NaCl was in the regenerant, which is processed in the gas production step of the overall N2kWh process (see Figure 2), further research will be needed to see if there are negative effects of this NaCl concentration.

At first, the difference between ED and RO are small. ED and RO start off very similar but ED was less efficient above CF 2. As shown in 4.2.2, as the difference between concentrations in concentrate and diluate increased during the ED experiment, the efficiency of the ED decreased. Applying an alternative staging design could have a positive effect on energy efficiency. When real reject water is used as feed water, efficiency will likely drop due to fouling. However, EDR is an effective measure to minimize the effects of fouling.

During RO laboratory experiments (due to pressure restrictions) an NH_4^+ concentration of only 4.5 g NH_4^+/L (CF=3) was reached, ROSA software was used to estimate higher CF. As with ED, when real reject water is the feed water, fouling will have a negative effect on the results. Necessary pre-treatment, to minimize the effects of fouling, will use more energy or add extra chemicals. Scaling will likely have a bigger impact on RO than ED. Furthermore, 5.4.2.4 showed that a higher percentage of the available NH_4^+ was not used by RO. Decreasing the amount of NH_4^+ that is wasted, would also result in an increase in energy use.

IEX seems to be the best candidate, with regards to energy used. However, ED can reach higher NH_4^+ concentrations. But ultimately the performance of the different (N2kWh) process steps together informs the choice of technology used in the concentration step. What is more important, a higher concentration or lower energy use? The graph in Figure 36 can be a valuable design tool, showing the cost of the desired CF when designing the entire process (from reject water to SOFC).

