

**Ammonia - from pollutant to power**

**Removal and recovery of total ammoniacal nitrogen from residual waters for electricity generation**

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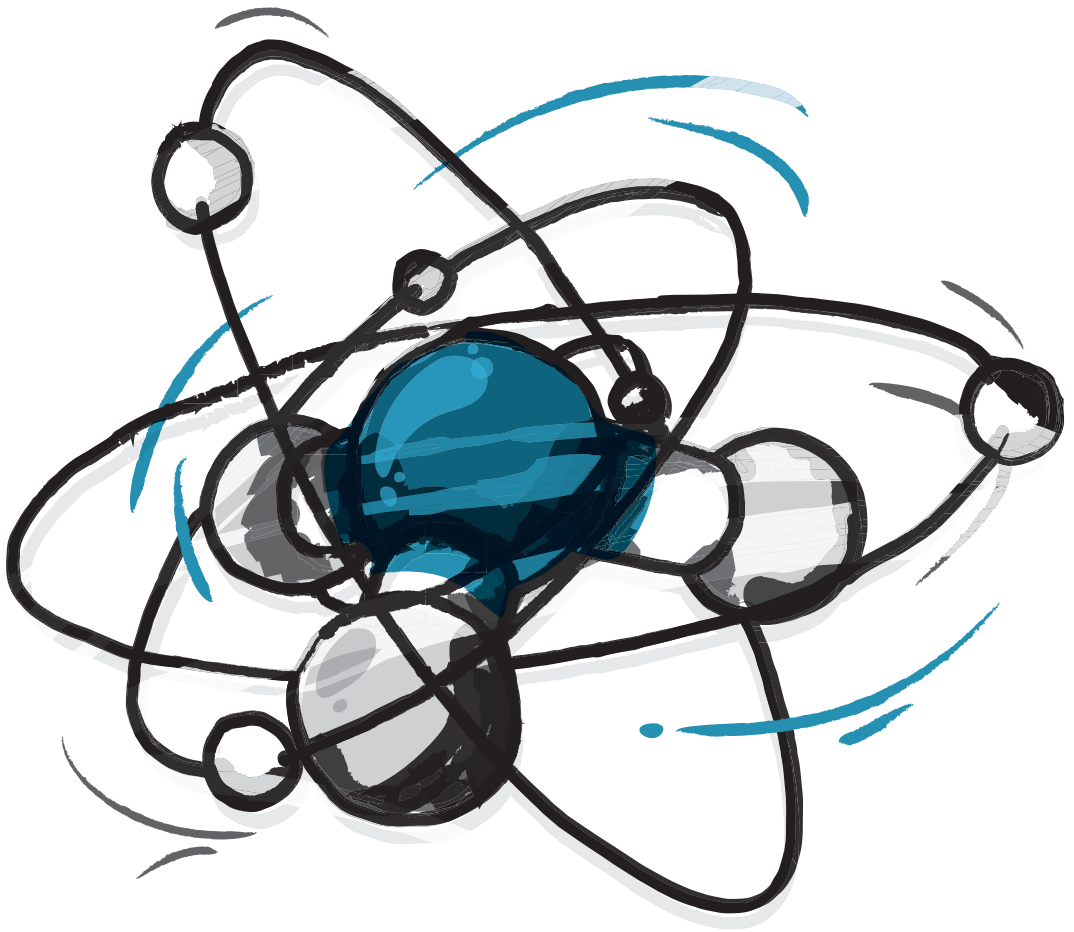
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# Ammonia – from pollutant to power

Removal and recovery of total ammoniacal nitrogen  
from residual waters for electricity generation



Niels van Linden

# Ammonia - from pollutant to power

Removal and recovery of total ammoniacal nitrogen from residual waters  
for electricity generation

## Dissertation

for the purpose of obtaining the degree of doctor  
at Delft University of Technology

by the authority of the Rector Magnificus Prof. dr. ir. T.H.J.J. van der Hagen,  
chair of the Board for Doctorates  
to be defended publicly on  
11<sup>th</sup> of July 2022 at 15:00 o'clock

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Keywords:

ammonia, electricity generation, electrodialysis, bipolar membrane electrodialysis, vacuum membrane stripping, pervaporation, solid oxide fuel cell

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# Abstract

Ammonia ( $\text{NH}_3$ ) is one of world's most-produced chemicals and is mostly used as a raw resource for fertilisers. From the used  $\text{NH}_3$ -based fertilisers, almost half of the  $\text{NH}_3$  ends up in receiving water bodies, leading to eutrophication, eventually resulting in species diversity loss in the aquatic environment. To minimise environmental damage, total ammoniacal nitrogen (TAN) should be removed from residual waters before discharge. Currently, the treatment of residual waters with high TAN concentrations (hereafter nitrogen (N)-loaded residual waters) by biological processes, such as partial nitrification in combined with anammox (reaching TAN removal efficiencies up to 90%), is challenged by the undesired emission of oxidised nitrogen species. In addition, current methods to recover TAN from N-loaded residual waters for reuse purposes require large amounts of energy and chemicals.

Interestingly,  $\text{NH}_3$  was recently acknowledged as a carbon-free carrier of energy, having an energy content of  $21 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . The fact that  $\text{NH}_3$  carries energy, opens possibilities to remove TAN from N-loaded residual waters and subsequently recover  $\text{NH}_3$  for the generation of electricity, potentially leading to energy-positive methods to remove TAN from N-loaded residual streams. The objective of this thesis was to assess the feasibility to achieve competitive (approximately 90%) TAN removal from N-loaded residual waters and to use the recovered  $\text{NH}_3$  for electricity generation purposes, using a combination of technologies without using chemicals. The used technologies in this thesis are electro dialysis (ED), bipolar membrane electro dialysis (BPMED), vacuum membrane stripping (VMS) and a solid oxide fuel cell (SOFC). To determine the suitability of the combination of technologies, the research conducted in this thesis focused on the mass transfer and achievable concentrations of the various TAN species (ammonium ( $\text{NH}_4^+$ ), dissolved  $\text{NH}_3$  and gaseous  $\text{NH}_3$ ), as well as the electrical energy aspects (consumption and generation) for the various technologies.

In this thesis, a literature study in Chapter 2 identifies thirteen potentially suitable N-loaded residual waters from which  $\text{NH}_3$  can be recovered for electricity generation purposes. In addition, the literature study provides an overview of potentially suitable technologies to remove TAN from N-loaded residual waters and to recover  $\text{NH}_3$  for electricity generation purposes. Each of the selected technologies subsequently served as a research topic in the chapters of this thesis. Research on ED in Chapter 3 shows that applying dynamic current density leads to higher concentration factors to produce concentrated  $\text{NH}_4^+$  solutions, at lower electrical energy consumption compared to applying fixed current density. Solutions with  $\text{NH}_4^+$  concentrations up to  $10 \text{ g}\cdot\text{L}^{-1}$  were produced by ED at an  $\text{NH}_4^+$  removal efficiency of approximately 90%, at an electrical energy consumption of  $5 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . Subsequently, research on BPMED in Chapter 4 shows that approximately 90%  $\text{NH}_4^+$  removal can be achieved by BPMED, while simultaneously concentrated solutions with  $\text{NH}_3$  concentrations of  $4.5 \text{ g}\cdot\text{L}^{-1}$  can be produced without using chemicals, at an electrical energy consumption of  $22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . Furthermore, research on the recovery of  $\text{NH}_3$  as a gas by VMS in Chapter 5 and

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6 shows that transfer of water ( $\text{H}_2\text{O}$ ) is inevitable, leading to the recovery of  $\text{NH}_3\text{-H}_2\text{O}$  mixtures when using VMS. Transfer of  $\text{H}_2\text{O}$  is even consistently preferred over the transfer of  $\text{NH}_3$ , for various feed water compositions, operating conditions and membrane types, when using VMS to recover gaseous  $\text{NH}_3$  from water. By providing  $\text{NH}_3$  feed water concentrations up to  $10 \text{ g}\cdot\text{L}^{-1}$ ,  $\text{NH}_3$  concentrations of 11 wt% can be obtained in the recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixtures. Research on the SOFC in Chapter 6 shows that  $\text{NH}_3\text{-H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations down to 5 wt% can still be used for electricity generation purposes: the SOFC generated of  $9 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$  of electrical energy. Research on real N-loaded residual streams in Chapter 7 shows the feasibility of ED to achieve competitive (approximately 90%) TAN removal from three real N-loaded residual waters: algae digestion reject water, sludge digestion reject water and fertiliser industry condensate. The treatment of fertiliser industry condensate was not hampered by implications due to the presence of other ions or organics in the feed water. ED, BPMED, VMS and an SOFC were combined to achieve approximately 90% TAN removal from fertiliser industry condensate and to ultimately generate energy from the recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixtures. The electrical energy consumption of ED, BPMED and VMS was  $38 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$ , whereas the SOFC generated  $11 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$ . The combination of technologies had a net electrical energy consumption of  $27 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$ , making the proposed system not yet energy-positive in terms of electricity.

For each of the technologies, more research on the mass transfer of the various TAN species, the used (membrane) materials and operating conditions is required to decrease the electrical energy consumption of the ED, BPMED and VMS and to increase the electricity generation of the SOFC, to potentially develop an energy-positive system to remove TAN from N-loaded residual waters.

# Samenvatting

Ammoniak ( $\text{NH}_3$ ) is een van 's werelds meest geproduceerde chemicaliën en wordt vooral gebruikt als grondstof voor kunstmest. Van alle gebruikte kunstmest op  $\text{NH}_3$  basis, eindigt bijna de helft van de  $\text{NH}_3$  in ontvangende waterlichamen, leidend tot eutrofiering, wat uiteindelijk resulteert in het verlies van soorten diversiteit in het waterige milieu. Om schade aan het milieu te minimaliseren, moet ammoniakale stikstof verwijderd worden van restwateren voordat deze geloosd worden. Momenteel wordt de behandeling van restwateren met hoge ammoniakale stikstof concentraties (hierna stikstof-rijke restwateren genoemd) door biologische processen zoals als partiele nitrificatie in combinatie met anammox (reikend tot ammoniakale stikstof verwijderingsefficiënties tot 90%) uitgedaagd door de onwenselijke uitstoot van geoxideerde stikstof soorten. Daarnaast hebben huidige methoden om ammoniakale stikstof uit stikstof-rijke restwateren terug te winnen voor hergebruik grote hoeveelheden energie en chemicaliën nodig.

Interessant genoeg werd  $\text{NH}_3$  recent erkend als koolstof-vrije energiedrager, met een energie inhoud van  $21 \text{ MJ} \cdot \text{kg-N}^{-1}$ . Het feit van  $\text{NH}_3$  energie draagt, opent mogelijkheden om ammoniakale stikstof uit stikstof-rijke restwateren te verwijderen en vervolgens de  $\text{NH}_3$  terug te winnen voor het opwekken van elektriciteit, wat mogelijk leidt tot energie-positieve methoden voor ammoniakale stikstof verwijdering uit stikstof-rijke restwateren. Het doel van dit proefschrift was het bepalen van de haalbaarheid om concurrerende (ongeveer 90%) ammoniakale stikstof verwijdering uit stikstof-rijke restwateren te behalen en om de teruggewonnen  $\text{NH}_3$  te gebruiken voor elektriciteitsopwekking, gebruikmakend van een combinatie van technologieën zonder gebruik van chemicaliën. De gebruikte technologieën in dit proefschrift zijn elektrolyse (ED), bipolaire membraan elektrolyse (BPMED), vacuüm membraan strippen (VMS) en een solid oxide fuel cell (SOFC). Om de geschiktheid van de combinatie van technologieën te bepalen, richt het onderzoek in dit proefschrift zich op de massaoverdracht en de haalbare concentraties van de verschillende ammoniakale stikstof soorten (ammonium ( $\text{NH}_4^+$ ), opgeloste  $\text{NH}_3$  en gasvormige  $\text{NH}_3$ ), alsmede op de elektrische energie aspecten (verbruik en opwekking) voor de verschillende technologieën.

In dit proefschrift identificeert een literatuurstudie in Hoofdstuk 2 dertien potentieel geschikte stikstof-rijke restwateren waar  $\text{NH}_3$  uit teruggewonnen kan worden voor elektriciteitsopwekkingsdoeleinden. Daarnaast verstrekt de literatuurstudie een overzicht van potentieel geschikte technologieën om ammoniakale stikstof uit stikstof-rijke restwateren te verwijderen en om  $\text{NH}_3$  terug te winnen voor elektriciteitsopwekkingsdoeleinden. Elk van de geselecteerde technologieën diende vervolgens als onderzoeksonderwerp in de hoofdstukken van dit proefschrift. Onderzoek naar ED in Hoofdstuk 3 toont aan dat het toepassen van een dynamische stroomsterktedichtheid leidt tot hogere concentratiefactoren om geconcentreerde  $\text{NH}_4^+$  oplossingen te produceren, voor een lager elektriciteitsverbruik dan het toepassen van een vaste stroomsterktedichtheid. Oplossingen met  $\text{NH}_4^+$  concentratie tot  $10 \text{ g} \cdot \text{L}^{-1}$  werden geproduceerd bij een verwijderingsefficiëntie van  $\text{NH}_4^+$  van ongeveer 90%, voor een elektrisch energieverbruik van 5

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$\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . Vervolgens toont onderzoek naar BPMED in Hoofdstuk 4 aan dat 90% verwijdering van  $\text{NH}_4^+$  haalbaar is voor BPMED, terwijl tegelijkertijd geconcentreerde oplossingen met  $\text{NH}_3$  concentraties van  $4.5 \text{ g}\cdot\text{L}^{-1}$  werden geproduceerd zonder gebruik van chemicaliën, voor een elektrisch energieverbruik van  $22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . Verder toont onderzoek in Hoofdstuk 5 en 6 naar het terugwinnen van  $\text{NH}_3$  als een gas met VMS aan dat overdracht van water ( $\text{H}_2\text{O}$ ) onvermijdbaar is, wat er toe leidt dat  $\text{NH}_3$  als  $\text{NH}_3\text{-H}_2\text{O}$  mengsel teruggewonnen wordt bij het gebruik van VMS. Overdracht van  $\text{H}_2\text{O}$  heeft zelfs consequent de voorkeur boven de overdracht van  $\text{NH}_3$ , voor verschillende voedingswatersamenstellingen, operationele condities en membraantypes, wanneer VMS wordt toegepast om gasvormig  $\text{NH}_3$  uit water terug te winnen. Door  $\text{NH}_3$  voedingswaterconcentraties van  $10 \text{ g}\cdot\text{L}^{-1}$  aan te leveren voor VMS, kunnen  $\text{NH}_3$  concentraties van 11 gewichtsprocent (m%) bereikt worden in de teruggewonnen  $\text{NH}_3\text{-H}_2\text{O}$  mengsels. Onderzoek naar de SOFC in Hoofdstuk 6 toont aan dat  $\text{NH}_3\text{-H}_2\text{O}$  mengsels met  $\text{NH}_3$  concentraties tot aan 5 m% nog steeds gebruikt kunnen worden voor elektriciteitsopwekkingsdoeleinden: de SOFC wekte  $9 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  aan elektriciteit op. Onderzoek met echte stikstof-rijke restwateren in Hoofdstuk 7 toont de haalbaarheid van ED aan om concurrerende (ongeveer 90%) ammoniakale stikstof verwijdering te behalen voor drie echte stikstof-rijke restwateren: algenvergiftingsrejectiewater, slibvergiftingsrejectiewater en condensaat uit de kunstmestindustrie. De behandeling van condensaat uit de kunstmestindustrie werd niet belemmerd door de aanwezigheid van andere ionen of organische stof in het voedingswater. ED, BPMED, VMS en een SOFC werden gecombineerd om een ammoniakale stikstof verwijderingsefficiëntie van 90% uit condensaat uit de kunstmestindustrie te behalen en uiteindelijk elektriciteit op te wekken uit de teruggewonnen  $\text{NH}_3\text{-H}_2\text{O}$  mengsels. Het elektriciteitsverbruik van ED, BPMED en VMS was  $38 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , terwijl de SOFC  $11 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  opwekte. De combinatie van de technologieën had een netto energieverbruik van  $27 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , wat het voorgestelde systeem nog niet energie-positief maakte in termen van elektriciteit.

Voor elk van de technologieën is meer onderzoek nodig naar de massa overdracht van de verschillende ammoniakale stikstof soorten, de gebruikte (membraan)materialen en de operationele condities om het elektriciteitsverbruik van ED, BPMED en VMS te verlagen en de elektriciteitsopwekking van de SOFC te verhogen, om zo mogelijk een elektrische energie-positieve methode te ontwikkelen om ammoniakale stikstof uit stikstof-rijke reststromen te verwijderen.

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# Chapter 1.

## Introduction



### 1.1. Production and fate of NH<sub>3</sub>

Ammonia (NH<sub>3</sub>) is one of the world's most-produced chemicals with more than 178 million tons of NH<sub>3</sub> produced annually (FAO, 2019; The Royal Society, 2020). About 80% of the produced NH<sub>3</sub> is used as fertiliser, while the rest is used as raw material for the fabrication of chemical compounds and explosives (Galloway et al., 2004; Erisman et al., 2008), as depicted in Figure 1-1. Almost 2% of the total world's generated energy is used in the Haber-Bosch process to produce NH<sub>3</sub>-based products, contributing to 2% of the global annual CO<sub>2</sub> emission (The Royal Society, 2020). The well-established Haber-Bosch process produces NH<sub>3</sub> from nitrogen (N<sub>2</sub>) and hydrogen gas (H<sub>2</sub>) at high temperatures (300–500 °C) and under high pressure (150–300 bar). The production of H<sub>2</sub> accounts for the largest part of the energy consumption (80%) of the Haber-Bosch process (The Royal Society, 2020). When H<sub>2</sub> is generated via methane (CH<sub>4</sub>) reforming, the energy consumption of the Haber-Bosch process equals 28 MJ·kg-N<sup>-1</sup> produced, whereas when H<sub>2</sub> is generated via water electrolysis, the energy consumption of the Haber-Bosch process equals 107 MJ·kg-N<sup>-1</sup> (Cherkasov et al., 2015). Even though the Haber-Bosch process has been largely improved and is economically attractive, alternative methods for NH<sub>3</sub> production, such as electrochemical routes, are actively studied (Giddey et al., 2013; Caragounis et al., 2019; The Royal Society, 2020).

While NH<sub>3</sub>-based fertilisers contribute immensely to feeding the world's human population, the (over)use of NH<sub>3</sub>-based fertilisers creates a huge environmental impact (Erisman et al., 2007; Erisman et al., 2008). As depicted in Figure 1-1, 15–55% of the total amount of the produced fertilisers ends up in the atmosphere and water bodies (Galloway et al., 2004; Erisman et al., 2007; Matassa et al., 2015). Emission of NH<sub>3</sub> to receiving water bodies via untreated or partially treated residual waters leads to oxygen depletion and eutrophication, resulting in species diversity loss (Erisman et al., 2007). The latter also applies for the emission of other nitrogen species, such as nitrite (NO<sub>2</sub><sup>-</sup>) and nitrate (NO<sub>3</sub><sup>-</sup>) to receiving water bodies, but this thesis focuses on the possibilities to manage the treatment of NH<sub>3</sub> in residual waters.

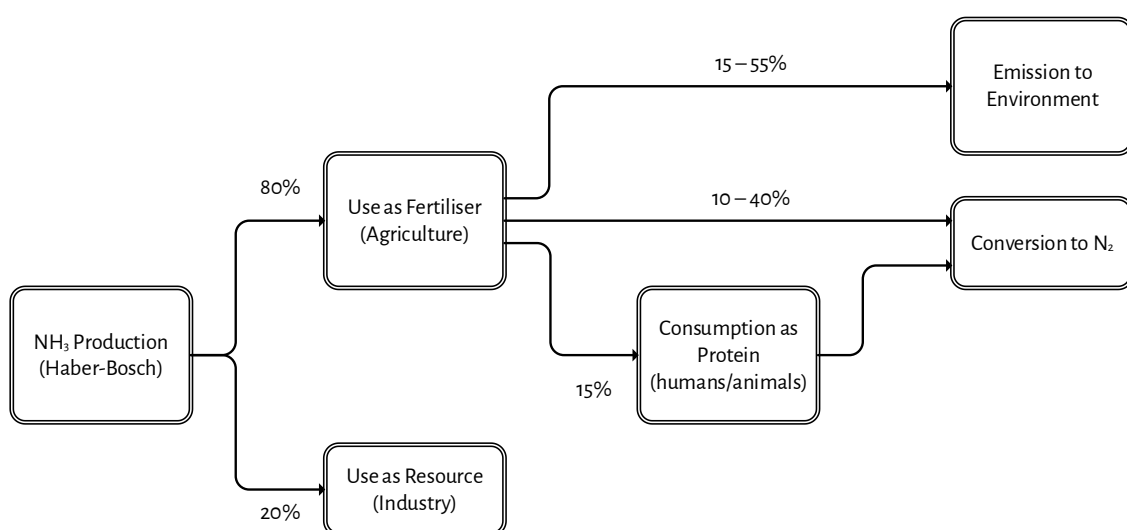


Figure 1-1 - Fate of produced NH<sub>3</sub> by the Haber-Bosch process, based on data provided by Galloway et al. (2004) and Erisman et al. (2008).

## 1.2. Current treatment of ammonia in residual waters

The presence of  $\text{NH}_3$  in water (aqueous solution) can be described as the total ammoniacal nitrogen (TAN) concentration, which is the sum of both dissolved  $\text{NH}_3$  gas and ammonium ( $\text{NH}_4^+$ ) ions. TAN can be present in water (aqueous solution) in both mentioned species, of which the distribution mainly depends on the temperature, the pH and the ionic strength of the solution (see Figure 1-3).

### 1.2.1. Biochemical processes to remove TAN from residual waters

To limit the emission of TAN to receiving water bodies, residual streams that contain TAN should be treated before discharge. Traditionally, TAN is removed by biochemical oxidation to  $\text{NO}_3^-$  in a process called nitrification, which occurs in biological treatment systems, such as (aerated) lagoons, trickling filters or activated sludge plants. To avoid excessive eutrophication of the receiving water bodies, oxidised N species subsequently needs to be reduced to  $\text{N}_2$  in a biochemical process called denitrification. At present, the nitrification-denitrification process (NDN) is commonly applied in sewage treatment and treatment processes for industrial residual waters to remove TAN. To achieve sufficient nitrogen removal, the application of (NDN) requires high hydraulic and solids retention times, which results in large physical installation footprints. However, sewage typically contains relatively low concentrations of TAN: up to  $50 \text{ mg}\cdot\text{L}^{-1}$ . This thesis focuses on the treatment of residual streams that are concentrated in TAN: higher than  $500 \text{ mg}\cdot\text{L}^{-1}$ .

For the treatment of concentrated (in TAN) residual waters, processes based on partial nitritation in combination with anaerobic ammonium oxidation (PN-anammox) are increasingly applied. An example of a concentrated residual water is the liquid fraction of sludge digestate (reject water) in sewage treatment plants. Through side stream treatment of sludge reject water by PN-anammox, the total TAN load to the NDN processes in the main stream (also called the water line) can be decreased by 15 – 25%, resulting in a decrease in the total energy consumption, compared to returning the sludge reject water back to the water line (Van Hulle et al., 2010; Lackner et al., 2014). In their review, Magri et al. (2013) mentioned that the side stream removal of TAN requires  $57 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  removed using NDN via nitrite, and that PN-anammox requires  $19 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  removed. Furthermore, Lackner et al. (2014) and Schaubroeck et al. (2015) reported that the energy consumption of side stream TAN removal in full-scale PN-anammox installations ranges between 3 and  $15 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  removed. Based on the study of Lackner et al. (2014), the removal efficiency of TAN by PN-anammox reaches up to approximately 90%. As PN-anammox is considered to be the state-of-the-art process for TAN removal from concentrated residual waters, in this thesis, 90% TAN removal is considered to be competitive TAN removal.

Despite the energy advantage of PN-anammox versus NDN, the application of PN-anammox is currently limited to warm side streams with low carbon to nitrogen ratios, as the preferred operating temperature of anammox bacteria is around  $35^\circ\text{C}$  and the growth of these bacteria is outcompeted by other bacteria species in the presence of high concentrations of biodegradable organic carbon in the feed water (Gonzalez-Martinez et al., 2018). Furthermore, there is consensus that the application of both NDN and PN-anammox

processes results in the production and emission of oxidised nitrogen species such as nitrous oxide ( $\text{N}_2\text{O}$ ), nitrogen oxide (NO) and nitrogen dioxide ( $\text{NO}_2$ ) ([Kampschreur et al., 2009](#)). Especially the emission of  $\text{N}_2\text{O}$  is undesirable, because it is a potent greenhouse gas, having a 296 times higher global warming potential than carbon dioxide ( $\text{CO}_2$ ), according to the IPCC ([Prather et al., 2001](#)). The fraction of  $\text{N}_2\text{O}$  emission relative to the total nitrogen load of full-scale biological water treatment plants is reported to be 0 – 15% ([Kampschreur et al., 2009](#); [Vasilaki et al., 2019](#)). The wide range in gaseous oxidised nitrogen emission is explained by the diversity in feed water compositions and applied operational conditions, which affect the production of gaseous oxidised nitrogen species by bacteria ([Kampschreur et al., 2009](#); [Desloover et al., 2012](#)). According to the review of [Desloover et al. \(2012\)](#), the emission of  $\text{N}_2\text{O}$  during biochemical processes can contribute to 80% of the total greenhouse emissions, expressed in  $\text{CO}_2$  equivalents of water treatment plants that process sewage, manure, landfill leachate or industrial effluents. Hence, even though wide ranges are reported for the energy consumption and the emission of gaseous oxidised nitrogen species, currently available literature shows that biochemical removal of TAN consumes energy and results in the emission of strong greenhouse gases. Finally, a recent study by [RIVM \(2019\)](#) showed the presence of legionella in various water treatment plants where PN-anammox is applied, which threatens the applicability of PN-anammox process due to danger to legionella spreading events.

### 1.2.2. Recovery of TAN from residual waters

In contrast to the application of biochemical technologies to remove TAN from residual waters by destruction, recovery of TAN offers multiple opportunities for reuse. In the last two decades, there has been a growing interest in the recovery of TAN as raw material for fertilisers, using mature technologies such as struvite (magnesium ammonium phosphate) precipitation and ammonia stripping using air or steam ([Mehta et al., 2015b](#)). However, recovery of TAN as a resource is not always desirable, because chemicals and energy are typically required to drive the recovery technologies. Moreover, the use of the recovered products can be challenging due to legislation, quality restrictions, storage and transportation costs, and supply and demand mismatches ([Mehta et al., 2015b](#); [Zarebska et al., 2015](#)).

Interestingly,  $\text{NH}_3$  was recently identified as a suitable energy carrier, as an alternative to carbon-based fuels such as oil and natural gas, because it is carbon-free and the storage and transportation systems are already established ([ISPT, 2017](#); [Valera-Medina et al., 2018](#); [The Royal Society, 2020](#)). The chemically bound energy in  $\text{NH}_3$  ( $21 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ) can actually be converted into electricity and heat, with  $\text{N}_2$  gas and  $\text{H}_2\text{O}$  as final products, while the emission of oxidised nitrogen species is avoided ([Staniforth & Ormerod, 2003](#)).

### 1.3. Research description

#### 1.3.1. General problem description

The generation of electricity from  $\text{NH}_3$  recovered from residual waters is a novel concept and opens new opportunities to manage TAN in residual waters. This concept was previously studied in a Dutch research project, in which TAN was removed from sludge reject water by struvite precipitation and  $\text{NH}_3$  gas was recovered after thermal struvite decomposition (STOWA, 2013). Subsequently, the recovered  $\text{NH}_3$  gas was used as the fuel for a solid oxide fuel cell (SOFC), as described in the papers of Hemmes et al. (2011) and Saadabadi et al. (2020). SOFCs can convert  $\text{NH}_3$  to  $\text{N}_2$  gas and  $\text{H}_2\text{O}$  while generating both electricity and heat, with the highest reported energy efficiency amongst energy-conversion technologies: up to 60% electrical efficiency, whereas an additional 30% of the chemical energy carried in the fuel can be recovered as heat and the residual part is assigned to the changes in entropy or lost by heat emission to the environment (Stambouli & Traversa, 2002; Lan & Tao, 2014b). However, stoichiometrically, one mole of struvite contains equal moles of nitrogen and phosphorus. Because residual waters that require TAN removal typically contain more nitrogen than phosphorus, struvite precipitation only accounts for limited (15 – 30%) TAN removal (Mehta et al., 2015a; Zarebska et al., 2015). Therefore, the concept as described in the study of STOWA (2013) is in this thesis not considered to be able to achieve competitive (90%) TAN removal. Furthermore, the studies of Xu et al. (2017) and Grasham et al. (2019) addressed the recovery of  $\text{NH}_3$  from residual waters for the generation of electricity, but did not elaborate on how to recover  $\text{NH}_3$  as a gas from water (aqueous solution), in what concentration  $\text{NH}_3$  can be recovered and how much energy can be generated when using gaseous  $\text{NH}_3$  recovered from water as a fuel. Hence, it was unclear how  $\text{NH}_3$  can be recovered from residual waters and whether the recovered  $\text{NH}_3$  can be used for electricity generation.

#### 1.3.2. General considerations

From this point onwards, this thesis will consistently use the following terminology, following the definitions as presented in Chapter 2.2:

- (N-loaded) residual streams: used as a collective term for all N-loaded streams that contain total Kjeldahl nitrogen concentrations higher than  $0.5 \text{ g}\cdot\text{L}^{-1}$  (aqueous, slurries, etc.);
- (N-loaded) residual waters: used when referring to aqueous solutions that contain TAN in concentrations higher than  $0.5 \text{ g}\cdot\text{L}^{-1}$ ;
- Feed waters: used to refer to aqueous solutions used for experiments;

Furthermore, the following terminology will be used for  $\text{NH}_3$  in its various forms and different contexts:

- Ammonia ( $\text{NH}_3$ ): used when referring to the gaseous form, either dissolved in water (aq) or as gas (g);
- Ammonium ( $\text{NH}_4^+$ ): used when referring to the ionised form, dissolved in water (aq);
- Total ammoniacal nitrogen (TAN): used as a collective term for the presence of ammoniacal nitrogen dissolved in water, or as recovered in gaseous mixtures, dissolved or solid form.

To recover  $\text{NH}_3$  from N-loaded residual waters for the generation of electricity, many different technologies can be considered. To narrow down the number of technologies and the associating research topics to be studied, this thesis focuses only on technologies that are applicable to the treatment of N-loaded residual waters, containing reduced (or total Kjeldahl) nitrogen in concentrations higher than  $0.5 \text{ g}\cdot\text{L}^{-1}$ . The limit  $0.5 \text{ g}\cdot\text{L}^{-1}$  is based on an assessment on the identification and characterisation of concentrated residual streams from which TAN currently is removed and recovered, presented in Chapter 2.2 of this thesis. Furthermore, Chapter 2.3 provides an assessment of various suitable technologies to remove and recover TAN from water. To further narrow down the options for technologies, the following considerations were taken into account:

- To be competitive with currently existing methods for TAN removal from N-loaded residual waters, the TAN removal efficiency of the combination of technologies should be around 90% ([Lackner et al., 2014](#));
- The SOFC is considered to be the most efficient electricity generation technology and can use  $\text{NH}_3$  directly as a fuel ([Stambouli & Traversa, 2002](#); [Valera-Medina et al., 2018](#)), as also can be concluded from the review on various fuel cell types in Chapter 2.4;
- As electrical energy is released during electricity generation from  $\text{NH}_3$ , this energy source could be used to drive the technologies for TAN removal and subsequent  $\text{NH}_3$  recovery, with the purpose to develop an energy-efficient and chemical-free system. This consideration excludes the potentially suitable application of zeolites and the subsequent regeneration with alkaline solutions to obtain  $\text{NH}_3$  as presented by [Vecino et al. \(2019\)](#).

### 1.3.3. Research objective

The research objective of this thesis is to assess the feasibility of a proposed combination of technologies to allow for competitive TAN removal from N-loaded residual waters and the subsequent generation of electricity from the recovered  $\text{NH}_3$ . In this thesis, the following aspects were extensively studied:

- Quantification of concentration of various nitrogen species:  $\text{NH}_4^+$  (aq),  $\text{NH}_3$  (aq) and  $\text{NH}_3$  (g) throughout the various studied technologies (in g/L and wt%);
- Electrical energy assessment: determining the required electrical energy consumption of the various technologies and the electrical energy generation of the SOFC, normalised per unit of mass of processed (unless stated differently) nitrogen ( $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ).

By acquiring information on the TAN concentrations and energy, the feasibility of the proposed system is assessed. Furthermore, by optimising the operation of the proposed technologies to remove TAN and recover  $\text{NH}_3$  for electricity generation in an SOFC, potentially an electrical energy-positive system may be developed: net generation of electricity during the removal of TAN from N-loaded residual waters, whereas to date, conventional TAN removal process still consumes electrical energy (as depicted in Figure 1-2). To achieve the main objective, this thesis considers various specific topics, focusing on the various proposed technologies.

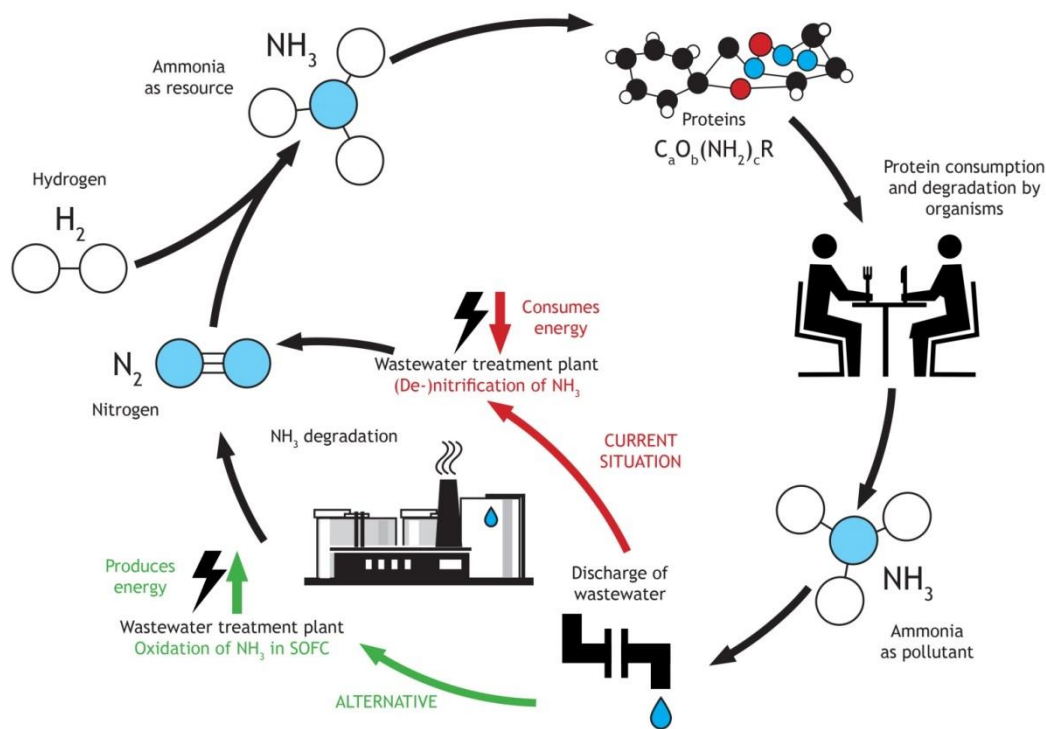


Figure 1-2 - The cycle of nitrogen via TAN, which currently requires energy to manage TAN in N-loaded residual waters (red route), while there are opportunities to generate energy from recovered NH<sub>3</sub> (green route).

#### 1.3.4. Specific technology-based research topics

##### 1.3.4.1. SOFC to generate energy from recovered NH<sub>3</sub>

According to Stambouli and Traversa (2002), SOFCs operate at a temperature ranging between 600 to 1,000 °C and typically use high purity gases as a fuel, such as methane (CH<sub>4</sub>) and H<sub>2</sub>. As extensively described in Chapter 2.4, SOFCs can also be used to generate energy using NH<sub>3</sub> as a fuel and are considered to be the most efficient energy-conversion technology to generate energy from NH<sub>3</sub>. However, there are certain quality restrictions for SOFC fuels. The presence of metal-based salts in the fuel is expected to cause scaling on the anode, whereas the presence of gaseous oxidants in the fuel, such as O<sub>2</sub> and hydrogen sulphide (H<sub>2</sub>S) may deactivate the present anode catalyst by oxidation (Papadimas et al., 2012). Since SOFCs use gaseous fuels, this thesis focuses on the recovery of NH<sub>3</sub> as a gas from N-loaded residual waters. The recovery of gaseous NH<sub>3</sub> from N-loaded residual waters simultaneously allows for the separation of NH<sub>3</sub> from contaminating metal-based salts and sulphur-based solutes, which are typically present in N-loaded residual waters.

To recover gaseous NH<sub>3</sub> from N-loaded residual waters, various gas stripping technologies can be used, as described in Chapter 2.3.2. Amongst the various gas stripping configurations to recover NH<sub>3</sub> as fuel for an SOFC, vacuum stripping is expected to be most suitable, as no O<sub>2</sub> (expected to act as an oxidant) is supplied, which is the case for conventional gas stripping using air. By using hydrophobic membranes (impermeable for liquids, but permeable for vapours) as physical barriers to separate the liquid (the feed water) and the by



vacuum extracted gas, high contact areas in small volumes can be achieved, leading to a flexible and modular system design. Therefore, in this thesis, vacuum membrane stripping (VMS) is selected for the recovery of gaseous  $\text{NH}_3$ . However, as described in Chapter 2.3.2, when gaseous  $\text{NH}_3$  is recovered from feed water in vacuum stripping applications, evaporation of water ( $\text{H}_2\text{O}$ ) takes place, leading to the recovery of  $\text{NH}_3\text{-H}_2\text{O}$  mixtures. Because  $\text{H}_2\text{O}$  cannot be used for electricity generation purposes in an SOFC, the presence of  $\text{H}_2\text{O}$  in the fuel should be minimised and thus the  $\text{NH}_3$  concentration in the  $\text{NH}_3\text{-H}_2\text{O}$  mixtures should be maximised. In this thesis, the fuel for the SOFC is expected to contain  $\text{H}_2\text{O}$ , but it is unknown how much  $\text{NH}_3$  should at least be present in the fuel to generate energy. Moreover, it is unknown how much energy can be generated from  $\text{NH}_3\text{-H}_2\text{O}$  mixtures. Therefore, the considerations for the use of  $\text{NH}_3\text{-H}_2\text{O}$  mixtures as fuels by SOFCs lead to the following specific research topic:

- A.  $\text{NH}_3$  concentration in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures for electricity generation by an SOFC and corresponding energy generation.

#### 1.3.4.2. VMS to recover concentrated gaseous $\text{NH}_3$

Stripping of  $\text{NH}_3$  is typically performed at a feed water pH of 9.5, because at this pH, TAN is predominantly present as volatile dissolved  $\text{NH}_3$  gas instead of non-volatile  $\text{NH}_4^+$  (see Figure 1-3). For stripping  $\text{NH}_3$  under vacuum, the driving force of the  $\text{NH}_3$  transfer is the  $\text{NH}_3$  vapour pressure difference between the liquid feed water and the gaseous permeate. Based on Henry's Law, the higher the dissolved  $\text{NH}_3$  concentration in the feed water, the higher the  $\text{NH}_3$  vapour pressure in the feed water. Higher  $\text{NH}_3$  vapour pressure differences, in their turn, lead to a higher  $\text{NH}_3$  transfer rate. By adjusting the feed water composition (TAN concentration, pH, temperature and ionic strength), the transfer of  $\text{NH}_3$  can be increased. On the contrary,  $\text{H}_2\text{O}$  transport is predominantly affected by the feed water temperature. Hence, increasing the  $\text{NH}_3$  concentration in the feed water may allow for the maximisation of the  $\text{NH}_3$  concentration in the recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixtures by VMS. Furthermore, the transfer of  $\text{NH}_3$  may be improved by adjusting the operating conditions and the membrane type. However, it is unknown how the feed water composition, operational conditions and membrane type affect the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  transfer. Moreover, it is unknown how much energy is needed to recover  $\text{NH}_3$  as  $\text{NH}_3\text{-H}_2\text{O}$  mixtures by VMS. To this end, the considerations for the recovery of  $\text{NH}_3$  by VMS lead to the following specific research topic:

- B.  $\text{NH}_3$  and  $\text{H}_2\text{O}$  transfer and corresponding energy consumption during  $\text{NH}_3$  recovery by VMS, as a function of the feed water composition, operational conditions and membrane type.