7 Recommendations

7.1 IEX

7.1.1 Loading, Regeneration, Reloading

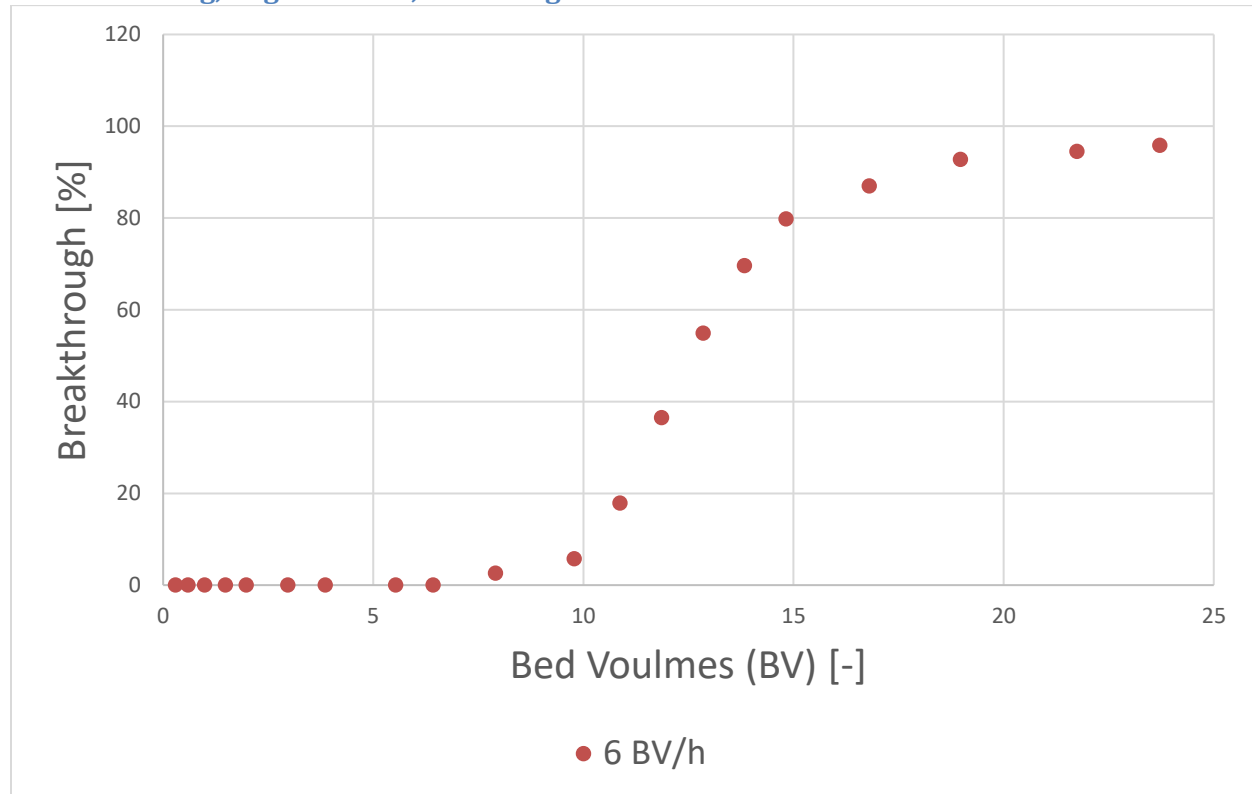


Figure 37: IEX Laboratory Set-Up: Breakthrough Curve of 1.5 g NH₄⁺/L feed Water; Feed flow of 6 BV/h. Sample points after IEX bed measure percentage of original (feed) concentration in effluent at different intervals.

To produce a high NH₄⁺ concentration with IEX, the regeneration was not fully carried out. With the reloading of the pre-loaded IEX bed, it was assumed that reloading would continue, following the graph that is shown in Figure 37. For example: when reloading starts with a saturation of 41% at 12 BV (after regeneration with 100 g NaCl/L), it takes 10 BV to get to 100 % saturation again. Extra experiments of loading-regenerating-reloading would have to be performed to check these assumptions.

7.1.2 Alternative Regeneration

To maximize the concentration of the regenerant, regeneration was stopped after 2.1 and 8.3 BV (when regenerating with a 100 g NaCl/L and a solution with pH of 12.5 respectively). So the IEX bed was still partly saturated (34 – 41 %) with NH₄⁺ when the bed was reloaded again.

An alternative to increasing the concentration, while fully regenerating the IEX bed comes from (Siegiers et al., 2001). Here multiple beds (in columns) are cycled on a carousel and loaded one after another. At the regeneration-section, multiple columns are regenerated with the same solution (see Figure 38; in the original research 30 columns are used).

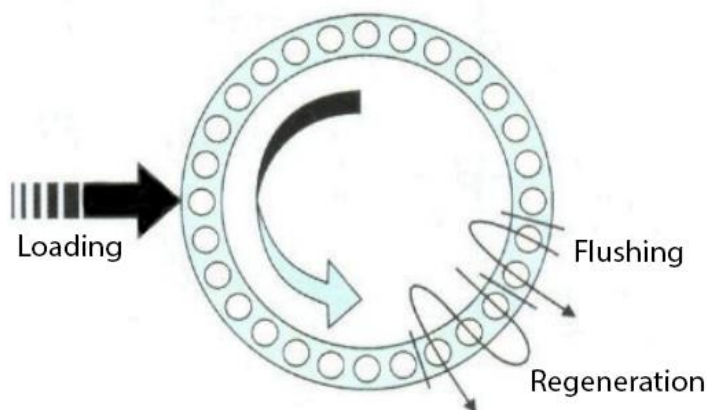


Figure 38: Schematization of Alternative Regeneration Set-Up

Regeneration is executed in counter-current, meaning that the most saturated IEX column is regenerated with regenerant with the highest NH_4^+ concentration (or “old” regenerant). And the most depleted IEX column with new regenerant. So with each new IEX column the concentration of NH_4^+ in the regenerant increases. While the technique was originally used to remove humic acid it could also work for NH_4^+ . Further research is needed to see how many columns are needed, how many columns are regenerated with the same regenerant and what concentration could be reached with this technique.

7.2 RO

Because the available RO laboratory set-up could only reach a pressure of about 15 bar, the ROSA Software is used to estimate the results of a full scale set-up. While experiments were able to validate the model for low (<15 bar) pressures, further research is needed to validate the ROSA model for applying high (>15 bar) pressures.

The software is not usually not used for scientific research. ROSA is a tool made by DOW chemicals, the ROSA software is usually used in the initial design stage to calculate what concentrations are to be expected, how many membranes are subsequently needed and the amount of energy that is needed. Experiments with a full scale set-up have to be performed to see how the results (achievable NH_4^+ concentrations and the energy used) line up with the ROSA software.

7.3 Reject Water

This thesis focused on a $1.5 \text{ g NH}_4^+/\text{L}$ solution to simulate reject water, but how these technologies would react to actual reject water instead is still unclear. What negative effects will occur and what pre-treatments are necessary (described in chapter 5), are dependant on the precise composition of the reject water. Further research is needed.

8 Appendix

8.1 Appendix A: ED

8.1.1 LCD calculation

During a run with a constant velocity, as the concentration of the diluate decreased so did the LCD. To calculate the LCD first, a constant velocity and concentration were chosen. Now the LCD for this velocity/concentration combination could be found (the concentration was kept constant by recirculating the diluate and concentrate in the same reservoir). For different current densities (15.6 to 109 A/m²) the average potential was measured and corresponding resistance calculated. The (inverse) current density with the lowest resistance was the LCD for that velocity/concentration (Ponce-de-Leon & Field, 2000) (see Figure 39).

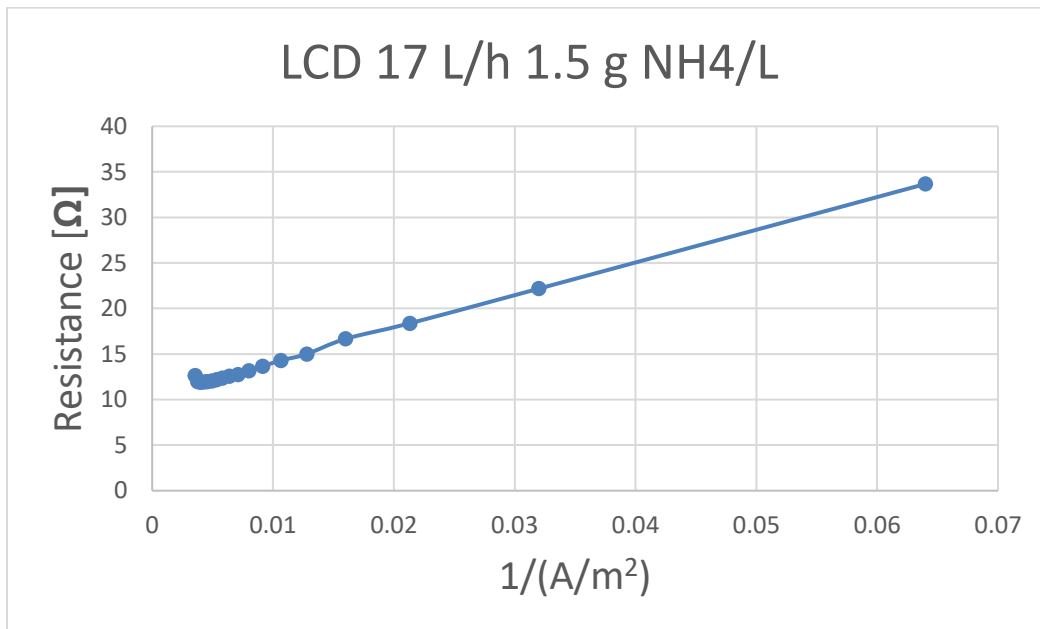


Figure 39: ED Laboratory Set-Up: LCD for Cross flow velocity = 43 m/h and Concentration = 1.5 g NH₄⁺/L

After repeating this process for other concentration with the same velocity, Figure 40 was produced. This process was repeated for other velocities as well. In the graph, the concentration was represented with EC because that was the parameter which could be monitored in real time during the experiments. So, as the EC dropped, the current density that was applied was adjusted, to make sure the LCD was not reached.