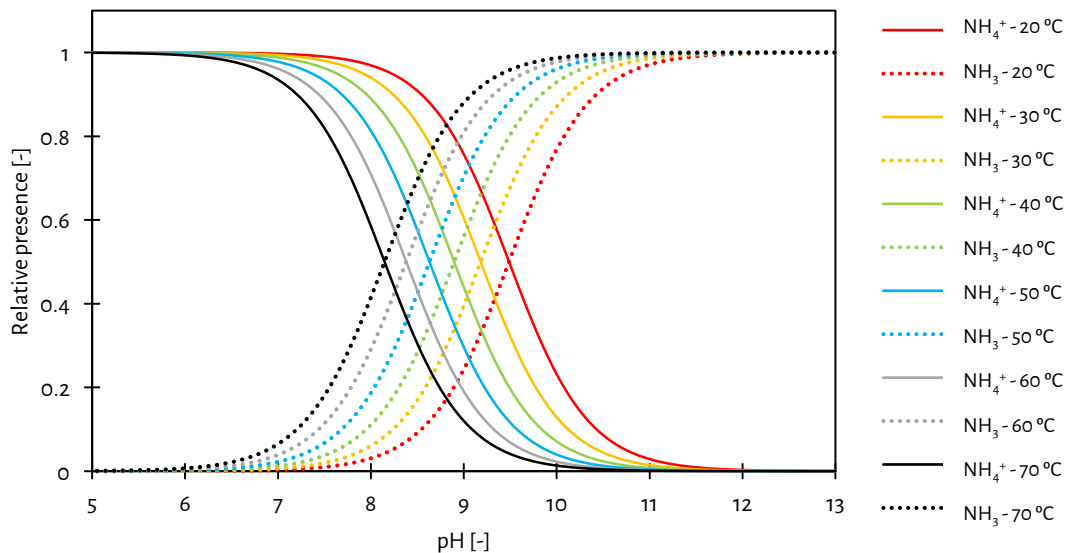


Figure 1-3 - The relative presence (or speciation) of  $\text{NH}_4^+$  and  $\text{NH}_3$  as a function of the solution pH and temperature. The effect of the ionic strength of the solution on the TAN speciation was not used as a variable in PHREEQC simulations, which provided the data for the graph.

#### 1.3.4.3. ED and BPMED to produce concentrated TAN solutions

To maximise the  $\text{NH}_3$  concentration in the recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixtures, maximisation of the  $\text{NH}_3$  concentration in the feed water is required. Obtaining high  $\text{NH}_3$  concentrations in feed waters can be achieved by the addition of chemicals to feed waters with high  $\text{NH}_4^+$  concentrations to increase the pH. According to Chapter 2.3.1, electrodialysis (ED) allows for competitive TAN removal from N-loaded residual waters, while simultaneously producing a concentrated  $\text{NH}_4^+$  solution. However, there is limited information available on how much energy is required to produce concentrated  $\text{NH}_4^+$  solution by ED and how the  $\text{NH}_4^+$  concentration can be maximised. To this end, the use of ED leads to the following specific research topic:

- C. Competitive  $\text{NH}_4^+$  removal and production of concentrated  $\text{NH}_4^+$  solutions by ED and corresponding electrical energy consumption;

Finally, according to Chapter 2.3.1, bipolar membrane electrodialysis (BPMED) can be used to produce concentrated  $\text{NH}_3$  solutions as a feed for VMS, without using an external supply of chemicals. However, it is unknown whether BPMED can produce concentrated  $\text{NH}_3$  solutions, while achieving competitive TAN removal from N-loaded residual waters. Moreover, there is no information on the energy consumption for BPMED to produce concentrated  $\text{NH}_3$  solutions. To this end, the use of BPMED leads to the following specific research topic:

- D. Competitive  $\text{NH}_4^+$  removal and production of concentrated  $\text{NH}_3$  solution and corresponding electrical energy consumption by BPMED;

1.3.5. Thesis structure

This thesis covers separate chapters on each specific research topic. All specific research topics are more elaborately introduced in the respective chapters. This thesis contains the following chapters:

1. Chapter 1: background information on the topic, problem description and research topics;
2. Chapter 2: literature review on potentially suitable N-loaded residual streams and technologies for TAN removal and the subsequent electricity generation from recovered  $\text{NH}_3$ ;
3. Chapter 3: ED for simultaneous  $\text{NH}_4^+$  removal and the production of concentrated  $\text{NH}_4^+$  solutions (specific research topic D);
4. Chapter 4: BPMED for simultaneous  $\text{NH}_4^+$  removal and production of concentrated  $\text{NH}_3$  solutions (specific research topic C);
5. Chapter 5: selectivity of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer during the recovery of  $\text{NH}_3$  by VMS, for various membranes and operational conditions (specific research topic B);
6. Chapter 6: achievable  $\text{NH}_3$  concentrations in  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures recovered during  $\text{NH}_3$  recovery by VMS and the use of the recovered  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures as a fuel for an SOFC (specific research topic A and B);
7. Chapter 7: removal and recovery of TAN from real residual streams using a combination of technologies;
8. Chapter 8: conclusions and recommendations.

Figure 1-4 shows a schematic representation of this thesis outline and how the chapters are linked by technologies to remove TAN from N-loaded residual waters and the subsequent generation of electricity from the recovered  $\text{NH}_3$ . Chapter 1 introduces this thesis and Chapter 2 provides an extensive literature review on potentially suitable N-loaded residual streams and suitable technologies that can be used for TAN removal and recovery. The selection of the selected technologies in this thesis (ED, BPMED, VMS and SOFC) is predominantly based on Chapter 2. The separate technologies were the main subject of research in Chapter 3 (ED), 4 (BPMED), 5 (VMS) and 6 (VMS and SOFC). In the Chapters 3, 4, 5 and 6, synthetic feed waters are used for the conducted experiments. To demonstrate the feasibility of the proposed concept of TAN removal and recovery of  $\text{NH}_3$  for electricity generation purposes, Chapter 7 focuses on the treatment of real N-loaded residual streams. Finally, Chapter 8 provides an overview of the conclusions and recommendations from this thesis.

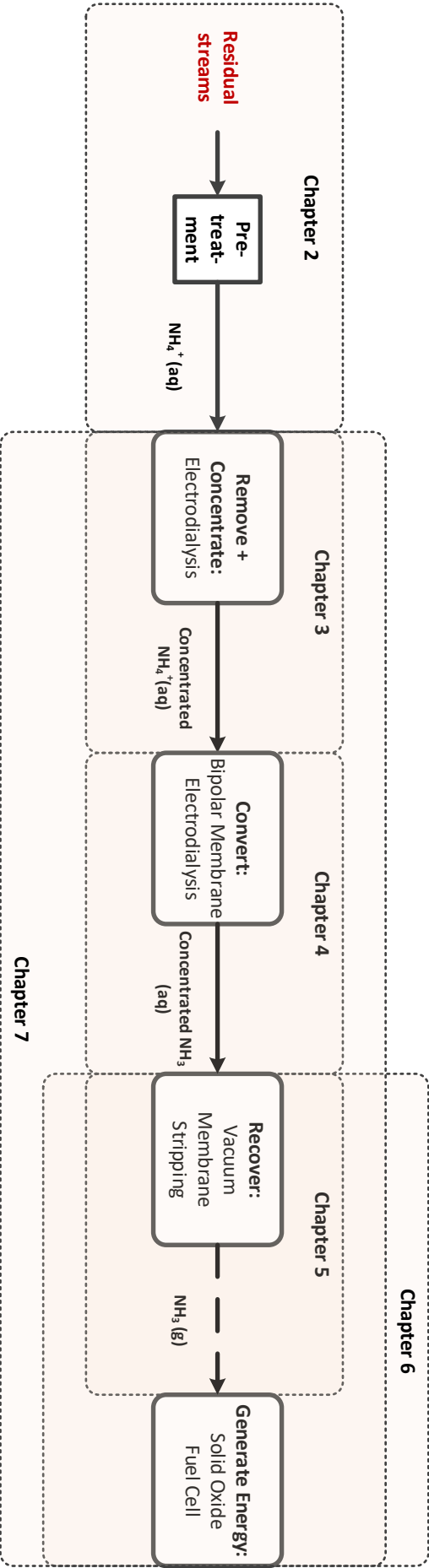


Figure 1-4 - A schematic representation of the structure of this thesis.

1.4. References

- Cherkasov, N., Ibhaddon, A. O., & Fitzpatrick, P. (2015). A review of the existing and alternative methods for greener nitrogen fixation. *Chemical Engineering and Processing: Process Intensification*, *90*, 24-33. doi:<https://doi.org/10.1016/j.cep.2015.02.004>
- Desloover, J., Vlaeminck, S. E., Clauwaert, P., Verstraete, W., & Boon, N. (2012). Strategies to mitigate N<sub>2</sub>O emissions from biological nitrogen removal systems. *Current Opinion in Biotechnology*, *23*(3), 474-482. doi:<https://doi.org/10.1016/j.copbio.2011.12.030>
- Erisman, J. W., Bleeker, A., Galloway, J., & Sutton, M. S. (2007). Reduced nitrogen in ecology and the environment. *Environmental Pollution*, *150*, 140-149. doi:<https://doi.org/10.1016/j.envpol.2007.06.033>
- Erisman, J. W., Sutton, M. A., Galloway, J., Klimont, Z., & Winiwarter, W. (2008). How a century of ammonia synthesis changed the world. *Nature Geoscience*, *1*, 636. doi:10.1038/ngeo0325
- FAO. (2019). *World fertilizer trends and outlook to 2022*. Rome, Italy
- Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., & Vo, C. J. (2004). Nitrogen cycles : past , present , and future. *Biogeochemistry*, *70*, 153-226.
- Garagounis, I., Vourros, A., Stoukides, D., Dasopoulos, D., & Stoukides, M. (2019). Electrochemical synthesis of ammonia: Recent efforts and future outlook. *Membranes*, *9*(9). doi:10.3390/membranes9090112
- Giddey, S., Badwal, S. P. S., & Kulkarni, A. (2013). Review of electrochemical ammonia production technologies and materials. *International Journal of Hydrogen Energy*, *38*(34), 14576-14594. doi:<https://doi.org/10.1016/j.ijhydene.2013.09.054>
- Gonzalez-Martinez, A., Muñoz-Palazon, B., Rodriguez-Sanchez, A., & Gonzalez-Lopez, J. (2018). New concepts in anammox processes for wastewater nitrogen removal: recent advances and future prospects. *FEMS Microbiology Letters*, *365*(6). doi:10.1093/femsle/fny031
- Grasham, O., Dupont, V., Camargo-Valero, M. A., García-Gutiérrez, P., & Cockerill, T. (2019). Combined ammonia recovery and solid oxide fuel cell use at wastewater treatment plants for energy and greenhouse gas emission improvements. *Applied Energy*, *240*, 698-708. doi:<https://doi.org/10.1016/j.apenergy.2019.02.029>
- ISPT. (2017). Power to Ammonia: From renewable energy to CO<sub>2</sub>-free ammonia as chemical feedstock and fuel [Press release]. Retrieved from <http://www.ispt.eu/media/P2A-press-release-March-2017.pdf>
- Kampschreur, M. J., Temmink, H., Kleerebezem, R., Jetten, M. S. M., & van Loosdrecht, M. C. M. (2009). Nitrous oxide emission during wastewater treatment. *Water Research*, *43*(17), 4093-4103. doi:<https://doi.org/10.1016/j.watres.2009.03.001>
- Lackner, S., Gilbert, E. M., Vlaeminck, S. E., Joss, A., Horn, H., & van Loosdrecht, M. C. M. (2014). Full-scale partial nitrification/anammox experiences - An application survey. *Water Research*, *55*, 292-303. doi:10.1016/j.watres.2014.02.032

- Lan, R., & Tao, S. (2014). Ammonia as a Suitable Fuel for Fuel Cells. *Frontiers in Energy Research*, 2(35). doi:10.3389/fenrg.2014.00035
- Magri, A., Beline, F., & Dabert, P. (2013). Feasibility and interest of the anammox process as treatment alternative for anaerobic digester supernatants in manure processing--an overview. *J Environ Manage*, 131, 170-184. doi:10.1016/j.jenvman.2013.09.021
- Matassa, S., Batstone, D. J., Hulsen, T., Schnoor, J., & Verstraete, W. (2015). Can direct conversion of used nitrogen to new feed and protein help feed the world? *Environmental Science and Technology*, 49(9), 5247-5254. doi:<https://doi.org/10.1021/es505432w>
- Mehta, C. M., Khunjar, W. O., Nguyen, V., Tait, S., & Batstone, D. J. (2015a). Technologies to Recover Nutrients from Waste Streams: A Critical Review. *Critical Reviews in Environmental Science and Technology*, 45(4), 385-427. doi:10.1080/10643389.2013.866621
- Mehta, C. M., Khunjar, W. O., Nguyen, V., Tait, S., & Batstone, D. J. (2015b). Technologies to Recover Nutrients From Waste Streams: A Critical Review. *Critical Reviews in Environmental Science and Technology*, 45, 385-427. doi:<https://doi.org/10.1080/10643389.2013.866621>
- Papadias, D. D., Ahmed, S., & Kumar, R. (2012). Fuel quality issues with biogas energy – An economic analysis for a stationary fuel cell system. *Energy*, 44(1), 257-277. doi:<https://doi.org/10.1016/j.energy.2012.06.031>
- Prather, M., Ehhalt, D., Dentener, F., Derwent, R., & Grubler, A. (2001). Atmospheric chemistry and greenhouse gases. In *Climate Change 2001: The Scientific Basis, Third Assessment Report*. IPCC: Working Group I of the Intergovernmental Panel on Climate Change.
- Schaubroeck, T., De Clippeleir, H., Weissenbacher, N., Dewulf, J., Boeckx, P., Vlaeminck, S. E., & Wett, B. (2015). Environmental sustainability of an energy self-sufficient sewage treatment plant: Improvements through DEMON and co-digestion. *Water Research*, 74, 166-179. doi:<https://doi.org/10.1016/j.watres.2015.02.013>
- Stambouli, A. B., & Traversa, E. (2002). Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. *Renewable and Sustainable Energy Reviews*, 6(5), 433-455. doi:[https://doi.org/10.1016/S1364-0321\(02\)00014-X](https://doi.org/10.1016/S1364-0321(02)00014-X)
- Staniforth, J., & Ormerod, R. M. (2003). Clean destruction of waste ammonia with consummate production of electrical power within a solid oxide fuel cell system. *Green Chemistry*, 5(5), 606-609. doi:10.1039/B307396N
- STOWA. (2013). *Struvietprecipitatie in combinatie met stikstofwinning en omzetting in een brandstofcel: evaluatie en verificatie technische en economische haalbaarheid* (9789057736353). Retrieved from Amersfoort: <https://www.stowa.nl/publicaties/struvietprecipitatie-combinatie-met-stikstofwinning-en-omzetting-een-brandstofcel>
- The Royal Society. (2020). *Ammonia: zero-carbon fertiliser, fuel and energy store*. Retrieved from [royalsociety.org/green-ammonia](https://royalsociety.org/green-ammonia)

Valera-Medina, A., Xiao, H., Owen-Jones, M., David, W. I. F., & Bowen, P. J. (2018). Ammonia for power.

*Progress in Energy and Combustion Science*, 69, 63-102.

doi:<https://doi.org/10.1016/j.pecs.2018.07.001>

Van Hulle, S. W. H., Vandeweyer, H. J. P., Meesschaert, B. D., Vanrolleghem, P. A., Dejans, P., & Dumoulin, A. (2010). Engineering aspects and practical application of autotrophic nitrogen removal from nitrogen rich streams.

*Chemical Engineering Journal*, 162(1), 1-20. doi:10.1016/j.cej.2010.05.037

Vasilaki, V., Massara, T. M., Stanchev, P., Fatone, F., & Katsou, E. (2019). A decade of nitrous oxide (N<sub>2</sub>O) monitoring in full-scale wastewater treatment processes: A critical review.

*Water Research*, 161, 392-412. doi:<https://doi.org/10.1016/j.watres.2019.04.022>

Vecino, X., Reig, M., Bhushan, B., Gibert, O., Valderrama, C., & Cortina, J. L. (2019). Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors.

*Chemical Engineering Journal*, 360, 890-899.

doi:<https://doi.org/10.1016/j.cej.2018.12.004>

Xu, L., Dong, F., Zhuang, H., He, W., Ni, M., Feng, S., & Lee, P. (2017). Energy upcycle in anaerobic treatment: ammonium, methane, and carbon dioxide reformation through a hybrid

electrodeionization-solid oxide fuel cell system. *Energy Conversion and Management*, 140, 157-166.

Zarebska, A., Romero Nieto, D., Christensen, K. V., Fjerbæk Sjøtoft, L., & Norddahl, B. (2015). Ammonium fertilizers production from manure: A critical review.

*Critical Reviews in Environmental Science and Technology*, 45(14), 1469-1521. doi:10.1080/10643389.2014.955630





## Chapter 2.

# Residual streams and technologies for ammoniacal nitrogen recovery and energy generation

Based on:

Recovery and applications of ammoniacal nitrogen from nitrogen-loaded residual streams: A review

Zhe Deng, Niels van Linden, Elena Guillen, Henri Spanjers, Jules B. van Lier (2021)

<https://doi.org/10.1016/j.jenvman.2021.113096>



### Abstract

In available literature, no studies assess potentially suitable residual streams for total ammoniacal nitrogen (TAN) removal, technologies for TAN recovery and the generation of electricity from ammonia (NH<sub>3</sub>). This chapter presents the results of a literature study on the assessment of the feasibility of residual streams used for TAN removal and technologies allowing for TAN removal and recovery and electricity generation from recovered NH<sub>3</sub>.

The first part describes the identification of thirteen (13) so-called nitrogen-loaded (N-loaded) residual streams, which contain at least 0.5 g·L<sup>-1</sup> of total Kjeldahl nitrogen (TKN), which were subsequently characterised and divided into three categories. Category 1 represents streams with a low TAN/TKN ratio (< 0.5), requiring conversion of organic-N to TAN before TAN recovery. Category 2 represents streams with a high TAN/TKN ratio (≥ 0.5) and high solids content (> 1 g·L<sup>-1</sup>), requiring solids removal before TAN recovery. Category 3 represents streams with a high TAN/TKN ratio (≥ 0.5) and low solids content (≤ 1 g·L<sup>-1</sup>), which are suitable for TAN recovery.

The second part describes the required inputs and obtained outputs of TAN of various TAN recovery technologies. Reverse and forward osmosis and electrodialysis produce concentrated ammonium (NH<sub>4</sub><sup>+</sup>) solutions, whereas (bio-)electrochemical cells and bipolar membrane electrodialysis produce concentrated NH<sub>3</sub> solutions. Struvite precipitation, air stripping followed by acid scrubbing and vacuum (membrane) stripping allow for the recovery of TAN as salt, NH<sub>4</sub><sup>+</sup>-salt solution or gaseous NH<sub>3</sub>, respectively. The respective technologies cover a wide range of feasible TAN concentrations, while the energy consumption is not consistently reported.

The third part discusses combustion-based and fuel cell technologies for the generation of electricity from NH<sub>3</sub>. Solid oxide fuel cells allow for the generation of electricity with negligible emission of oxidised N-species, which is still a challenge for combustion-based technologies. Finally, currently available literature lacks information on the generation of electricity using NH<sub>3</sub> recovered from N-loaded residual streams or aqueous solutions as a fuel.

The provided overview may be used to define strategies for TAN recovery from N-loaded streams, based on the composition of the respective stream, suitable recovery technologies and the desired use of the recovered TAN.

### Keywords

ammoniacal nitrogen; nitrogen-loaded; residual streams; resource recovery; anaerobic digestion;



## 2.1. Introduction

### 2.1.1. Ammoniacal nitrogen recovery

In the last decades, recovery of total ammoniacal nitrogen (TAN) from residual streams by both mature technologies such as chemical precipitation and stripping gained traction, as well as studies to novel technologies such as reverse osmosis (RO) and electrodialysis (ED) (Mehta et al., 2015a; Xie et al., 2016). However, currently available studies discuss the state-of-the-art of different available technologies from the perspective of one specific TAN application: the use of recovered TAN as a resource for fertilisers (Mehta et al., 2015a; Zarebska et al., 2015). Moreover, published review studies overlook or do not explore an important aspect of the TAN recovery potential, which is the existing available residual streams and their composition.

### 2.1.2. Research objective

This chapter assesses the feasibility of residual streams and technologies that are potentially suitable for TAN removal, TAN recovery in different forms and generation of electricity from recovered  $\text{NH}_3$ . This chapter is based on an extensive literature study. This chapter aims to provide a wider view on technologies that allow for the recovery of TAN from residual streams, especially residual waters, other than only for energy generation. More detailed information on the application of TAN as a fertiliser or as a resource for chemical and biochemical processes can be found in the review of Deng et al. (2021), which also assesses the application of anaerobic digestion (AD) to convert organically bound nitrogen (N), or total Kjeldahl nitrogen (TKN) to TAN. This chapter contains:

- The identification, characterisation and categorisation of residual streams that are potentially suitable for TAN recovery;
- An overview of various technologies that can be used for  $\text{NH}_3$  recovery, based on their principle (concentrate TAN as  $\text{NH}_4^+$ ,  $\text{NH}_3$  or recover TAN as  $\text{NH}_3$  from the liquid), the main energy input, the end product and challenges;
- An overview of various technologies that can be used for electricity generation using  $\text{NH}_3$  as a fuel.