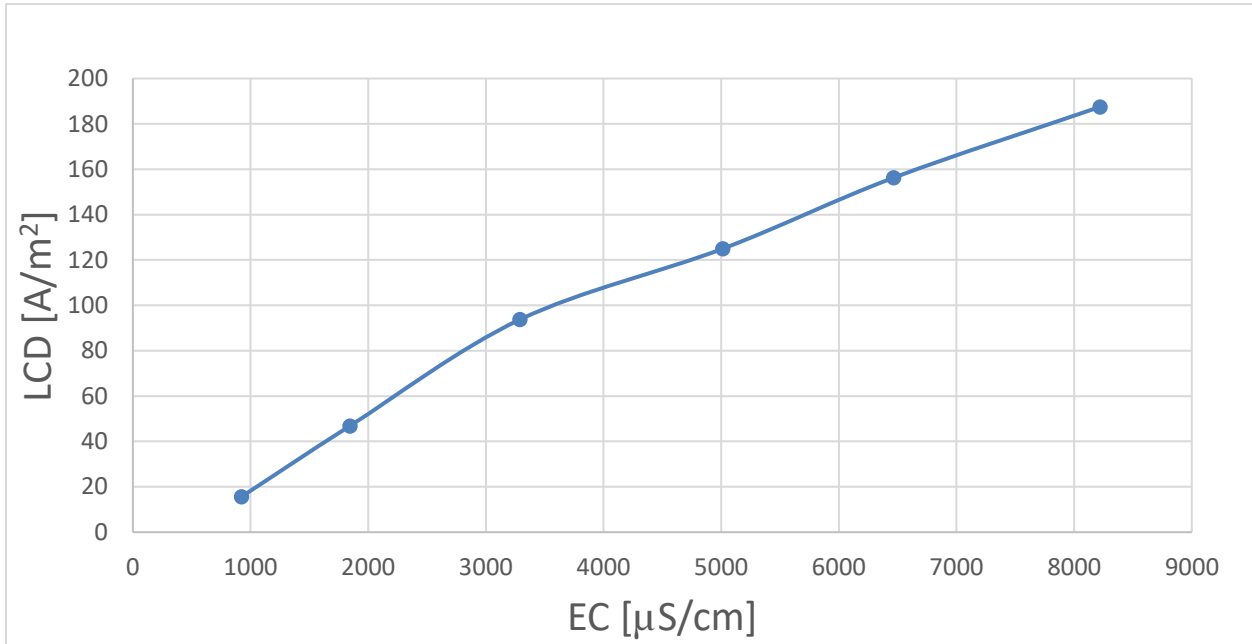


Figure 40: ED Laboratory Set-Up: LCD for Cross flow velocity = 43 m/h

8.1.2 Achieved NH₄⁺ concentration

In Table 15 an overview was given of the concentrations of the concentrate and diluate and the energy used, per reservoir of diluate replaced.

Table 15: ED; Achievable NH₄⁺ concentrations and Energy used, for laboratory scale and full scale set-up

Diluate Reservoir	time [h]	EC Diluate [μS/cm]	Concentration Diluate [mg NH ₄ ⁺ /L]	EC Concentrate [μS/cm]	Concentration Concentrate [mg NH ₄ ⁺ /L]	Energy Used (Lab Scale) [Wh]	Volume Concentrate [L]	Energy Used (Full Scale) [kWh]
1	0	8600	1457	8070	1486	0.00	1	0.00
	3	952	126	13980	2538	1.06	1.03	1.03
2	3	7910	1455	13840	2538	1.06	1.03	1.03
	5	854	109	18280	3505	2.14	1.07	2.00
3	5	8070	1498	18070	3435	2.14	1.07	2.00
	8	987	136	21700	4165	3.30	1.13	2.92
4	8	8000	1493	21400	4165	3.30	1.13	2.92
	11	1014	141	24400	5065	4.58	1.20	3.83
5	11	7810	1496	24300	5065	4.60	1.20	3.85
	15	1014	150	26500	5165	5.90	1.27	4.67
6	15	8160	1462	26200	5165	5.90	1.27	4.67
	18	964	148	28200	5560	7.34	1.24	5.92
7	18	8040	1458	27800	5560	7.34	1.24	5.92
	22	816	124	29400	6190	8.87	1.43	6.19
8	22	8130	1440	29300	5870	8.87	1.43	6.19
	26	1006	148	30400	6140	10.38	1.52	6.82
9	26	7990	1491	30000	6140	10.38	1.52	6.82
	30	990	159	30900	6600	11.95	1.62	7.36
10	30	8380	1482	30700	6590	11.95	1.62	7.36
	34	986	158	31500	6780	13.72	1.72	7.97
11	34	7990	1504	31100	6780	13.72	1.72	7.97
	38	985	41	31800	6840	15.51	1.84	8.41
12	38	8270	1483	31300	6820	15.51	1.84	8.41
	42	994	167	31800	7230	17.31	1.95	8.89
13	42	8000	1537	31600	7230	17.31	1.95	8.89
	47	981	172	31900	6870	19.09	2.05	9.32
14	47	8130	1519	31800	6920	19.09	2.05	9.32
	51	1001	167	32200	7130	20.79	2.17	9.59
15	51	8010	1482	31900	7130	20.79	2.17	9.59
	55	996	170	32300	7270	22.55	2.25	10.02
16	55	8240	1571	32500	7440	22.55	2.25	10.02
	60	992	170	32800	7100	24.35	2.36	10.33