During the identification of suitable residual streams, a wide range of descriptions of the term “nitrogen-loaded”: “nitrogen rich”, “high nitrogen content” and “high strength nitrogen” was encountered. In this chapter, the term “nitrogen-loaded” (hereafter N-loaded) refers to residual streams containing TKN concentrations of at least  $0.5 \text{ g}\cdot\text{L}^{-1}$  or  $\text{g}\cdot\text{kg}^{-1}$ . Furthermore, in this chapter, the term “N-loaded residual streams” refers to all N-loaded streams (aqueous, slurries, etc.), whereas the term “N-loaded residual waters” refers to aqueous solutions.

## 2.2. N-loaded residual streams

### 2.2.1. Parameters for characterisation of N-loaded residual streams

To characterise the N-loaded residual streams, this chapter assesses only collected data on various key parameters that should be considered for their treatment to allow for TAN recovery. These parameters concern concentrations of: total suspended solids (TSS), chemical oxygen demand (COD), TKN and TAN. To report consistently, the TSS, COD, TKN and TAN concentrations were normalised to parts per thousand, which corresponds to  $\text{g}\cdot\text{kg}^{-1}$  and  $\text{g}\cdot\text{L}^{-1}$  for solid and liquid streams (assuming a liquid density of  $1,000 \text{ g}\cdot\text{L}^{-1}$ ), respectively. The TSS indicates the feasibility to use directly physicochemical technologies for the recovery of TAN or the need for pre-treatment by for example filtration. The COD is an indication of the presence of organic matter, which must be decreased before discharge to receiving water bodies. Also, a high COD is likely to induce fouling in the physicochemical technologies for TAN recovery, indicating the need for pre-treatment.

The absolute TKN content is an indication of the amount of nitrogen that is present as both organic nitrogen and TAN. The TAN/TKN ratio indicates the dominant present form of N. Data collected for this chapter suggests that physicochemical technologies, such as stripping and precipitation, can be used for direct TAN recovery, for example, pre-treatment steps such as the conversion of organic nitrogen to TAN or solids removal is not needed, at a TAN/TKN ratio higher than 0.5; TAN/TKN ratios lower than 0.5 suggest that the organic nitrogen must be first converted to TAN to allow for recovery of TAN.

When it is necessary to convert organic nitrogen to TAN, the COD/N ratio must also be considered. Typically, when the COD/N ratio of residual streams falls within a certain range (for example, 20 - 30), biochemical technologies such as AD are suitable to decrease the organic matter content, without potential problems of nitrogen shortage or inhibition ([Rajagopal et al., 2013](#)). Regarding the nitrogen in the COD/N ratio, this could refer to either the TN (including organic and inorganic N) or the TKN. It must be noted that under anaerobic conditions TKN is assumed to be equal to TN so the COD/N ratio can be calculated with TKN or TN.

### 2.2.2. Identification and characterisation of N-loaded residual streams

For this chapter, data on N-loaded residual streams from approximately 150 studies was obtained, all using real residual streams either for analytical or experimental research purposes. For each identified N-loaded residual stream, at least three independent references were used and the average, minimum and maximum values of the characteristic parameters are reported. The N-loaded residual streams are divided into four different groups, based on their origins: solid residual streams, manure, liquid residual streams (all domestic) and residual streams reported to originate from industrial processes. The obtained average, minimum and maximum values are presented in Figure 2-1. In the text, only average values are referred to. More details on the consulted references, such as the TSS, COD, TKN and TAN content, the respective units, used treatment technologies and reference details can be found in the supplementary material of the review of [Deng et al. \(2021\)](#).

#### 2.2.2.1. Solid residual streams

The first group includes: bio- and food waste, the organic fraction of municipal solid waste (OFMSW) and spent biomass, such as the waste activated sludge from wastewater treatment plants (WWTPs) and algal sludge (Mata-Alvarez et al., 2000). Typical TSS values for bio- and food waste and OFMSW are 269 and 333  $\text{g}\cdot\text{kg}^{-1}$  (ranges can be consulted in Figure 2-1), respectively, while the COD content is 428 and 644  $\text{g}\cdot\text{kg}^{-1}$ , respectively. For the spent biomass streams, the TSS and COD are considerably lower than for bio- and food waste and OFMSW: 49 and 50  $\text{g}\cdot\text{kg}^{-1}$ , respectively. The typical TAN content of the solid residual streams is 1  $\text{g}\cdot\text{kg}^{-1}$ . Furthermore, the TKN ranges between 3 – 12  $\text{g}\cdot\text{kg}^{-1}$  and is mainly represented by the presence of proteins (Braguglia et al., 2018; Ganesh Saratale et al., 2018). The relatively low TAN/TKN ratios (ranging from 0 to 0.3) indicate that direct TAN recovery will be challenging. To allow for effective TAN recovery, the TAN/TKN ratio must be increased by converting organic nitrogen to TAN. For bio- and food waste and OFMSW, the COD/N ratio is 47 and 60, respectively, whereas for spent biomass the COD/N ratio is 14, because of the lower COD content. Anaerobic (co-)digestion is a widely applied technology to treat these solid residual streams, due to the relatively high COD ( $> 10 \text{ g}\cdot\text{kg}^{-1}$ ) and nitrogen contents ( $> 0.5 \text{ g}\cdot\text{kg}^{-1}$ ) (Hartmann & Ahring, 2005; Keucken et al., 2018). Anaerobic (co-)digestion allows for the simultaneous decrease of the solids and COD content of the residual streams, while the organic nitrogen is converted to TAN, increasing the TAN/TKN ratio.

#### 2.2.2.2. Manure

The second group concerns manure, which is frequently reported to contain high levels of TAN and TSS, and is often considered to be problematic for its treatment via AD (Massé et al., 2014; Rodriguez-Verde et al., 2018). Manure is divided into poultry, cattle and swine manure. Poultry manure has the highest TSS, COD and TKN: 521, 661 and 35  $\text{g}\cdot\text{kg}^{-1}$ , respectively. Despite the low TAN/TKN ratio (TAN/TKN close to 0) of poultry manure, its absolute TAN content is high, for example, 2  $\text{g}\cdot\text{kg}^{-1}$ , practically 92% nitrogen is present as organic nitrogen in poultry manure. Cattle and swine manure have a much lower content of TSS, for example, 81 and 24  $\text{g}\cdot\text{kg}^{-1}$ , respectively, COD, for example, 58 and 36  $\text{g}\cdot\text{kg}^{-1}$ , respectively, and TKN, for example, 4  $\text{g}\cdot\text{kg}^{-1}$ . The TAN of cattle manure is 1  $\text{g}\cdot\text{kg}^{-1}$ , whereas swine manure has a TAN of 4  $\text{g}\cdot\text{kg}^{-1}$ . The nitrogen in cattle manure is predominantly present as organic nitrogen (TAN/TKN ratio is 0.4), whereas in swine manure nitrogen is already present predominantly as TAN (TAN/TKN ratio is 0.7). The COD/N ratio of the various types of manure ranges between 8 and 32. According to the consulted studies, manure is mainly treated by AD but, due to the high level of TAN, is often co-digested with other organic residues to suppress the negative effects of the presence of TAN during the AD processes (Hartmann & Ahring, 2005; Mata-Alvarez et al., 2014).

#### 2.2.2.3. Liquid residual streams (residual waters)

The third group includes leachate, the liquid fraction of raw swine manure (swine liquid) and human (source-separated) urine. The TSS of swine liquid and urine streams is below 1  $\text{g}\cdot\text{L}^{-1}$ , whereas conversely, leachates can contain high amounts of suspended solids (19  $\text{g}\cdot\text{L}^{-1}$ ). Regarding COD, leachates and swine

liquid contain 26 and 31 g·L<sup>-1</sup>, respectively, whereas human urine ranges between 5 and 10 g·L<sup>-1</sup>. The TKN content for all the liquid N-loaded residual streams (N-loaded residual waters) ranges between 3 and 7 g·L<sup>-1</sup>. For leachate, swine liquid and stored human urine, the TAN/TKN is at least 0.8. Fresh human urine, however, has a TAN/TKN ratio of 0.0, because nitrogen is still present as urea. When urine is stored, urea is hydrolysed to TAN, increasing the TAN/TKN ratio. When leachates contain high TSS and COD and have a high COD/N ratio, anaerobic (co-)digestion can be applied for the treatment of the organic fraction ([Lei et al., 2018](#); [Montusiewicz et al., 2018](#)).

#### 2.2.2.4. Industrial residual streams

The fourth group concerns those N-loaded residual streams that have an industrial origin, such as mining and fertiliser industry and fish/fishmeal processing. Amongst these industrial N-loaded residual streams, fishery residual water has the highest COD content (110 g·L<sup>-1</sup>) and TKN content (3 g·L<sup>-1</sup>), and the TKN is mostly present as organic nitrogen (TAN/TKN ratio of 0.3). Residual streams originating from mining and fertiliser industries have a much lower COD content (1 and 0 g·L<sup>-1</sup>, respectively), while all nitrogen is present as TAN (TAN/TKN is 1.0). The TAN content of mining and fertiliser industry residual streams is 5 and 2 g·L<sup>-1</sup>, respectively. For the treatment of fishery residual streams, AD has been used ([Guerrero et al., 1999](#)), whereas physicochemical TAN recovery technologies and biological oxidation processes were used to treat mining and fertiliser residual water ([Noworyta et al., 2003](#); [Huang et al., 2011](#)). Finally, there are also specific (industrial) N-loaded residual streams that are not represented in Figure 2-1, but are considered to be N-loaded and therefore potentially interesting for recovery. For example, TAN content of glutamate wastewater ranges between 16 - 19 g·L<sup>-1</sup> ([Yang et al., 2005](#); [Wang et al., 2011](#)); pectin wastewater can contain around 1.4 g·L<sup>-1</sup> ([Degn Pedersen et al., 2003](#)); slaughterhouse wastewater ~ 0.7 g·L<sup>-1</sup> ([Kundu et al., 2013](#)); nuclear wastewater ~ 35 g·L<sup>-1</sup> ([Gain et al., 2002](#)); coking wastewater can contain between 0.2 - 0.6 g·L<sup>-1</sup> ([Jin et al., 2013](#); [Lin et al., 2018](#)) and ion exchange brine up to 3.9 g·L<sup>-1</sup> ([Vecino et al., 2019](#)). These residual streams also have a high potential for TAN recovery, but insufficient information on their composition and current treatment is available for further assessment.



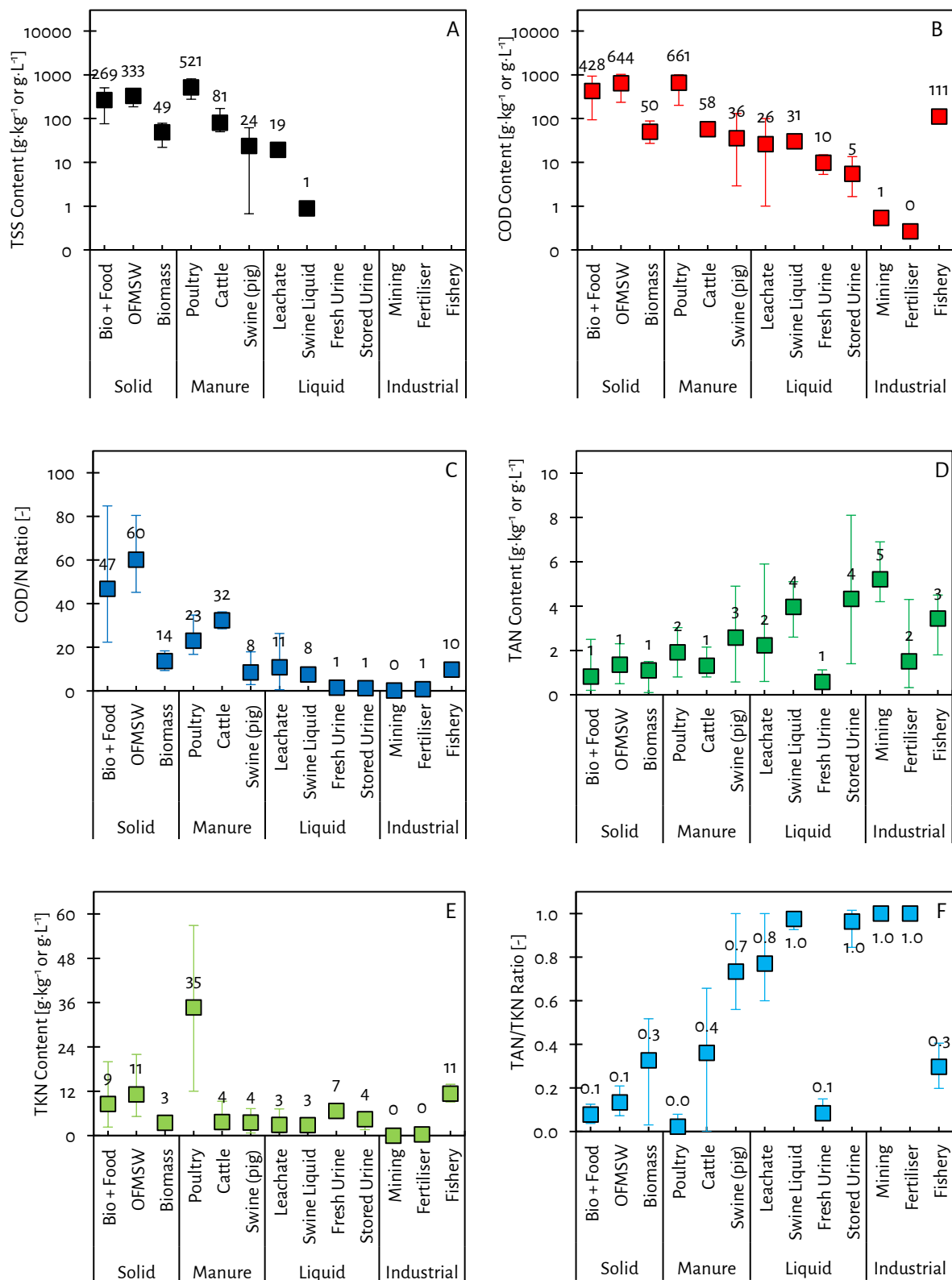


Figure 2-1 - An overview of the identified N-loaded residual streams and their characteristics in terms of TSS (A), COD (B), TKN (D) and TAN (E) content and the respective calculated COD/N (C) and TAN/TKN (F) ratios. The presented values and error bars represent the averages and minimum and maximum values of at least three independently consulted references. The consulted references are extensively presented and referred to in the Supporting Information of the review of [Deng et al. \(2021\)](#).

2.2.3. Category 1: TAN/TKN < 0.5

2.2.3.1. Category 1: TAN/TKN < 0.5

Category 1 contains N-loaded residual streams with a TAN/TKN ratio < 0.5 and a TSS and COD content both higher than 24 and 36 g·kg<sup>-1</sup>, respectively. For these streams, the TAN/TKN must be increased to at least 0.5 to allow for subsequent effective TAN recovery. The N-loaded residual streams that require this organic nitrogen to TAN conversion step are bio- and food waste, OFMSW, spent biomass, poultry and cattle manure. Various biochemical and physicochemical processes, such as AD, can be used to increase the TAN/TKN ratio by conversion of organic nitrogen to TAN, while simultaneously the TSS and COD content is decreased. The conversion of organic nitrogen to TAN by AD is discussed in the review of [Deng et al. \(2021\)](#).

2.2.3.2. Category 2: TAN/TKN ≥ 0.5, TSS > 1 g·L<sup>-1</sup>

Category 2 contains N-loaded residual streams with a TAN/TKN ratio greater than 0.5 and TSS concentrations higher than 1 g·L<sup>-1</sup>. The application of AD to treat various organic N-loaded residual streams from category 1 leads to the generation of digestate (which falls into this category), having a TAN/TKN ratio greater than 0.5. Direct TAN recovery is possible by solids-tolerant recovery technologies, such as struvite precipitation and air stripping (see 2.3) for digestate with TSS up to 1 g·L<sup>-1</sup>. However, for recovery technologies that are prone to fouling (mostly membrane-based technologies), the feed stream must be made free from solids by using solid-liquid separation (centrifugation or belt-press filtration), sedimentation, sand filtration, micro- or ultrafiltration.

2.2.3.3. Category 3: TAN/TKN ≥ 0.5, TSS ≤ 1 g·L<sup>-1</sup>

Category 3 contains N-loaded residual streams with a TAN concentration higher than 0.5 g·L<sup>-1</sup>, a TAN/TKN ratio greater than 0.5 and TSS ≤ 1 g·L<sup>-1</sup>. Within category 3, the liquid residual streams (residual waters), such as solids-free leachate, filtered swine liquid and urine and various industrial N-loaded residual streams coming from mining and fertiliser industry are placed. According to the obtained data with respect to applied treatment technologies, these residual streams are considered suitable for direct TAN recovery by technologies discussed in 2.3.

2.2.4. Interpretation of categories of N-loaded residual streams

The proposed categories indicate the suitability and the path for TAN recovery. For category 1 streams, the organic nitrogen needs to be converted to TAN to increase the TAN/TKN ratio, which is usually achieved by AD. Then the TAN must be separated from the solids to make the liquid stream or N-loaded residual water suitable for TAN recovery. Hence, category 1 streams require the most (pre-)treatment steps, whereas category 3 streams, require the least. The N-loaded residual waters in category 3 can be found in specific industries, such as mining and chemical industries, and have a high potential for TAN recovery because of their high TAN concentrations and low TSS content. However, access to this information is usually limited.

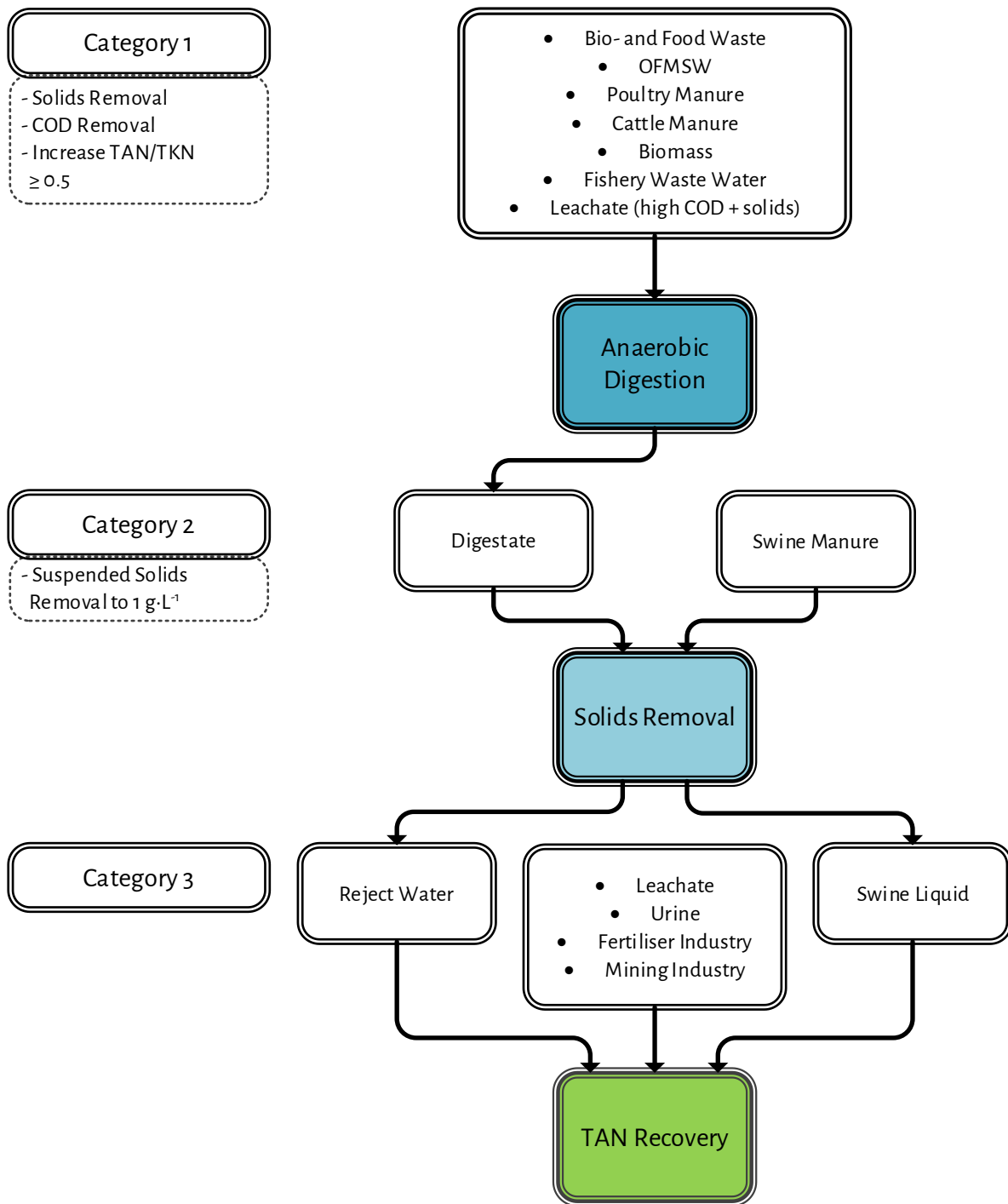


Figure 2-2 - A strategic categorisation of the various N-loaded residual streams, based on their characteristics and required (pre-)treatment before TAN recovery.

### 2.3. Technologies to recover TAN from N-loaded residual waters

#### 2.3.1. Technologies to concentrate TAN

Solid-liquid separation or complete solids removal is preferred before TAN recovery. To this end, mature technologies such as centrifugation, filter presses, media (sand) filtration or microfiltration and ultrafiltration, can be applied to reduce the TSS concentration to below  $1 \text{ g}\cdot\text{L}^{-1}$  (2%) ([Masse et al., 2007](#); [Zarebska et al., 2015](#)). The technologies discussed below are considered to be used at a TSS concentration lower than  $1 \text{ g}\cdot\text{L}^{-1}$  or else after full solids removal.

##### 2.3.1.1. Reverse and forward osmosis

In reverse osmosis (RO), the N-loaded residual water is pressurised to allow for water permeation through a membrane that rejects practically all dissolved substances. To effectively use RO as concentration technology by rejecting TAN and decreasing the volume of the N-loaded residual water, TAN must be present as  $\text{NH}_4^+$ , because uncharged  $\text{NH}_3$  can easily permeate through the membrane ([Masse et al., 2008](#)). For example, [Mondor et al. \(2008a\)](#) and [Gong \(2013\)](#) reported final TAN concentrations of  $12.8$  and  $12 \text{ g}\cdot\text{L}^{-1}$  in the concentrate after using RO to treat filtered swine manure reject water, respectively. The concentration factor (CF), relating the final achieved concentration to the ingoing concentration of the respective N-loaded residual water, was  $1.5$  and  $3.6$ , respectively. [Ledda et al. \(2013\)](#) achieved TAN concentrations of  $5.7$  and  $7.3 \text{ g}\cdot\text{L}^{-1}$ , with a CF of  $4$ , after treating cow and swine reject water pre-treated by ultrafiltration, respectively. In addition, [Schoeman and Strachan \(2009a\)](#) obtained  $1.8 \text{ g}\cdot\text{L}^{-1}$ , CF of  $2$ , after concentrating solid waste leachate by RO. Finally, [Fu et al. \(2011\)](#) used RO to concentrate TAN in simulated acid scrubber effluent and reported a final TAN concentration of  $12.6 \text{ g}\cdot\text{L}^{-1}$  (CF of  $3$ , based on the reported volume reduction and  $\text{NH}_4^+$  rejection) and [Noworyta et al. \(2003\)](#) produced an RO concentrate with a TAN concentration of  $11 \text{ g}\cdot\text{L}^{-1}$  (CF of  $8$ ) after treating  $\text{NH}_4\text{NO}_3$  condensate from fertiliser industry.

Forward osmosis (FO) uses a saline draw solution to force water permeation from the feed water by osmosis, while most (except volatile) dissolved substances are rejected by a membrane. [Holloway et al. \(2007\)](#) reported a water recovery of  $70\%$  and an  $\text{NH}_4^+$  rejection of  $92\%$  for the use of FO to concentrate nutrients in filtered sludge reject water, resulting in a final TAN concentration of  $4 \text{ g}\cdot\text{L}^{-1}$  (CF of  $3$ ). Interestingly, even though the same water recovery was achieved on manure digestate by [Li et al. \(2020\)](#), the authors did not succeed to concentrate TAN by FO as the rejection of  $\text{NH}_4^+$  was less than  $40\%$ .

According to the consulted studies, the maximum CF that can be achieved by RO and FO for TAN in N-loaded residual waters is about  $6$  and  $3$ , respectively. The CF for RO and FO is mainly limited by the water recovery. Furthermore, as a result of the effective rejection (and thus concentration) of substances such as humic acids and multivalent ions by RO and FO, membrane fouling was observed in many studies ([Holloway et al., 2007](#); [Masse et al., 2007](#); [Xie et al., 2016](#); [Li et al., 2020](#)), even when pre-treatment by (membrane) filtration was applied. Hence, extensive membrane cleaning is required, to allow for the stable operation to concentrate TAN by RO and FO when substances in the feed stream are present that induce particulate fouling, scaling

or organic fouling. Finally, because the membranes reject practically everything, also other concentrated compounds (organics and salts) are present in the concentrated  $\text{NH}_4^+$  solution.

#### 2.3.1.2. (Bio-)electrochemical cells

In (bio-)electrochemical cells ((B)ECs), TAN is transported as  $\text{NH}_4^+$  from the anode compartment, through a cation exchange membrane, to the cathode compartment when an electric current is applied. In the last decade, these technologies have been widely applied to recover TAN from N-loaded residual waters as urine and reject water, containing  $\text{NH}_4^+$  feed concentrations up to  $4 \text{ g}\cdot\text{L}^{-1}$  (Rodríguez Arredondo et al., 2015; Kuntke et al., 2018). The various types of (B)ECs comprise microbial fuel cells (MFCs), microbial electrolysis cells (MECs) and electrochemical cells (ECs). While MFCs are actually able to recover TAN and simultaneously produce energy, the highest reported  $\text{NH}_4^+$  fluxes ( $0.08 \text{ kg}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) are 6.5 times lower than for MECs ( $0.52 \text{ kg}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) and 4.8 times lower than for ECs ( $0.38 \text{ kg}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ) (Kuntke et al., 2018). The higher  $\text{NH}_4^+$  fluxes in MECs and ECs are attained at the expense of external electricity supply, which results in a higher electrical energy consumption for MECs ( $4 - 22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ) and ECs ( $18 - 94 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ) compared to the energy-producing MFCs ( $- 10 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ) (Kuntke et al., 2018). The wide range of reported electrical energy consumptions by the (B)ECs can be explained by the very wide range of achieved TAN removal efficiencies (1 – 100%). Based on the reported (B)ECs data, the efforts to decrease the electrode and membrane areas, for which increased  $\text{NH}_4^+$  fluxes are required, led to higher electrical energy consumptions.

(B)ECs are actually used to concentrate TAN, and are mostly combined with stripping and scrubbing of  $\text{NH}_3$ , allowing for actual TAN recovery (Kuntke et al., 2018). Hence, very little attention is paid to the concentrations of TAN obtained in the cathode compartment. The study of Ledezma et al. (2017) reported a final concentration of  $26.2 \text{ g}\cdot\text{N}\cdot\text{L}^{-1}$  (CF of 4.5) in the cathode during the recovery of TAN from synthetic urine by a novel MEC, while Kuntke et al. (2014) achieved a concentration of  $7 \text{ g}\cdot\text{N}\cdot\text{L}^{-1}$  when concentrating TAN in an MEC (CF of 10). A convenient aspect of (B)ECs is the reduction of water at the cathode side, resulting in the generation of  $\text{OH}^-$ , allowing for an in-situ pH increase while no chemicals are needed. Hence, the concentrated TAN solution produced by (B)ECs contains dissolved  $\text{NH}_3$ . Interestingly, no limitations by fouling were reported in the reviews of Kuntke et al. (2018) and Rodríguez Arredondo et al. (2015) while urine, (pig) digestate, reject water leachate were used as feed streams. The apparent tolerance of (B)ECs to blockage by solids and fouling is possibly explained by the relatively wide anode compartments and the fact that the feed water is not pressurised and forced through the membrane.

#### 2.3.1.3. (Bipolar membrane) electro dialysis

Similar to (B)ECs, TAN is transported as  $\text{NH}_4^+$  from the N-loaded residual water when an electric current is applied in electro dialysis processes. Because ED contains alternating cation and anion exchange membranes, alternating feed water and concentrate channels are formed. Eventually, the transported TAN ends up as concentrated  $\text{NH}_4^+$  in the so-called ED concentrate. Pronk et al. (2006b) applied ED to concentrate 93% of the TAN from source-separated urine and achieved a final concentration of  $14.2 \text{ g}\cdot\text{L}^{-1}$  (CF of 2.9).

Studies performed by [Mondor et al. \(2008a\)](#) and [Ippersiel et al. \(2012\)](#) showed that ED can be used to remove TAN by 75 – 85% from filtered manure reject water and that final TAN concentrations between 14 – 21 g·L<sup>-1</sup> can be achieved (CF up to 5.6) for an electrical energy consumption ranging between 66 and 71 MJ·kg-N<sup>-1</sup>. Furthermore, [Ward et al. \(2018\)](#) achieved a CF of 8.5 in the ED concentrate of 120 L by removing 23% of the TAN from 5,400 L sludge reject water at an electrical energy consumption of 18 MJ·kg-N<sup>-1</sup>, leading to a final TAN concentration of 7 g·L<sup>-1</sup>. Furthermore, by optimising the applied current density (which will minimise osmotic water transport and ion back-diffusion), the TAN concentration can be increased from 1.5 to 10 g·L<sup>-1</sup> (CF of 6.7) for 90% TAN removal at an electrical energy consumption of 5 MJ·kg-N<sup>-1</sup> ([van Linden et al., 2019b](#)). By using bipolar membrane electrodialysis (BPMED), TAN can be transported from the N-loaded residual water as NH<sub>4</sub><sup>+</sup> and simultaneously be concentrated as dissolved NH<sub>3</sub> due to the production of OH<sup>-</sup> by bipolar membranes, which only requires electricity ([van Linden et al., 2020](#)). According to the study of [van Linden et al. \(2020\)](#), at least 85% TAN removal can be achieved by BPMED for the production of 5 g·L<sup>-1</sup> of NH<sub>3</sub> at the expense of 19 MJ·kg-N<sup>-1</sup>. Dissolved NH<sub>3</sub> concentrations of 46 and 54 g-NH<sub>3</sub>·L<sup>-1</sup> starting from synthetic NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> solutions containing 37 and 45 g-NH<sub>4</sub><sup>+</sup>·L<sup>-1</sup>, respectively, were achieved by [Li et al. \(2016\)](#) and [Gain et al. \(2002\)](#), respectively. A study performed by [Pronk et al. \(2006c\)](#) resulted in the production of a solution containing 2.5 g-NH<sub>3</sub>·L<sup>-1</sup> after treating diluted urine with an initial TAN concentration of 4.9 g·L<sup>-1</sup> by BPMED, while [Shi et al. \(2018\)](#) used BPMED to completely remove TAN from synthetic pig manure reject water at the expense of 58 MJ·kg-N<sup>-1</sup>, reaching a final concentration of 13.8 g-NH<sub>3</sub>·L<sup>-1</sup>.

Similar to FO and RO, feed waters with low solids concentrations are desired for ED and BPMED, to avoid particulate fouling between the spacers and membranes. Besides, in available studies on ED to concentrate TAN, organic fouling and scaling on the membranes was reported ([Mondor et al., 2009](#); [Shi et al., 2019](#)). Fouling in ED can be reversed and limited by chemical cleaning, reversing the electrode polarity ([Shi et al., 2019](#)) or by avoiding the transport of scaling substances (multivalent ions) and humic acids by using selective membranes ([Kim et al., 2002](#)). In the few published studies on BPMED to recover TAN from N-loaded residual waters, no information on fouling was reported.

### 2.3.2. Technologies to recover TAN

#### 2.3.2.1. Struvite precipitation

The addition of magnesium to N-loaded residual waters containing both TAN and phosphate within the optimum pH range (pH = 8 – 9) leads to the precipitation of struvite crystals (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O, having an NH<sub>4</sub><sup>+</sup> content of 7 wt%), which can be used as fertiliser ([Mehta et al., 2015a](#); [Zarebska et al., 2015](#)). Struvite precipitation is widely applied to avoid undesired scaling in pipelines during the transport of digestate and for the recovery of phosphorus. Moreover, struvite formation can directly be achieved in manure reject water, suggesting that struvite precipitation has a high tolerance to the presence of solids in the N-loaded residual water ([Mehta et al., 2015a](#); [Zarebska et al., 2015](#)). However, in N-loaded residual waters, TAN is present in excess molar concentrations with respect to phosphate (equal molar concentrations required to form struvite) resulting in a TAN removal efficiency of struvite precipitation limited to 15 - 30% ([Mehta et al.,](#)

2015a; Zarebska et al., 2015). The energy consumption of chemical precipitation for the removal and recovery of TAN was reported by Magrí et al. (2013) to be  $59 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , taking the use of chemicals into account.

### 2.3.2.2. (Air) stripping and acid scrubbing

TAN can also be recovered as  $\text{NH}_3$  by air stripping (AS), for example from manure and sludge reject water (Magrí et al., 2013; Zarebska et al., 2015) and recovery of TAN from cathode solutions produced by (B)ECs (Kuntke et al., 2018). Because the vapour pressure of  $\text{NH}_3$  in fresh air is negligibly low,  $\text{NH}_3$  transport from the N-loaded residual water to the air takes place. TAN recovery by AS in stripping towers has a high tolerance of solids as studies reported that no pre-treatment of digestate was required (Mehta et al., 2015a; Zarebska et al., 2015), while it should be noted that scaling of minerals requires cleaning. However, before  $\text{NH}_3$  effectively can be stripped, the pH of the N-loaded residual water must be increased to convert  $\text{NH}_4^+$  to  $\text{NH}_3$ , by means of chemical addition,  $\text{CO}_2$  stripping or electrochemical reactions (water reduction or water dissociation).

The actual concentrations of  $\text{NH}_3$  in the air after  $\text{NH}_3$  stripping according to the study of Wang et al. (2010) are below 9,000 ppm (corresponding to 0.9 wt%). Besides, based on the reported  $\text{NH}_3$  mass flows and the used air flow rates, the concentration of  $\text{NH}_3$  in the air is well below 1 wt% according to the studies of Bonmati and Flotats (2003) and Lei et al. (2007). Hence, by using AS, only diluted gaseous  $\text{NH}_3$  is obtained. By subsequent scrubbing of the  $\text{NH}_3$  gas-containing air with acid, dissolved  $\text{NH}_4^+$  solutions or even solid  $\text{NH}_4^+$  salts such as ammonium sulphate ( $(\text{NH}_4)_2\text{SO}_4$ ), ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) or ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) can be obtained (Bonmati & Flotats, 2003; Ukwuani & Tao, 2016; Kuntke et al., 2018). The energy consumption of AS and subsequent scrubbing in acid ranges from 14 to  $50 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  and depends strongly on the TAN concentration and temperature of the N-loaded residual water (Mehta et al., 2015a; Zarebska et al., 2015). However, not all reported values consistently consider the energy for the addition of heat and the addition of chemicals.

By using hydrophobic membranes, which are impermeable for liquids, but permeable for vapours and gases, to separate the liquid and gas phase, small installation footprints can be realised by providing a large contact area per unit of volume between the feed water and the permeate. Moreover, the pressure of the liquid can be controlled independently of the pressure of the gas. When an acidic solution is recirculated in the permeate side and the feed water contains dissolved  $\text{NH}_3$ , stripping and direct scrubbing takes place, resulting in the direct production of a solution containing  $\text{NH}_4^+$ . This configuration of  $\text{NH}_3$  stripping and scrubbing is called direct membrane contactors (DMCS) or transmembrane chemisorption (TMCS).

According to the review studies of Zarebska et al. (2015), Mehta et al. (2015a) and Kuntke et al. (2018), the DMCS or TMCS was widely applied to directly scrub the stripped  $\text{NH}_3$  from digestates, reject waters, stored urine and from the cathode compartment solutions from (B)ECs, even though TSS concentrations of up to  $20 \text{ g}\cdot\text{L}^{-1}$  were present. The review of Beckinghausen et al. (2020) reported that the energy consumption was about  $4 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , but it remains unclear whether this includes the use of heat and chemicals such as  $\text{H}_2\text{SO}_4$ .

### 2.3.2.3. Vacuum (membrane) stripping

Finally, stripping of  $\text{NH}_3$  also can be achieved by applying a vacuum, which avoids the presence of air in the vapour that contains the stripped  $\text{NH}_3$ . [Ukwuani and Tao \(2016\)](#) successfully used vacuum stripping (VS) in combination with acid scrubbing to recover  $\text{NH}_3$  from water (aqueous solution) at various feed water temperatures and vacuum pressures from manure, food waste, sludge digestate and landfill leachate (containing  $1.0\text{--}6.4\text{ g}\cdot\text{L}^{-1}$  of  $\text{NH}_3$ ). According to the review of [Beckinghausen et al. \(2020\)](#), the required energy for TAN recovery by VS was  $215\text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , which is mainly required for increasing the feed water temperature. However, besides the stripping of  $\text{NH}_3$ , also water is evaporated during VS and vacuum membrane stripping (VMS) resulting in a gaseous  $\text{NH}_3$  and water vapour mixture ([He et al., 2018](#)). In fact, the ratio of the  $\text{NH}_3$  flux to the total flux (water and  $\text{NH}_3$ ) during VMS to recover at  $\text{NH}_3$  at TAN feed concentrations ranging  $1\text{--}4\text{ g}\cdot\text{L}^{-1}$  was only 1% ( $\text{NH}_3$  concentration of 1 wt%) in unfiltered digestate in the studies of [He et al. \(2017\)](#) and [He et al. \(2018\)](#). However, according to the study of [El-Bourawi et al. \(2007\)](#), the  $\text{NH}_3$  in the recovered gas increases from 1.2 to 6.8 wt% when the concentration of  $\text{NH}_3$  in the liquid feed is increased from 5 to  $20\text{ g}\cdot\text{NH}_3\cdot\text{L}^{-1}$ , respectively.

### 2.3.3. Discussion on TAN concentration and recovery technologies

Table 2-1 provides an extensive overview of the key information of the various technologies to concentrate and recover TAN. For almost all technologies (except for struvite precipitation), the actual energy consumption depends heavily on the feed water characteristics, the operational conditions and the actual performance. In currently available literature, the energy consumption for RO and FO is not directly reported. Hence, to concentrate TAN by RO and FO, high TAN rejections and water recoveries must be achieved, leading to an increase in osmotic pressure throughout the operation, which will ultimately translate to a higher energy consumption. Also, the required information to determine the energy consumption to concentrate TAN is lacking. Therefore, there is a need to assess and normalise the energy consumption to concentrate TAN by RO and FO, which will be a function of the TAN feed concentration and rejection, the water recovery and flow rate, transmembrane membrane pressure and pump efficiency. The same holds for (B)ECs and (BPM)ED, for which the energy consumption to concentrate TAN strongly depends on the feed concentration, the amount of TAN transported, the efficiency of using electric charge and the resistance of the cell and membrane stacks. When sufficient data is available, there is potential to normalise the data and derive technology-specific energy values to concentrate TAN.

Finally, to actually recover TAN as gaseous  $\text{NH}_3$ ,  $\text{NH}_4^+$  solution or solid  $\text{NH}_4^+$  crystals, the energy consumption must be expressed including the required amount of heat and energy to produce chemicals and to increase the pH and scrub the  $\text{NH}_3$ . Only when normalised information is available on the various strategies and technologies to recover TAN, fair comparisons between technologies can be made. Eventually, the choice to use a certain technology or combination of technologies will depend on the availability of local resources, the potential to use the recovered products and the financial implications.



Table 2-1 - An overview of the various technologies that can be used to concentrate or recover TAN from N-loaded residual waters.