8.1.3 Energy Used - ED Pumps

To estimate the energy use of the pumps during the experiments, two Festo SPAU pressure sensors were used. The sensors were placed before the ED cell to see the pressure drop over the cell (the pressure after the ED cell was zero). The pressure drop of the concentrate, diluate and electrolyte were all measured separately. With this pressure drop, the power of the pumps can be estimated by:

$$P = Q * \rho * g * h \text{ [W]}$$

With Q = Flow [m^3/s], ρ = density [kg/m^3], g = gravity [m/s^2] and h = pressure drop [m]



Figure 41: Photo of Pressure Sensors: Calculating Power [W] of the Pumps used in ED Laboratory Experiments.

The average pressure drops over the ED cell for the different flows were given in Table 16. The energy used by the pumps were added to the total energy used by the ED cell in Table 17 (assuming a pump efficiency of 60 %). Note that the set-up combination of high cross flow velocity, low current still used the lowest amount of energy.

Table 16: ED Laboratory Set-Up: ED Efficiency Test: Calculating Pressure Drop over the ED Cell

Feed flow [L/h]	Pressure Drops [bar]			Average pressure drop [bar]
	Elec	Conc	Dil	
17	0.04	0.05	0.05	0.04
5.5	0.04	0.03	0.03	0.03

Table 17: ED Laboratory Set-Up: ED Efficiency Test: Total Energy Used by ED and Pumps

Set Up	Flow [m ³ /s]	Pressure Drop [m]	Total Time [h]	Energy Used ED [Wh]	Power Pumps [W]	Energy used Pumps [Wh]	Total Energy use [Wh]
43 m/h LCD	5.00E-06	0.43	0.9	2.76	1.1E-01	9.0E-02	2.85
43 m/h 0,5 LCD	5.00E-06	0.43	1.4	1.58	1.1E-01	1.4E-01	1.72
43 m/h 15.6 A/m ²	5.00E-06	0.43	2.7	0.93	1.1E-01	2.8E-01	1.21
14 m/h LCD	2.00E-06	0.33	1.9	1.67	3.3E-02	6.33E-02	1.73
14 m/h 0,5 LCD	2.00E-06	0.33	3.8	1.10	3.3E-02	1.25E-01	1.23
14 m/h 15.6 A/m ²	2.00E-06	0.33	2.7	1.34	3.3E-02	8.70E-02	1.43