Recovery of TAN	Concentrating TAN						References	
	Technology	TAN Feed Conc.	Required Input	Solids Tolerance	End products	Product Conc.		Energy Consumption
		g·L <sup>-1</sup>	-	-	-	m% TAN	MJ·kg-N <sup>-1</sup>	
	RO	0.9–8.5	Electricity	Low	NH <sub>4</sub> <sup>+</sup> (aq)	1.3	n.r.	(Mondor et al., 2008a; Schoeman & Strachan, 2009b)
	FO	1.3	Electricity, + salt solution	Low	NH <sub>4</sub> <sup>+</sup> (aq)	0.4	n.r.	(Holloway et al., 2007)
	(B)ES	0.7–5.8	Electricity	Low	NH <sub>3</sub> (aq)	0.7 - 2.6	-10 - 94*	(Kuntke et al., 2018)
	ED	0.8–4.9	Electricity	Low	NH <sub>4</sub> <sup>+</sup> (aq)	0.7 - 2.1	18 - 71	(Mondor et al., 2008a; Ippersiel et al., 2012; Ward et al., 2018)
	BPMED	4.9-45	Electricity	Low	NH <sub>3</sub> (aq)	0.5-1.4	58	(Shi et al., 2018)
	Precipitation	n.r.	Base and salt	High	MgNH <sub>4</sub> PO <sub>4</sub> (6H <sub>2</sub> O) (s)	7	59	(Magri et al., 2013)
	AS (+ Scrub)	0.5–6:7	Electricity, heat and base (acid)	High	NH <sub>3</sub> -air (g) (NH <sub>4</sub> <sup>+</sup> (aq))	0.9 (7 -14)	14 - 50	(Mehta et al., 2015b; Zarebska et al., 2015)
	V(M)S	1-12	Electricity, heat and base	High	NH <sub>3</sub> -water (g)	1.0 - 6.8	215	(Beckinghausen et al., 2020)

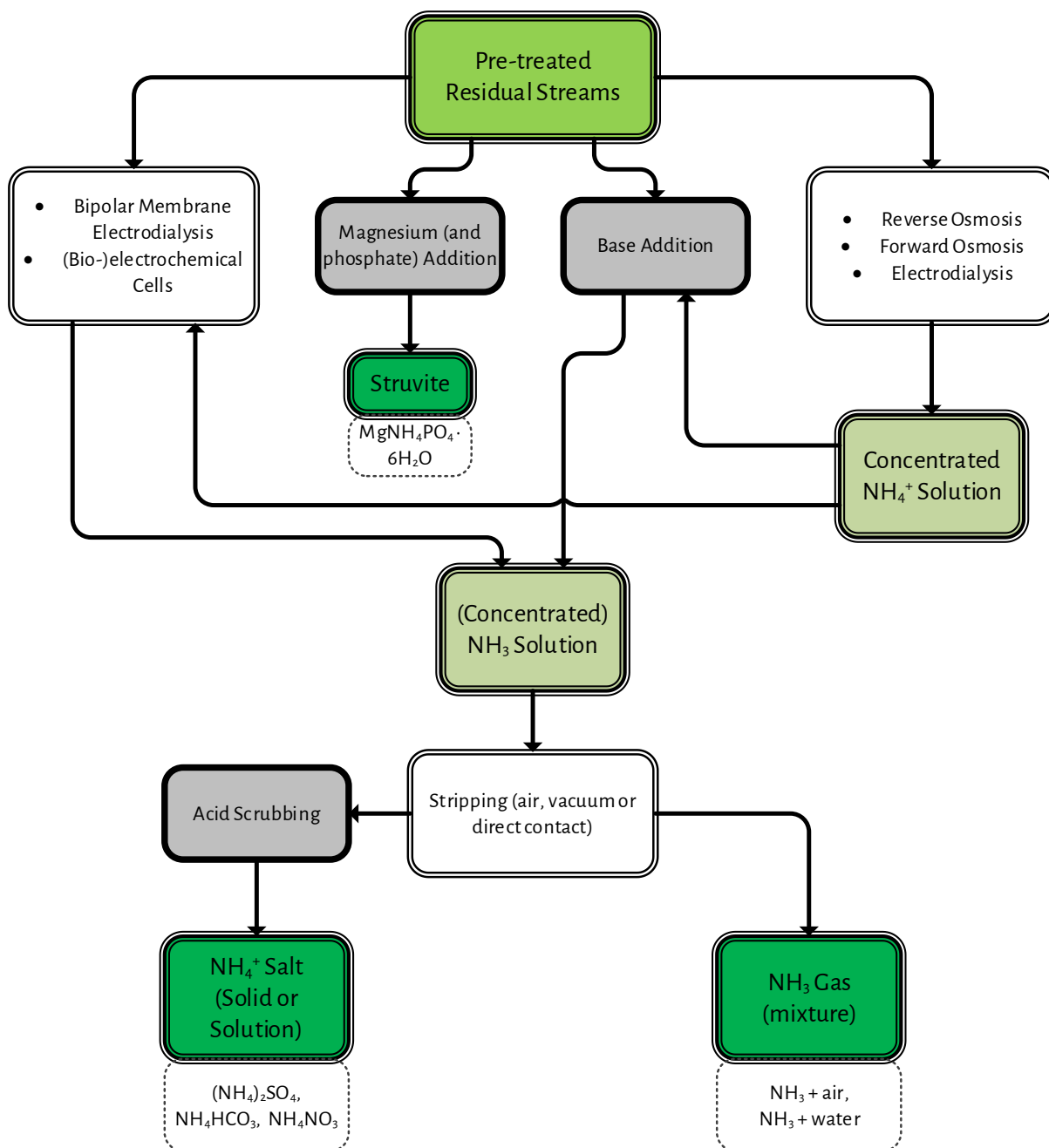


Figure 2-3 - A schematic overview of the various TAN recovery technologies to obtain various TAN products (concerning concentrated  $\text{NH}_4^+$  solutions,  $\text{NH}_3$  solutions, struvite, solid or dissolved  $\text{NH}_4^+$  salts and gaseous  $\text{NH}_3$ ).

#### 2.4. Technologies to generate energy from NH<sub>3</sub>

As extensively mentioned, NH<sub>3</sub> can be used as a fuel for the generation of electricity. This chapter focuses on two energy-generation technologies: combustion-based and fuel cell technologies. According to the available information, more research focused on the application of fuel cells, especially due to their scalability advantage, compared to combustion-based technologies. Based on collected data, a general overview of direct NH<sub>3</sub> fuel cells and their operational characteristics and peak power densities is provided in

Table 2-2 ([Ni et al., 2009](#); [Lan & Tao, 2014a](#); [Afif et al., 2016](#)).

##### 2.4.1. Combustion technologies

NH<sub>3</sub> can be used as fuel in thermal combustion and propulsion technologies. This is normally done in combination with other fuels, such as H<sub>2</sub>, CH<sub>4</sub> or other carbon-based fuels ([Valera-Medina et al., 2018](#)). Recent developments in the maritime shipping industry are focusing on using NH<sub>3</sub> in internal combustion engines ([Lesmana et al., 2019](#)). In fact, NH<sub>3</sub> is regarded as a key carbon-neutral energy carrier, particularly in the retrofitting of the existing fleet. However, according to the review studies of [Kobayashi et al. \(2019\)](#) and [Dimitriou and Javaid \(2020\)](#), there are challenges when using NH<sub>3</sub> regarding low flammability, emission of unprocessed NH<sub>3</sub> and oxidised nitrogen species (NO<sub>x</sub>, N<sub>2</sub>O, etc.). Unfortunately, studies with respect to the use of recovered NH<sub>3</sub> and electricity generation with combustion-based technologies are not currently available.

##### 2.4.2. Alkaline (membrane) fuel cells

Alkaline fuel cells (AFCs) use dissolved or molten hydroxide for the transport of hydroxide (OH<sup>-</sup>) from the cathode to the anode, whereas alkaline membrane fuel cells (AMFCs) use an anion exchange membrane. In both AFCs and AMFCs, NH<sub>3</sub> is directly electrochemically oxidised by OH<sup>-</sup> at the anode, while at the cathode O<sub>2</sub> and water react together with the supplied electrons to OH<sup>-</sup> ([Lan & Tao, 2014a](#)). However, [Lan and Tao \(2010\)](#) mentioned that the low operational temperature of 25 °C resulted in a long stabilisation time of the established electric potential difference between the anode and cathode of their AMFC, indicating slow kinetics of the processes. Furthermore, research conducted by [Suzuki et al. \(2012\)](#) showed that the performance of AMFCs is limited by fuel cross-over, caused by the diffusion of NH<sub>3</sub> from the anode to the cathode. Moreover, [Suzuki et al. \(2012\)](#) also showed that poisoning of the metal catalysts with adsorbed nitrogen species takes place at the anode. Finally, the reported maximum power densities for AFCs and AMFCs are only 40 and 16 mW·cm<sup>-2</sup>, respectively, ([Ganley, 2008](#); [Lan & Tao, 2010](#)), which is an order of magnitude lower than high-temperature fuel cells.

### 2.4.3. Solid oxide fuel cells

SOFCs can be divided, based on their ability, to either conduct protons (SOFC-H) or oxygen ions (SOFC-O) through the solid ceramic electrolyte. Because in both SOFC types the operational temperature is well above 500 °C, NH<sub>3</sub> is spontaneously cracked at the anode in the presence of a nickel catalyst, resulting in the production of H<sub>2</sub> and N<sub>2</sub>. Initially, nickel was used as a catalyst for H<sub>2</sub>-fueled SOFCs ([Mahato et al., 2015](#)) and later also appeared to be a good catalyst to crack NH<sub>3</sub> ([Fournier et al., 2006](#)). In SOFC-Hs, the electrolyte is proton-conducting, while in SOFC-Os, the electrolyte is oxygen-conducting, implying different reactions to take place. According to the study of [Ni et al. \(2008\)](#), the application of SOFC-Hs could lead to higher electrical efficiencies than SOFC-Os when using NH<sub>3</sub> as fuel due to the place where the oxidation reaction takes place, which affects the activity of the reactants. However, available literature reports higher power densities for SOFC-Os than for SOFC-Hs ([Ni et al., 2009](#); [Afif et al., 2016](#)), which is mainly attributed to the low resistance of the oxygen-conducting electrolytes. A maximum power density of 1,190 mW·cm<sup>-2</sup> for SOFC-Os was reported by [Meng et al. \(2007\)](#), compared to 580 mW·cm<sup>-2</sup> for SOFC-Hs ([Aoki et al., 2018](#)), both using NH<sub>3</sub> directly (without external cracking) as fuel. The higher power density reported for SOFC-O is probably a result of more intensive research activities. Based on review papers of ([Ni et al., 2009](#)) and ([Afif et al., 2016](#)), it can be concluded that also the design of the cell is important, as the use of anode-supported planar cells results in superior power densities, compared to the use of tubular-supported or tubular cells. Unfortunately, most research on NH<sub>3</sub>-fueled SOFCs only reports the achieved power density. In addition to the maximum power density, it is also important how efficient the fuel is used, to determine the actual electrical efficiency. Only a limited number of studies reported the actual electrical efficiency (for example, conversion of chemical energy to electrical energy), which can go up to 70% ([Dekker & Rietveld, 2006](#)). A more general review paper on SOFCs by [Stambouli and Traversa \(2002\)](#) also reported that electrical efficiencies of 60% are feasible, while an additional 30% of the chemical energy from the fuels can be used as a high-grade heat. Therefore, SOFCs can potentially effectively use 90% of the total energy content of NH<sub>3</sub>, making the SOFC the most efficient technology to reclaim energy from NH<sub>3</sub>.

Another advantage of SOFCs over combustion-based technologies and A(M)FCs is the negligible production of oxidised N-species. [Staniforth and Ormerod \(2003\)](#), [Ma et al. \(2006\)](#) and [Okanishi et al. \(2017\)](#) analysed the anode off-gas, and concluded that the concentration of oxidised N-species is below the detection limit, and 0.5 ppm by [Dekker and Rietveld \(2006\)](#). Moreover, the application of SOFC-Hs using NH<sub>3</sub> as fuel will even less likely produce oxidised N-species, because N<sub>2</sub> and O<sub>2</sub> will not be in direct contact, as only H<sup>+</sup> is transported through the proton-conducting electrolyte ([Ni et al., 2009](#)). However, a potential challenge for the use of SOFCs is nickel nitridation, which is the formation of nickel-nitrogen (Ni<sub>3</sub>N) species at the anode. Nitridation of nickel at the nickel/yttria-stabilised zirconia anode was observed by [Yang et al. \(2015\)](#), who linked this to a decrease in electric potential over the operational run time at an operational temperature ranging 600 – 700 °C. These findings were confirmed by [Stoeckl et al. \(2019b\)](#), who also observed a decrease in electric potential at 700 °C, while using a nickel/yttria-stabilised zirconia anode. However, interestingly,

Stoeckl et al. (2019b) also observed a stable electric potential at an operational temperature of 800 °C. In a subsequent study by Stoeckl et al. (2020), the electric potential decreased only by 1% over an operational run time of 1,000 hours, when an temperature ranging 815 – 845 °C was maintained. The authors reported that no structural damage was observed at the anode. However, in this study, a nickel/gadolinium-doped ceria anode was used. Therefore, it remains unclear under what operational conditions and for what anode materials nickel nitridation affects the stable operation of NH<sub>3</sub> in SOFC-Os. For SOFC-Hs, no studies were found that reported on nitridation or production of oxidised N-species.

There are no studies that use NH<sub>3</sub> actually recovered from N-loaded residual streams or waters as a fuel in a fuel cell. In case of recovery from water (aqueous solution), NH<sub>3</sub> will be accompanied by water vapour and potentially by contaminants. Interestingly, the main components of biogas (CH<sub>4</sub> and CO<sub>2</sub>), can also be fed to the SOFC-Os, because after CH<sub>4</sub> reforming with steam or CO<sub>2</sub>, the produced H<sub>2</sub> and CO also serve as fuel (Gür, 2016; Saadabadi et al., 2019). However, research conducted by Papadimas et al. (2012) showed that SOFCs are especially sensitive to contaminants such as H<sub>2</sub>S (typically present in biogas), HCl and siloxanes, which deactivate the nickel catalyst and decrease the effective surface of the anode, suggesting that gas cleaning is required before using recovered gases as fuels. Finally, studies on SOFC-Os conducted by Wojcik et al. (2003), Cinti et al. (2016), Stoeckl et al. (2019a) and Stoeckl et al. (2020) showed that it is actually feasible to use mixtures of NH<sub>3</sub> and water vapour as fuel for SOFC-Os. However, the minimum concentration of NH<sub>3</sub> in the fuel was 17% (Wojcik et al., 2003) and it remains unclear whether NH<sub>3</sub> in this concentration can (directly) be recovered from water (aqueous solution). Therefore, more research is required to determine what concentrations of NH<sub>3</sub> can be realised when NH<sub>3</sub> is recovered as a gas from N-loaded residual waters or aqueous solutions and whether SOFCs can work with these concentrations.

Table 2-2 - Various direct NH<sub>3</sub> fuel cells and their operational characteristics and peak power densities according to the review studies of (Ni et al., 2009); Lan and Tao (2014a); (Afif et al., 2016)

Type	Operating Temperature	Electrolyte	Mobile ion	Peak Power Density
AMFC	25 °C	Anion Exchange Membrane	OH <sup>-</sup>	16 mW·cm <sup>-2</sup>
AFC	50 – 450 °C	Dissolved/molten OH <sup>-</sup>	OH <sup>-</sup>	40 mW·cm <sup>-2</sup>
SOFC-H	450 – 750 °C	Ceramic Membrane	H <sup>+</sup>	580 mW·cm <sup>-2</sup>
SOFC-O	500 – 1,000 °C	Ceramic Membrane	O <sup>2-</sup>	1,190 mW·cm <sup>-2</sup>

#### 2.4.4. Discussion on technologies to generate from NH<sub>3</sub>

If used as a fuel, the obtained NH<sub>3</sub> concentration is the key. The presence of water vapour or any other additional inert gas stream may reduce the performance of the technology. Additionally, for the fuel cells and in particular, for SOFCs, the presence of certain chemical compounds such as H<sub>2</sub>S might deactivate the

catalysts (catalyst poisoning) and potentially need gas cleaning before entering the cell. In the case of the  $\text{NH}_3$ -fueled combustion engines,  $\text{NO}_x$  formation and low performance related to the low  $\text{NH}_3$  combustion rate are the main challenges. The use of combustion promoters (a second fuel) or partial  $\text{NH}_3$  cracking before the combustion are approaches being explored for this challenge.

## 2.5. Conclusions

Based on the literature study on the identification of N-loaded residual waters and suitable technologies for TAN recovery and technologies for generating energy from  $\text{NH}_3$ , the following can be derived:

- There is a large potential for TAN recovery from N-loaded residual streams, as thirteen (13) domestic and industrial N-loaded residual streams with a minimum TKN concentration of  $0.5 \text{ g-N}\cdot\text{L}^{-1}$  are identified;
- Categorisation of various N-loaded residual streams can be divided into three categories, based on the required treatment strategy to allow TAN recovery, using the respective TAN/TKN ratio and TSS content:
  - Category 1, representing residual streams with a TAN/TKN ratio  $< 0.5$ : require the conversion of organic nitrogen to TAN before TAN recovery;
  - Category 2, representing residual streams with a TAN/TKN ratio  $\geq 0.5$  and TSS concentration  $> 1 \text{ g}\cdot\text{L}^{-1}$ ; the removal of solids to enhance the TAN recovery;
  - Category 3, representing residual streams with a TAN/TKN ratio  $\geq 0.5$  and a TSS concentration  $\leq 1 \text{ g}\cdot\text{L}^{-1}$  (residual waters): suitable for direct TAN recovery.
- Various water treatment technologies are suitable to contribute to the recovery of TAN from N-loaded residual waters:
  - Production of concentrated  $\text{NH}_4^+$  solutions by reverse and forward osmosis and electro dialysis (13, 4 and  $14 \text{ g}\cdot\text{L}^{-1}$ , respectively);
  - (Bio-)electrochemical cells and bipolar membrane electro dialysis for the production of concentrated  $\text{NH}_3$  solutions ( $26$  and  $54 \text{ g}\cdot\text{L}^{-1}$ , respectively);
  - Struvite precipitation and (air) stripping and subsequent acid scrubbing for the production of  $\text{NH}_4^+$  salt (struvite) and  $\text{NH}_4^+$ -salt solutions, respectively;
  - Vacuum (membrane) stripping for the recovery of  $\text{NH}_3$  gas (up to 7 wt%);
- The (normalised) energy consumption for the technologies suitable for TAN recovery is not consistently reported in currently available literature;
- Both combustion-based and fuel cell technologies can be used to generate energy using  $\text{NH}_3$  as a fuel:
  - Fuel cell technologies can emit negligible amounts of oxidised N-species, whether  $\text{NO}_x$  emission is still a challenge for combustion-based technologies;
  - SOFCs outcompete A(M)FCs in terms of power density for generation of electricity using  $\text{NH}_3$  as a fuel;
- No information is available on the use of  $\text{NH}_3$  recovered from N-loaded residual waters or aqueous solutions as a fuel for combustion-based and fuel cell technologies;

2.6. References

- Afif, A., Radenahmad, N., Cheok, Q., Shams, S., Kim, J. H., & Azad, A. K. (2016). Ammonia-fed fuel cells: a comprehensive review. *Renewable and Sustainable Energy Reviews*, *60*, 822-835.  
doi:<http://dx.doi.org/10.1016/j.rser.2016.01.120>
- Aoki, Y., Yamaguchi, T., Kobayashi, S., Kowalski, D., Zhu, C., & Habazaki, H. (2018). High-Efficiency Direct Ammonia Fuel Cells Based on BaZr<sub>0.1</sub>Ce<sub>0.7</sub>Y<sub>0.2</sub>O<sub>3-δ</sub>/Pd Oxide-Metal Junctions. *Global Challenges*, *2*(1), 1700088. doi:10.1002/gch2.201700088
- Beckinghausen, A., Odlare, M., Thorin, E., & Schwede, S. (2020). From removal to recovery: An evaluation of nitrogen recovery techniques from wastewater. *Applied Energy*, *263*, 114616.  
doi:<https://doi.org/10.1016/j.apenergy.2020.114616>
- Bonmati, A., & Flotats, X. (2003). Air stripping of ammonia from pig slurry: characterisation and feasibility as a pre- or post-treatment to mesophilic anaerobic digestion. *Waste Management*, *23*(3), 261-272.  
doi:[http://dx.doi.org/10.1016/S0956-053X\(02\)00144-7](http://dx.doi.org/10.1016/S0956-053X(02)00144-7)
- Braguglia, C. M., Gallipoli, A., Gianico, A., & Pagliaccia, P. (2018). Anaerobic bioconversion of food waste into energy: A critical review. *Bioresource Technology*, *248*, 37-56.  
doi:10.1016/j.biortech.2017.06.145
- Cinti, G., Discepoli, G., Sisani, E., & Desideri, U. (2016). SOFC operating with ammonia: Stack test and system analysis. *International Journal of Hydrogen Energy*, *41*(31), 13583-13590.  
doi:<http://dx.doi.org/10.1016/j.ijhydene.2016.06.070>
- Degn Pedersen, P., Jensen, K., Lyngsie, P., & Henrik Johansen, N. (2003). Nitrogen removal in industrial wastewater by nitrification and denitrification - 3 years of experience. *Water Science and Technology*, *47*(11), 181-188. doi:10.2166/wst.2003.0603
- Dekker, N. J. J., & Rietveld, G. (2006). Highly efficient conversion of ammonia in electricity by solid oxide fuel cells. *Journal of Fuel Cell Science and Technology*, *3*(4), 499-502. doi:10.1115/1.2349536
- Deng, Z., van Linden, N., Guillen, E., Spanjers, H., & van Lier, J. B. (2021). Recovery and applications of ammoniacal nitrogen from nitrogen-loaded residual streams: A review. *Journal of Environmental Management*, *295*, 113096. doi:<https://doi.org/10.1016/j.jenvman.2021.113096>
- Dimitriou, P., & Javaid, R. (2020). A review of ammonia as a compression ignition engine fuel. *International Journal of Hydrogen Energy*, *45*(11), 7098-7118. doi:<https://doi.org/10.1016/j.ijhydene.2019.12.209>
- El-Bourawi, M. S., Khayet, M., Ma, R., Ding, Z., Li, Z., & Zhang, X. (2007). Application of vacuum membrane distillation for ammonia removal. *Journal of Membrane Science*, *301*(1-2), 200-209.  
doi:10.1016/j.memsci.2007.06.021
- Fournier, G. G. M., Cumming, I. W., & Hellgardt, K. (2006). High performance direct ammonia solid oxide fuel cell. *Journal of Power Sources*, *162*(1), 198-206.  
doi:<http://dx.doi.org/10.1016/j.jpowsour.2006.06.047>