8.2 Appendix B: NH₄⁺ Measurements

8.2.1 Electrical Conductivity

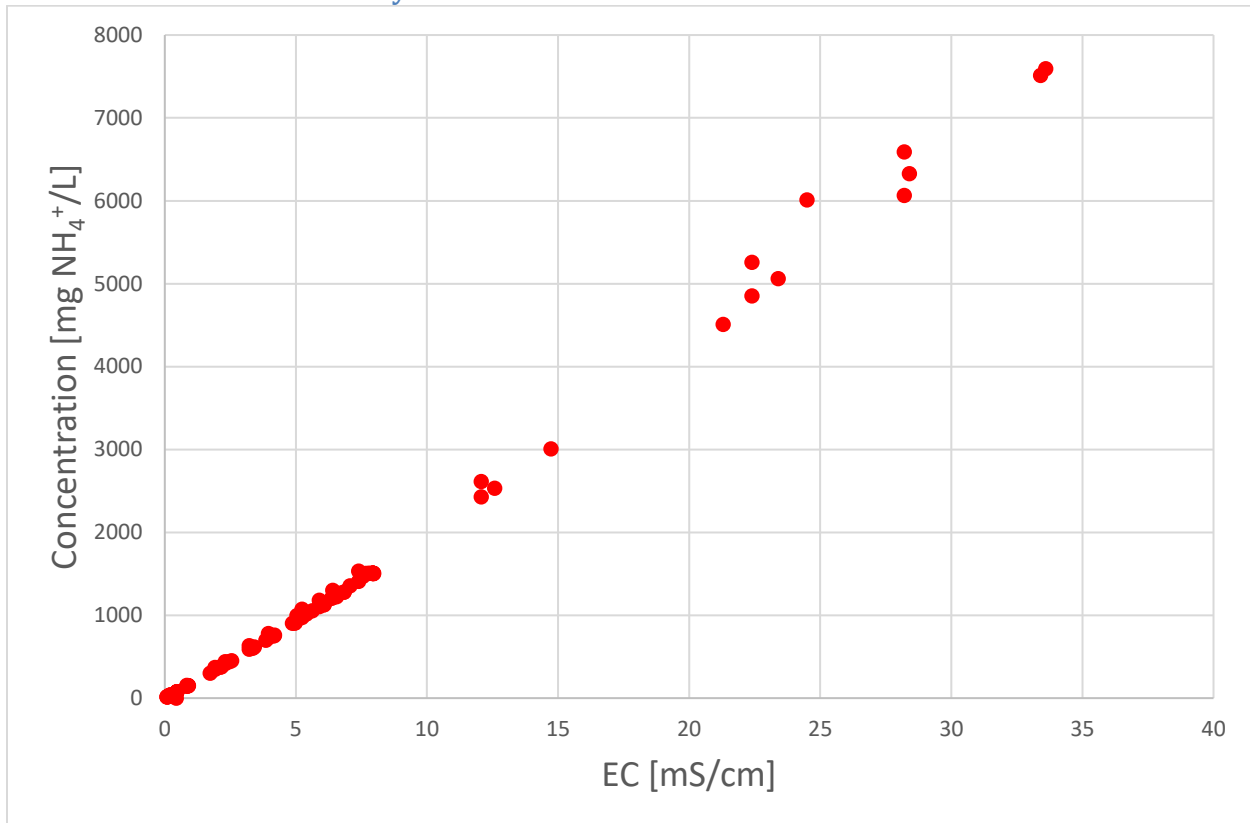


Figure 42: EC; Measured EC vs Known concentrations

The relationship between the EC and NH₄⁺ concentration (in mg NH₄⁺/L) was (see Figure 42):

$$226x - 150 = \text{NH}_4^+ \text{ concentration [mg/L]}$$

With $x = \text{EC [mS/cm]}$

8.2.2 Analysis of NH_4^+

However, the MN test kits were found to be much more precise and were used to compare the three technologies. The deviation between known (weighed) concentrations and measured concentrations with the MN test kits were less than 5%. In Figure 43 an almost perfect, 45° graph was produced.

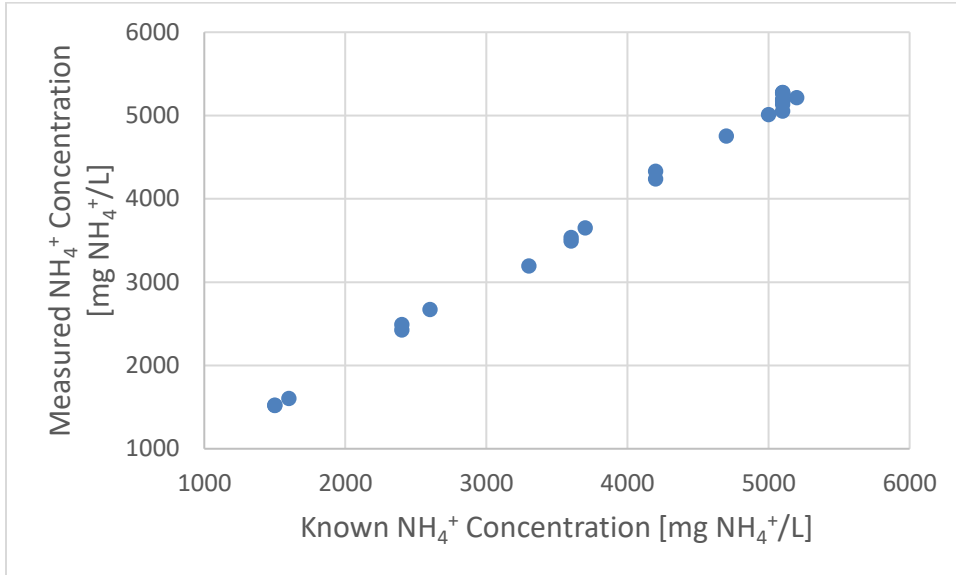


Figure 43: Measured vs Known NH_4^+ concentration

8.3 Appendix C: IEX Energy Used Calculations

In 4.1.3.1 the used energy was calculated for regeneration with a 100 g NaCl/L solution. Here the calculations for the energy used by regeneration with the other methods were given. The initial loading was always the same, however, differences occurred during regeneration and the subsequent reloading.

8.3.1 Regeneration NaOH - pH = 12.5

Regeneration was performed with a solution with pH = 12.5, an overview of the regeneration and reloading step applied to the vessel, described in 3.4.4.1, were given in Table 18 and Table 19 (The “breakthrough” and “fully loaded after” was taken from Figure 18).

The IEX was not fully regenerated, to maximize the concentration of the regenerant. Regeneration stopped after 8.3 BV to achieve a 1.67 g NH₄⁺/L concentration in the regenerant. A regenerant volume of 8.3 BV (52.2 m³) with a concentration of 1.67 g NH₄⁺/L held 87 kg of NH₄⁺. Only 87 of the 132 kg in the IEX bed was released during regeneration, this means that when the bed was loaded a second time the IEX was already 34% saturated. During this second (and subsequent) loading the IEX bed was fully loaded after 1.8 h (see Table 19).

Table 18: IEX Full Scale Set-Up: IEX Regeneration with pH = 12.5 Solution

Feed Flow	12.5	BV/h
Feed Flow	78	m ³ /h
Feed Flow	0.02	m ³ /s
Velocity	25	m/h
Velocity	0.007	m/s
Max Concentration Regenerant after	8.3	BV
Volume Regenerant	52.2	m ³
Run Time	0.67	h
Concentration	1.67	g/L
Total NH ₄ Removed	87	kg

Table 19: IEX Full Scale Set-Up: Subsequent Loading (Regeneration with pH = 12.5 Solution)

NH ₄ ⁺ in IEX bed	45	kg
Saturation	34	%
Fully Loaded after	10.5	BV
Fully Loaded after	1.8	h
Total Volume Exchanged	66	m ³

8.3.2 Regeneration Recirculation with Small Volume

Regeneration was applied with a smaller volume that was recirculated over the saturated IEX bed. First with a 100 g NaCl/L solution. An overview of the regeneration and reloading step, applied to the vessel, described in 3.4.4.1, were given in Table 20 and Table 21 (The “breakthrough” and “fully loaded after” was taken from Figure 18).

The IEX was not fully regenerated, the regeneration was stopped when an equilibrium was reached. Regeneration stops after 5 BV to achieve a 4.97 g NH₄⁺/L concentration in the regenerant. A regenerant volume of 1.6 BV (10.2 m³) with a concentration of 4.97 g NH₄⁺/L held 81 kg of NH₄⁺. Only 81 of the 132 kg in the IEX bed was released during regeneration, this means that when the bed was loaded a second time the IEX was already 61% saturated. During this second (and subsequent) loading the IEX bed was fully loaded after 1.5 h (see Table 21).

Table 20: IEX Full Scale Set-Up: IEX Regeneration by Recirculating Small volume (100 g NaCl/L)

Feed Flow	12.5	BV/h
Feed Flow	78	m ³ /h
Feed Flow	0.02	m ³ /s
Velocity	25	m/h
Velocity	0.007	m/s
Volume Regenerant	1.6	BV
Volume Regenerant	10.2	m ³
Run Time	5	BV
Run Time	0.4	h
Concentration	4.97	g/L
Total NH ₄ Removed	51	kg

Table 21: IEX Full Scale Set-Up: Subsequent Loading (Regeneration by Small Volume; 100 g NaCl/L)

NH ₄ ⁺ in IEX bed	81	kg
Saturation	61	%
Fully Loaded after	9	BV
Fully Loaded after	1.5	h
Total Volume Exchanged	57	m ³

Second, the IEX bed was recirculated with a pH = 12.5 solution. An overview of the regeneration and reloading step, applied to the vessel described in 3.4.4.1, were given in Table 22 and Table 23 (the “breakthrough” and “fully loaded after” was taken from Figure 18).