- Fu, G., Cai, T., & Li, Y. (2011). Concentration of ammoniacal nitrogen in effluent from wet scrubbers using reverse osmosis membrane. *Biosystems Engineering*, *109*(3), 235-240.  
doi:<http://dx.doi.org/10.1016/j.biosystemseng.2011.04.005>
- Gain, E., Laborie, S., Viers, P., Rakib, M., Hartmann, D., & Durand, G. (2002). Ammonium nitrate wastewaters treatment by an electromembrane process. *Desalination*, *149*(1-3), 337-342.  
doi:10.1016/S0011-9164(02)00806-8
- Ganesh Saratale, R., Kumar, G., Banu, R., Xia, A., Periyasamy, S., & Dattatraya Saratale, G. (2018). A critical review on anaerobic digestion of microalgae and macroalgae and co-digestion of biomass for enhanced methane generation. *Bioresource Technology*, *262*, 319-332.  
doi:<https://doi.org/10.1016/j.biortech.2018.03.030>
- Ganley, J. C. (2008). An intermediate-temperature direct ammonia fuel cell with a molten alkaline hydroxide electrolyte. *Journal of Power Sources*, *178*(1), 44-47.  
doi:<https://doi.org/10.1016/j.jpowsour.2007.11.093>
- Gong, H. Y., Z.: Liang, K. Q.: Jin, Z. Y.: Wang, K. J. (2013). Concentrating process of liquid digestate by disk tube-reverse osmosis system. *Desalination*, *326*, 30-36.  
doi:<http://dx.doi.org/10.1016/j.desal.2013.07.010>
- Guerrero, L., Omil, F., Mendez, R., & Lema, J. M. (1999). Anaerobic Hydrolysis and Acidogenesis of Wastewaters From Food Industries With High Content of Organic Solids and Protein. *Water Research*, *33*(15), 3281-3290.
- Gür, T. M. (2016). Comprehensive review of methane conversion in solid oxide fuel cells: Prospects for efficient electricity generation from natural gas. *Progress in Energy and Combustion Science*, *54*, 1-64. doi:<https://doi.org/10.1016/j.pecs.2015.10.004>
- Hartmann, H., & Ahring, B. K. (2005). Anaerobic digestion of the organic fraction of municipal solid waste: Influence of co-digestion with manure. *Water Research*, *39*(8), 1543-1552.  
doi:<https://doi.org/10.1016/j.watres.2005.02.001>
- He, Q., Tu, T., Yan, S., Yang, X., Duke, M., Zhang, Y., & Zhao, S. (2018). Relating water vapor transfer to ammonia recovery from biogas slurry by vacuum membrane distillation. *Separation and Purification Technology*, *191*(Supplement C), 182-191.  
doi:<https://doi.org/10.1016/j.seppur.2017.09.030>
- He, Q., Yu, G., Tu, T., Yan, S., Zhang, Y., & Zhao, S. (2017). Closing CO<sub>2</sub> Loop in Biogas Production: Recycling Ammonia As Fertilizer. *Environmental Science & Technology*, *51*(15), 8841-8850.  
doi:10.1021/acs.est.7b00751
- Holloway, R. W., Childress, A. E., Dennett, K. E., & Cath, T. Y. (2007). Forward osmosis for concentration of anaerobic digester centrate. *Water Research*, *41*(17), 4005-4014.  
doi:<http://dx.doi.org/10.1016/j.watres.2007.05.054>

- Huang, H. M., Xiao, X. M., Yang, L. P., & Yan, B. (2011). Removal of ammonium from rare-earth wastewater using natural brucite as a magnesium source of struvite precipitation. *Water Science and Technology*, 63(3), 468-474. doi:10.2166/wst.2011.245
- Ippersiel, D., Mondor, M., Lamarche, F., Tremblay, F., Dubreuil, J., & Masse, L. (2012). Nitrogen potential recovery and concentration of ammonia from swine manure using electro dialysis coupled with air stripping. *Journal of Environmental Management*, 95, S165-S169. doi:<http://dx.doi.org/10.1016/j.jenvman.2011.05.026>
- Jin, X., Li, E., Lu, S., Qiu, Z., & Sui, Q. (2013). Coking wastewater treatment for industrial reuse purpose: Combining biological processes with ultrafiltration, nanofiltration and reverse osmosis. *Journal of Environmental Sciences*, 25(8), 1565-1574. doi:[https://doi.org/10.1016/S1001-0742\(12\)60212-5](https://doi.org/10.1016/S1001-0742(12)60212-5)
- Keucken, A., Habagil, M., Batstone, D., Jeppsson, U., & Arnell, M. (2018). Anaerobic Co-Digestion of Sludge and Organic Food Waste—Performance, Inhibition, and Impact on the Microbial Community. *Energies*, 11(9), 2325. Retrieved from <https://www.mdpi.com/1996-1073/11/9/2325>
- Kim, D. H., Moon, S.-H., & Cho, J. (2002). Investigation of the adsorption and transport of natural organic matter (NOM) in ion-exchange membranes. *Desalination*, 151(1), 11-20. doi:[https://doi.org/10.1016/S0011-9164\(02\)00968-2](https://doi.org/10.1016/S0011-9164(02)00968-2)
- Kobayashi, H., Hayakawa, A., Somarathne, K. D. Kunkuma A., & Okafor, Ekenechukwu C. (2019). Science and technology of ammonia combustion. *Proceedings of the Combustion Institute*, 37(1), 109-133. doi:<https://doi.org/10.1016/j.proci.2018.09.029>
- Kundu, P., Debsarkar, A., & Mukherjee, S. (2013). Treatment of slaughterhouse wastewater in a sequencing batch reactor: Performance evaluation and biodegradation kinetics. *BioMed Research International*, 2013. doi:10.1155/2013/134872
- Kuntke, P., Sleutels, T. H. J. A., Rodríguez Arredondo, M., Georg, S., Barbosa, S. G., ter Heijne, A., Hamelers, H. V. M., & Buisman, C. J. N. (2018). (Bio)electrochemical ammonia recovery: progress and perspectives. *Applied Microbiology and Biotechnology*, 102(9), 3865-3878. doi:10.1007/s00253-018-8888-6
- Kuntke, P., Sleutels, T. H. J. A., Saakes, M., & Buisman, C. J. N. (2014). Hydrogen production and ammonium recovery from urine by a Microbial Electrolysis Cell. *International Journal of Hydrogen Energy*, 39(10), 4771-4778. Retrieved from <https://edepot.wur.nl/352760>
- Lan, R., & Tao, S. (2010). Direct Ammonia Alkaline Anion-Exchange Membrane Fuel Cells. *Electrochemical and Solid-State Letters*, 13(8), B83-B86. doi:<https://doi.org/10.1149/1.3428469>
- Lan, R., & Tao, S. (2014a). Ammonia as a Suitable Fuel for Fuel Cells. *Frontiers in Energy Research*, 2, 35. doi:<https://doi.org/10.3389/fenrg.2014.00035>
- Ledda, C., Schievano, A., Salati, S., & Adani, F. (2013). Nitrogen and water recovery from animal slurries by a new integrated ultrafiltration, reverse osmosis and cold stripping process: A case study. *Water Research*, 47(16), 6157-6166. doi:<http://dx.doi.org/10.1016/j.watres.2013.07.037>

- Ledezma, P., Jermakka, J., Keller, J., & Freguia, S. (2017). Recovering Nitrogen as a Solid without Chemical Dosing: Bio-Electroconcentration for Recovery of Nutrients from Urine. *Environmental Science and Technology Letters*, 4(3), 119-124. doi:<https://doi.org/10.1021/acs.estlett.7b00024>
- Lei, X., Sugiura, N., Feng, C., & Maekawa, T. (2007). Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification. *Journal of Hazardous Materials*, 145(3), 391-397. doi:<https://doi.org/10.1016/j.jhazmat.2006.11.027>
- Lei, Y., Wei, L., Liu, T., Xiao, Y., Dang, Y., Sun, D., & Holmes, D. E. (2018). Magnetite enhances anaerobic digestion and methanogenesis of fresh leachate from a municipal solid waste incineration plant. *Chemical Engineering Journal*, 348(March), 992-999. doi:10.1016/j.cej.2018.05.060
- Lesmana, H., Zhang, Z., Li, X., Zhu, M., Xu, W., & Zhang, D. (2019). NH<sub>3</sub> as a Transport Fuel in Internal Combustion Engines: A Technical Review. *J. Energy Resour. Technol.*, 141(7), 070703. doi:<https://doi.org/10.1115/1.4042915>
- Li, Y., Shi, S., Cao, H., Wu, X., Zhao, Z., & Wang, L. (2016). Bipolar membrane electro dialysis for generation of hydrochloric acid and ammonia from simulated ammonium chloride wastewater. *Water Research*, 89(Supplement C), 201-209. doi:<https://doi.org/10.1016/j.watres.2015.11.038>
- Li, Y., Xu, Z., Xie, M., Zhang, B., Li, G., & Luo, W. (2020). Resource recovery from digested manure centrate: Comparison between conventional and aquaporin thin-film composite forward osmosis membranes. *Journal of Membrane Science*, 593, 117436. doi:<https://doi.org/10.1016/j.memsci.2019.117436>
- Lin, P. H., Horng, R. Y., Hsu, S. F., Chen, S. S., & Ho, C. H. (2018). A Feasibility Study of Ammonia Recovery from Coking Wastewater by Coupled Operation of a Membrane Contactor and Membrane Distillation. *International journal of environmental research and public health*, 15(3), 441. doi:<https://doi.org/10.3390/ijerph15030441>
- Ma, Q., Peng, R., Tian, L., & Meng, G. (2006). Direct utilization of ammonia in intermediate-temperature solid oxide fuel cells. *Electrochemistry Communications*, 8(11), 1791-1795. doi:<http://dx.doi.org/10.1016/j.elecom.2006.08.012>
- Magrí, A., Béline, F., & Dabert, P. (2013). Feasibility and interest of the anammox process as treatment alternative for anaerobic digester supernatants in manure processing - An overview. *Journal of Environmental Management*, 131, 170-184. doi:10.1016/j.jenvman.2013.09.021
- Mahato, N., Banerjee, A., Gupta, A., Omar, S., & Balani, K. (2015). Progress in material selection for solid oxide fuel cell technology: A review. *Progress in Materials Science*, 72, 141-337. doi:<https://doi.org/10.1016/j.pmatsci.2015.01.001>
- Massé, D. I., Rajagopal, R., & Singh, G. (2014). Technical and operational feasibility of psychrophilic anaerobic digestion biotechnology for processing ammonia-rich waste. *Applied Energy*, 120, 49-55. doi:10.1016/j.apenergy.2014.01.034

- Masse, L., Massé, D. I., & Pellerin, Y. (2007). The use of membranes for the treatment of manure: a critical literature review. *Biosystems Engineering*, 98(4), 371-380.  
doi:<https://doi.org/10.1016/j.biosystemseng.2007.09.003>
- Masse, L., Massé, D. I., & Pellerin, Y. (2008). The effect of pH on the separation of manure nutrients with reverse osmosis membranes. *Journal of Membrane Science*, 325(2), 914-919.  
doi:<http://dx.doi.org/10.1016/j.memsci.2008.09.017>
- Mata-Alvarez, J., Dosta, J., Romero-Güiza, M. S., Fonoll, X., Peces, M., & Astals, S. (2014). A critical review on anaerobic co-digestion achievements between 2010 and 2013. *Renewable and Sustainable Energy Reviews*, 36, 412-427. doi:10.1016/j.rser.2014.04.039
- Mata-Alvarez, J., Macé, S., & Llabrés, P. (2000). Anaerobic digestion of organic solid wastes. An overview of research achievements and perspectives. *Bioresource Technology*, 74(1), 3-16. doi:10.1016/S0960-8524(00)00023-7
- Mehta, C. M., Khunjar, W. O., Nguyen, V., Tait, S., & Batstone, D. J. (2015a). Technologies to Recover Nutrients From Waste Streams: A Critical Review. *Critical Reviews in Environmental Science and Technology*, 45, 385-427. doi:<https://doi.org/10.1080/10643389.2013.866621>
- Mehta, C. M., Khunjar, W. O., Nguyen, V., Tait, S., & Batstone, D. J. (2015b). Technologies to Recover Nutrients from Waste Streams: A Critical Review. *Critical Reviews in Environmental Science and Technology*, 45(4), 385-427. doi:10.1080/10643389.2013.866621
- Meng, G., Jiang, C., Ma, J., Ma, Q., & Liu, X. (2007). Comparative study on the performance of a SDC-based SOFC fueled by ammonia and hydrogen. *Journal of Power Sources*, 173(1), 189-193.  
doi:<http://dx.doi.org/10.1016/j.jpowsour.2007.05.002>
- Mondor, M., Ippersiel, D., Lamarche, F., & Masse, L. (2009). Fouling characterization of electro dialysis membranes used for the recovery and concentration of ammonia from swine manure. *Bioresource Technology*, 100(2), 566-571. doi:<https://doi.org/10.1016/j.biortech.2008.06.072>
- Mondor, M., Masse, L., Ippersiel, D., Lamarche, F., & Massé, D. I. (2008a). Use of electro dialysis and reverse osmosis for the recovery and concentration of ammonia from swine manure. *Bioresource Technology*, 99, 7363-7368. doi:<https://doi.org/10.1016/j.biortech.2006.12.039>
- Montusiewicz, A., Bis, M., Pasieczna-Patkowska, S., & Majerek, D. (2018). Mature landfill leachate utilization using a cost-effective hybrid method. *Waste Management*, 76, 652-662.  
doi:10.1016/j.wasman.2018.03.012
- Ni, M., Leung, D. Y. C., & Leung, M. K. H. (2008). Thermodynamic analysis of ammonia fed solid oxide fuel cells: Comparison between proton-conducting electrolyte and oxygen ion-conducting electrolyte. *Journal of Power Sources*, 183(2), 682-686. doi:<https://doi.org/10.1016/j.jpowsour.2008.05.022>
- Ni, M., Leung, M. K. H., & Leung, D. Y. C. (2009). Ammonia-fed solid oxide fuel cells for power generation—A review. *International Journal of Energy Research*, 33(11), 943-959. doi:10.1002/er.1588

- Noworyta, A., Koziol, T., & Trusek-Holownia, A. (2003). A system for cleaning condensates containing ammonium nitrate by the reverse osmosis method. *Desalination*, *156*(1), 397-402.  
doi:[https://doi.org/10.1016/S0011-9164\(03\)00373-4](https://doi.org/10.1016/S0011-9164(03)00373-4)
- Okanishi, T., Okura, K., Srafa, A., Muroyama, H., Matsui, T., Kishimoto, M., Saito, M., Iwai, H., Yoshida, H., Saito, M., Koide, T., Iwai, H., Suzuki, S., Takahashi, Y., Horiuchi, T., Yamasaki, H., Matsumoto, S., Yumoto, S., Kubo, H., Kawahara, J., Okabe, A., Kikkawa, Y., Isomura, T., & Eguchi, K. (2017). Comparative Study of Ammonia-fueled Solid Oxide Fuel Cell Systems. *Fuel Cells*, *17*(3), 383-390.  
doi:10.1002/fuce.201600165
- Papadias, D. D., Ahmed, S., & Kumar, R. (2012). Fuel quality issues with biogas energy – An economic analysis for a stationary fuel cell system. *Energy*, *44*(1), 257-277.  
doi:<https://doi.org/10.1016/j.energy.2012.06.031>
- Pronk, W., Biebow, M., & Boller, M. (2006b). Electrodialysis for Recovering Salts from a Urine Solution Containing Micropollutants. *Environmental Science and Technology*, *40*(7), 2414-2420.  
doi:<https://doi.org/10.1021/es051921i>
- Pronk, W., Biebow, M., & Boller, M. (2006c). Treatment of source-separated urine by a combination of bipolar electrodialysis and a gas transfer membrane. *Water Science and Technology*, *53*(3), 139-146. doi:10.2166/wst.2006.086
- Rajagopal, R., Massé, D. I., & Singh, G. (2013). A critical review on inhibition of anaerobic digestion process by excess ammonia. *Bioresource Technology*, *143*, 632-641. doi:10.1016/j.biortech.2013.06.030
- Rodriguez-Verde, I., Regueiro, L., Lema, J. M., & Carballa, M. (2018). Blending based optimisation and pretreatment strategies to enhance anaerobic digestion of poultry manure. *Waste Management*, *71*, 521-531. doi:10.1016/j.wasman.2017.11.002
- Rodríguez Arredondo, M., Kuntke, P., Jeremiassé, A. W., Sleutels, T. H. J. A., Buisman, C. J. N., & ter Heijne, A. (2015). Bioelectrochemical systems for nitrogen removal and recovery from wastewater. *Environmental Science: Water Research and Technology*, *1*(1), 22-33.  
doi:<https://doi.org/10.1039/C4EW00066H>
- Saadabadi, S. A., Thallam Thattai, A., Fan, L., Lindeboom, R. E. F., Spanjers, H., & Aravind, P. V. (2019). Solid Oxide Fuel Cells fuelled with biogas: Potential and constraints. *Renewable Energy*, *134*, 194-214.  
doi:<https://doi.org/10.1016/j.renene.2018.11.028>
- Schoeman, J. J., & Strachan, L. (2009a). Performance of tubular reverse osmosis for the desalination/concentration of a municipal solid waste leachate. *Water SA*, *35*(3), 323-328.  
doi:10.4314/wsa.v35i3.76776
- Schoeman, J. J., & Strachan, L. (2009b). Performance of tubular reverse osmosis for the desalination/concentration of a municipal solid waste leachate. *Water SA*, *35*, 323-328.  
doi:10.4314/wsa.v35i3.76776

- Shi, L., Hu, Y., Xie, S., Wu, G., Hu, Z., & Zhan, X. (2018). Recovery of nutrients and volatile fatty acids from pig manure hydrolysate using two-stage bipolar membrane electrodialysis. *Chemical Engineering Journal*, 334, 134-142. doi:<https://doi.org/10.1016/j.cej.2017.10.010>
- Shi, L., Xie, S., Hu, Z., Wu, G., Morrison, L., Croot, P., Hu, H., & Zhan, X. (2019). Nutrient recovery from pig manure digestate using electrodialysis reversal: Membrane fouling and feasibility of long-term operation. *Journal of Membrane Science*, 573, 560-569. doi:<https://doi.org/10.1016/j.memsci.2018.12.037>
- Stambouli, A. B., & Traversa, E. (2002). Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. *Renewable and Sustainable Energy Reviews*, 6(5), 433-455. doi:[https://doi.org/10.1016/S1364-0321\(02\)00014-X](https://doi.org/10.1016/S1364-0321(02)00014-X)
- Staniforth, J., & Ormerod, R. M. (2003). Clean destruction of waste ammonia with consummate production of electrical power within a solid oxide fuel cell system. *Green Chemistry*, 5(5), 606-609. doi:10.1039/B307396N
- Stoeckl, B., Preininger, M., Subotić, V., Gaber, C., Seidl, M., Sommersacher, P., Schroettner, H., & Hochenauer, C. (2019a). High Utilization of Humidified Ammonia and Methane in Solid Oxide Fuel Cells: An Experimental Study of Performance and Stability. *Journal of The Electrochemical Society*, 166(12), F774-F783. doi:10.1149/2.0781912jes
- Stoeckl, B., Preininger, M., Subotić, V., Megel, S., Folgner, C., & Hochenauer, C. (2020). Towards a wastewater energy recovery system: The utilization of humidified ammonia by a solid oxide fuel cell stack. *Journal of Power Sources*, 450, 227608. doi:<https://doi.org/10.1016/j.jpowsour.2019.227608>
- Stoeckl, B., Subotić, V., Preininger, M., Schwaiger, M., Evic, N., Schroettner, H., & Hochenauer, C. (2019b). Characterization and performance evaluation of ammonia as fuel for solid oxide fuel cells with Ni/YSZ anodes. *Electrochimica Acta*, 298, 874-883. doi:<https://doi.org/10.1016/j.electacta.2018.12.065>
- Suzuki, S., Muroyama, H., Matsui, T., & Eguchi, K. (2012). Fundamental studies on direct ammonia fuel cell employing anion exchange membrane. *Journal of Power Sources*, 208(Supplement C), 257-262. doi:<https://doi.org/10.1016/j.jpowsour.2012.02.043>
- Ukwuani, A. T., & Tao, W. (2016). Developing a vacuum thermal stripping - acid absorption process for ammonia recovery from anaerobic digester effluent. *Water Research*, 106, 108-115. doi:<https://doi.org/10.1016/j.watres.2016.09.054>
- Valera-Medina, A., Xiao, H., Owen-Jones, M., David, W. I. F., & Bowen, P. J. (2018). Ammonia for power. *Progress in Energy and Combustion Science*, 69, 63-102. doi:<https://doi.org/10.1016/j.pecs.2018.07.001>
- van Linden, N., Bandinu, G. L., Vermaas, D. A., Spanjers, H., & van Lier, J. B. (2020). Bipolar membrane electrodialysis for energetically competitive ammonium removal and dissolved ammonia