The IEX was not fully regenerated, the regeneration was stopped when an equilibrium was reached. Regeneration stops after 5 BV to achieve a 2.02 g NH₄⁺/L concentration in the regenerant. A regenerant volume of 1.6 BV (10.2 m³) with a concentration of 2.02 g NH₄⁺/L held 21 kg of NH₄⁺. Only 21 of the 132 kg in the IEX bed was released during regeneration, this means that when the bed was loaded a second time the IEX was already 84% saturated. During this second (and subsequent) loading the IEX bed was fully loaded after 1.0 h (see Table 23).

Table 22: IEX Full Scale Set-Up: IEX Regeneration by Recirculating Small volume (pH = 12.5)

Feed Flow	12.5	BV/h
Feed Flow	78	m ³ /h
Feed Flow	0.02	m ³ /s
Velocity	25	m/h
Velocity	0.007	m/s
Volume Regenerant	1.6	BV
Volume Regenerant	10.2	m ³
Run Time	5	BV
Run Time	0.4	h
Concentration	2.02	g/L
Total NH ₄ Removed	21	kg

Table 23: IEX Full Scale Set-Up: Subsequent Loading (Regeneration by Small Volume; pH = 12.5)

NH ₄ ⁺ in IEX bed	111	kg
Saturation	84	%
Fully Loaded after	6	BV
Fully Loaded after	1.0	h
Total Volume Exchanged	38	m ³

The achievable NH₄⁺ concentrations and energy use of the four regeneration methods are given in Table 24.

Table 24: IEX Full Scale Set-Up: Achievable NH₄⁺ Concentration + Energy Used by IEX, using various Regeneration Methods (per m³ of produced concentrated NH₄⁺ solution)

Regeneration Method	Regenerant Concentration [g NH ₄ ⁺ /L]	Energy Used 1st Run [kWh]	Energy Used subsequent runs [kWh]
Regeneration NaOH; pH = 12.5	1.7	0.08	0.05
Recirculation Small Volume (NaOH pH = 12.5)	2.0	0.34	0.13
Recirculation Small Volume (100 g NaCl/L)	4.9	0.34	0.17
Regeneration 100 g NaCl/L	6.0	0.24	0.12

8.4 Appendix D: ROSA Energy Used

The feed flow, recovery, membrane choice and number of stages were used as input for the ROSA software. The software then calculated the expected concentration, permeate flow and energy use. Multiple flows/recovery combinations were run through the software and the achieved NH_4^+ concentrations and energy used by the full scale set-up were presented in Figure 36.

The result of one flow/recovery combination, i.e. a feed flow of $0.6 \text{ m}^3/\text{h}$ and a recovery of 73% over 9 stages, was given in Table 25. The reported energy used was 1.7 kWh per m^3 of produced concentrated NH_4^+ solution. The concentrate concentration of $4.97 \text{ g NH}_4^+/\text{L}$ and 1.7 kWh energy used was reported in Table 25.

Table 25: RO ROSA Software Results: Simulation with Feed Concentration = $1.5 \text{ NH}_4^+/\text{L}$; Feed Flow = $0.6 \text{ m}^3/\text{h}$; Recovery = 73 %; 9 Stages

Stage	Feed Flow	Feed Press	Conc Flow	Concentrate Pressure	Permeate Flow	Permeate NH_4^+	TMP	Concentration NH_4^+ [mg NH_4^+/L]	
	[m^3/h]	[bar]	[m^3/h]	[bar]	[m^3/h]	[mg NH_4^+/L]		Concentrate	Permeate
1	0.60	13.32	0.48	13.11	0.12	286.68	13.215	1992	187
2	0.48	12.76	0.38	12.61	0.10	438.88	12.685	2437	221
3	0.38	12.26	0.31	12.15	0.07	695.69	12.205	2930	278
4	0.31	11.80	0.26	11.72	0.05	1123.24	11.76	3417	372
5	0.26	11.37	0.23	11.30	0.03	1791.53	11.335	3846	521
6	0.23	10.96	0.20	10.90	0.02	2719.89	10.93	4200	727
7	0.20	10.56	0.19	10.50	0.02	4029.57	10.53	4501	1020
8	0.19	10.16	0.17	10.11	0.01	5281.00	10.135	4751	1300
9	0.17	9.77	0.16	9.73	0.01	6396.43	9.75	4971	1550
				Total Permeate	0.430	m^3/h		Total permeate	387

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