- production. *Journal of Cleaner Production*, 120788.  
doi:<https://doi.org/10.1016/j.jclepro.2020.120788>
- van Linden, N., Spanjers, H., & van Lier, J. B. (2019b). Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electro dialysis. *Water Research*, 163, 114856. doi:<https://doi.org/10.1016/j.watres.2019.114856>
- Vecino, X., Reig, M., Bhushan, B., Gibert, O., Valderrama, C., & Cortina, J. L. (2019). Liquid fertilizer production by ammonia recovery from treated ammonia-rich regenerated streams using liquid-liquid membrane contactors. *Chemical Engineering Journal*, 360, 890-899.  
doi:<https://doi.org/10.1016/j.cej.2018.12.004>
- Wang, Q., Yang, P., & Cong, W. (2011). Cation-exchange membrane fouling and cleaning in bipolar membrane electro dialysis of industrial glutamate production wastewater. *Separation and Purification Technology*, 79(1), 103-113. doi:<https://doi.org/10.1016/j.seppur.2011.03.024>
- Wang, Y., Pelkonen, M., & Kotro, M. (2010). Treatment of High Ammonium–Nitrogen Wastewater from Composting Facilities by Air Stripping and Catalytic Oxidation. *Water, Air, and Soil Pollution*, 208(1), 259-273. doi:10.1007/s11270-009-0164-z
- Ward, A. J., Arola, K., Thompson Brewster, E., Mehta, C. M., & Batstone, D. J. (2018). Nutrient recovery from wastewater through pilot scale electro dialysis. *Water Research*, 135, 57-65.  
doi:<https://doi.org/10.1016/j.watres.2018.02.021>
- Wojcik, A., Middleton, H., Damopoulos, I., & Van herle, J. (2003). Ammonia as a fuel in solid oxide fuel cells. *Journal of Power Sources*, 118(1–2), 342-348. doi:[http://dx.doi.org/10.1016/S0378-7753\(03\)00083-1](http://dx.doi.org/10.1016/S0378-7753(03)00083-1)
- Xie, M., Shon, H. K., Gray, S. R., & Elimelech, M. (2016). Membrane-based processes for wastewater nutrient recovery: Technology, challenges, and future direction. *Water Research*, 89, 210-221.  
doi:<http://dx.doi.org/10.1016/j.watres.2015.11.045>
- Yang, J., Molouk, A. F. S., Okanishi, T., Muroyama, H., Matsui, T., & Eguchi, K. (2015). A Stability Study of Ni/Yttria-Stabilized Zirconia Anode for Direct Ammonia Solid Oxide Fuel Cells. *ACS Applied Materials and Interfaces*, 7(51), 28701-28707. doi:<https://doi.org/10.1021/acsami.5b11122>
- Yang, Q., Yang, M., Zhang, S., & Lv, W. (2005). Treatment of wastewater from a monosodium glutamate manufacturing plant using successive yeast and activated sludge systems. *Process Biochemistry*, 40, 2483-2488. doi:10.1016/j.procbio.2004.09.009
- Zarebska, A., Romero Nieto, D., Christensen, K. V., Fjerbæk Sjøftoft, L., & Norddahl, B. (2015). Ammonium fertilizers production from manure: A critical review. *Critical Reviews in Environmental Science and Technology*, 45(14), 1469-1521. doi:10.1080/10643389.2014.955630





## Chapter 3.

# Electrodialysis for ammonium removal and producing concentrated ammonium solutions

Based on:

Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electrodialysis

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Abstract

Electrodialysis (ED) can be used for total ammoniacal nitrogen (TAN) removal efficiencies by transporting ammonium ( $\text{NH}_4^+$ ) from treating nitrogen-loaded (N-loaded) residual streams, while simultaneously producing concentrated  $\text{NH}_4^+$  solutions. However, the effect of osmosis and back-diffusion increases when the  $\text{NH}_4^+$  concentration gradient between the diluate and the concentrate increases, resulting in a limitation of the concentration factor and an increase in electrical energy consumption. This chapter shows that operation at dynamic current density (DCD) decreased the effect of osmosis and back-diffusion, due to a 75% decrease of the operational run time, compared to operation at a fixed current density (FCD). The concentration factor increased from 4.5 for an FCD to 6.7 for DCD, while the electrical energy consumption of 90%  $\text{NH}_4^+$  removal from synthetic sludge reject water at DCD remained stable at  $5.4 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .

Keywords

electrodialysis; current density; ammonium; concentration factor; energy consumption; current efficiency;



### 3.1. Introduction

Chapter 2 identifies electrodialysis (ED) as a potentially suitable technology to achieve 90% removal of total ammoniacal nitrogen (TAN), while simultaneously producing concentrated ammonium ( $\text{NH}_4^+$ ) solutions. Subsequently, the literature review presented in Chapter 2 of this thesis confirms that ED is a suitable technology for TAN removal from nitrogen-loaded (N-loaded) residual waters, but that the achievable removal efficiency, concentration factor and energy consumption deviate in currently reported literature. Because this chapter focuses on the transport of ions, the main addressed form of TAN is  $\text{NH}_4^+$ .

#### 3.1.1. Concentrating $\text{NH}_4^+$ by ED

Pronk et al. (2006a) removed  $\text{NH}_4^+$  for 85% from source-separated urine for nutrient recovery purposes and concentrated  $\text{NH}_4^+$  by a factor of 3.2 with an energy consumption of  $96 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . In addition, Mondor et al. (2008b) and Ippersiel et al. (2012) used ED for  $\text{NH}_4^+$  recovery from digested swine manure and removed 75% and 87%, respectively, while achieving a concentration factor for  $\text{NH}_4^+$  of 2.8 and 5.6, respectively. The energy consumption for removing and concentrating  $\text{NH}_4^+$  in these two studies ranged between 18 and  $71 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . Furthermore, Wang et al. (2015) achieved full removal of  $\text{NH}_4^+$  from sludge reject water by ED for nutrient recovery purposes and obtained a concentration factor of 18. However, the energy consumption was an order of magnitude higher than the other reported studies:  $202 - 258 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . Finally, Ward et al. (2018) used ED to recover  $\text{NH}_4^+$  from sludge reject water on pilot scale, achieving a concentration factor of 8.5 for  $\text{NH}_4^+$ . However, the removal of  $\text{NH}_4^+$  from the sludge reject water was limited to 23%, while the energy consumption was competitive to partial nitrification in combination with anammox:  $18 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .

#### 3.1.2. Problems with concentrating $\text{NH}_4^+$ with ED

The concentration factor for concentrating ions by ED is limited by water ( $\text{H}_2\text{O}$ ) transfer (Pronk et al., 2006a; Mondor et al., 2008b; Rottiers et al., 2014; Ward et al., 2018). The ion concentration gradient that establishes across the membranes between the diluate and concentrate causes osmosis (Strathmann, 2004a), resulting in dilution of the concentrate. In addition, the ion concentration gradient causes the concentrated ions to diffuse from the concentrate back to the diluate (back-diffusion) (Strathmann, 2004b). The diffused ions need to be transported back and forth, requiring an additional supply of electrical charge (and thus consumed energy). Back-diffusion, therefore, results in a decrease in current efficiency (Strathmann, 2004b) and an increase in energy consumption. The reported studies on concentrating  $\text{NH}_4^+$  by ED either applied a fixed voltage or a fixed current density (FCD). When a fixed voltage is applied, the limiting current density (LCD) may be exceeded at low ion concentrations in the diluate.  $\text{H}_2\text{O}$  dissociates into  $\text{H}^+$  and  $\text{OH}^-$  when the LCD is exceeded, resulting in a decreased current efficiency and an increase in energy consumption (Strathmann, 2010). When an FCD is applied, a current density equal to or lower than the LCD of the aimed diluate ion concentration is applied. However, the application of low current densities leads to low ion transport fluxes, indicating inefficient use of membranes and high operational run times. By decreasing the

operational run time, the effect of osmosis and back-diffusion can be decreased, because an ion concentration gradient will inevitably establish when concentrating ions such as  $\text{NH}_4^+$ .

3.1.3. Research objective

Previous research showed that ED can effectively be applied to remove  $\text{NH}_4^+$  from side streams. This chapter assesses the operation of ED at dynamic current density (DCD) and FCD, aiming to maximise the concentration factor and minimise energy consumption. For DCD operation, the current density is dynamically adjusted in agreement with the decreasing ion concentration of the diluate, without exceeding the LCD. The effect of the current density on the concentrating factor and energy consumption was studied by assessing the  $\text{H}_2\text{O}$  transfer and the  $\text{NH}_4^+$  current efficiency during sequencing batch experiments at both the application of an FCD and DCD.

3.2. Materials and methods3.2.1. Materials

Figure 3-1 presents a schematic representation of the used experimental set-up. A bench-scale PC-Cell 64002 ED cell was used, consisting of a Pt/Ir coated titanium anode and a V4A steel cathode, with an electrode area of  $8 \times 8 \text{ cm}^2$ . In between the electrodes, a ten cell pair membrane stack was placed, consisting of two PCA SC cation exchange end (CEEM), ten PCA SA standard anion exchange (AEM) and nine PCA SK standard cation exchange membranes (CEM) (PCA, 2016b). The membrane stack contained polyethylene/silicone spacers to separate the electrodes and membranes, creating electrode rinse, diluate and concentrate channels. The spacers had a thickness of 0.5 mm and a void fraction of 59%. The lay-out of the electrodes, flow channels and membranes is schematically represented in Figure 3-2.

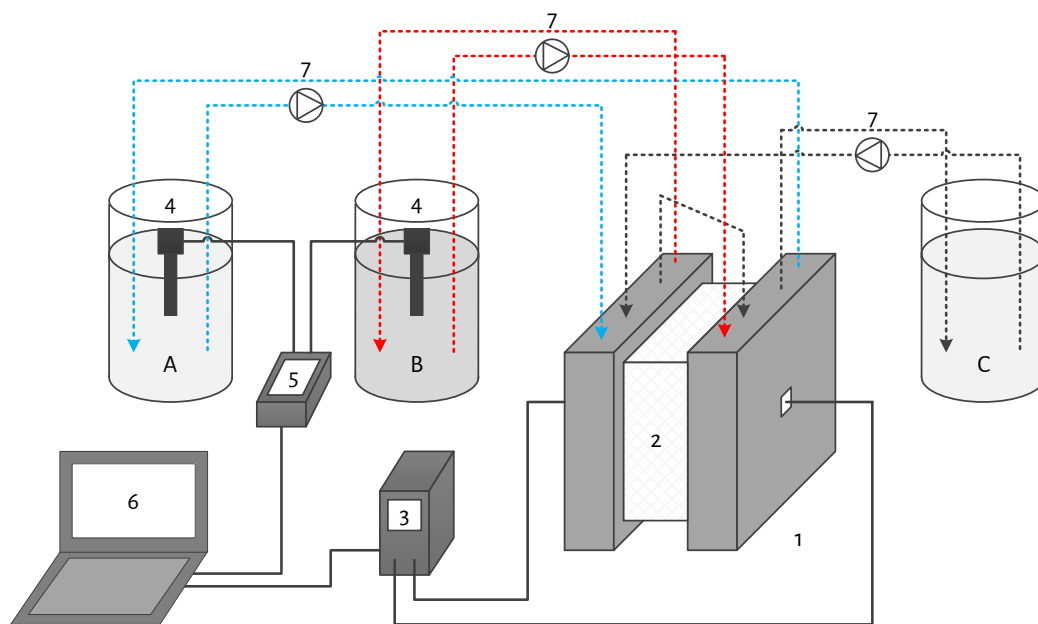


Figure 3-1 - A schematic representation of the used experimental set-up, including the ED cell (1), membrane stack (2), power supply (3), EC sensors (4), multimeter (5), laptop (6), peristaltic pumps (7) and the diluate (A), concentrate (B) and electrode rinse (C) solution.

The diluate and concentrate solutions were recirculated through the ED cell at a cross-flow velocity of  $2 \text{ cm} \cdot \text{s}^{-1}$ , following the recommendations of [Strathmann \(2010\)](#). The cross-flow velocity was controlled by using a calibrated peristaltic Watson-Marlow 520S pump at a flow rate of  $19 \text{ L} \cdot \text{h}^{-1}$ . The electrodes were rinsed with an electrode rinse solution at the same flow rate used for the diluate and concentrate. Separate Watson-Marlow 323 pump heads were used for each solution. For the application of electrical current, a Tenma 72-2535 power supply with an electrical current and electrical potential range of  $0.001 - 3.000 \text{ A}$  and  $0.01 - 30.00 \text{ V}$ , respectively, was used. The electrical conductivity (EC) and pH of the electrode rinse, diluate and concentrate were measured in the respective solution bottles, using two calibrated TetraCon 925 EC-sensors and a calibrated IDS SenTix 940 pH sensors, respectively, on a WTW Multi 3630 IDS multi-meter.

$\text{NH}_4^+$  concentrations were measured with Machery-Nagel NANOCOLOR Ammonium 200 (range: 0.04 – 0.2  $\text{g}\cdot\text{L}^{-1}$ ) and 2,000 (range: 0.4 – 2.0  $\text{g}\cdot\text{L}^{-1}$ ) test kits. Solution volumes were determined using calibrated volumetric cylinders.

Initial diluate and concentrate solutions consisting of 6.6  $\text{g}\cdot\text{L}^{-1}$   $\text{NH}_4\text{HCO}_3$  were used, equal to an  $\text{NH}_4^+$  concentration of 1.5  $\text{g}\cdot\text{L}^{-1}$ , simulating  $\text{NH}_4^+$  concentrations commonly present in sludge reject waters. Synthetic solutions were used to be able to study the effect of back-diffusion and (electro-)osmosis as a function of the  $\text{NH}_4^+$  concentration gradient on the concentration factor and energy consumption at different current density operations. The initial electrode rinse solutions consisted of 1 M  $\text{NaNO}_3$ . The salts were of analytical grade (Sigma Aldrich Reagent Plus,  $\geq 99\%$ ) and were added to 1 L of demi-water. The experiments were conducted at room temperature ( $T = 22 \pm 1^\circ\text{C}$ ).

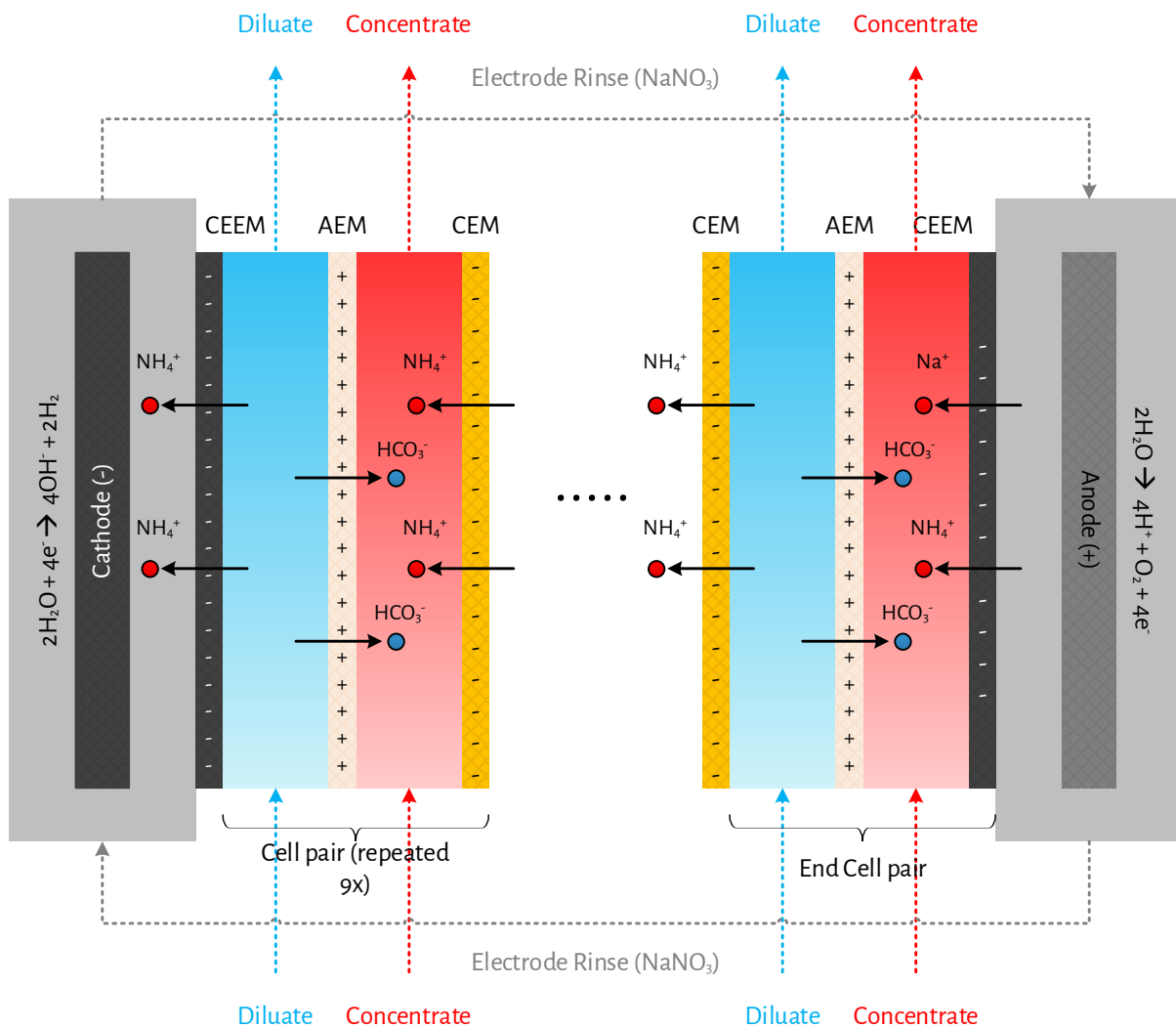


Figure 3-2 - A schematic representation of the membrane and flow channel sequence in the membrane stack, including ion transport due to the electrical current. The transport of cations at the electrodes through the CEEMs explains the accumulation of  $\text{NH}_4^+$  in the electrode rinse:  $\text{NH}_4^+$  is transported from the diluate to the electrode rinse at the cathode, while the same amount of charge transported through the CEEM at the anode is represented by both  $\text{NH}_4^+$  and  $\text{Na}^+$ .





3.2.2. Performance indicators

To assess H<sub>2</sub>O transfer, it was determined how much H<sub>2</sub>O was transported from the diluate to the concentrate. By relating the H<sub>2</sub>O transfer to the initial H<sub>2</sub>O mass, the relative H<sub>2</sub>O transfer was determined (Eq. 3-1). H<sub>2</sub>O transfer to the electrode rinse was neglected, as only one diluate and concentrate channel were in contact with the electrode chambers. Besides, extra thick CEEMs were placed next to electrode compartments to minimise H<sub>2</sub>O transfer.

$$\theta_{H_2O,t} = \frac{V_{d,i} \cdot \rho_{H_2O} - V_{d,f} \cdot \rho_{H_2O}}{V_{d,i} \cdot \rho_{H_2O}} \cdot 100\% \quad \text{Eq. 3-1}$$

Where  $\theta_{H_2O,t}$  = total H<sub>2</sub>O transfer from the diluate (unitless),  $V_{d,i}$  and  $V_{d,f}$  = initial and final diluate volume, respectively (in L) and  $\rho_{H_2O}$  = density of H<sub>2</sub>O (in g·L<sup>-1</sup>,  $\rho_{H_2O} = 995 \text{ g}\cdot\text{L}^{-1}$  at  $T = 22 \text{ }^\circ\text{C}$ ).

Water transfer in ED is caused by an ion concentration gradient (osmosis), resulting in H<sub>2</sub>O transfer from the diluate to the concentrate. In addition, H<sub>2</sub>O transfer is caused by the application of electrical current, which causes H<sub>2</sub>O transfer in the hydration shell of the transported ions from the diluate to the concentrate (electro-osmosis). The electro-osmotic H<sub>2</sub>O transfer (Eq. 3-2) was determined based on the amount of transported ions and their respective H<sub>2</sub>O transfer numbers (Strathmann, 2004a). It was assumed that for every transported mole of NH<sub>4</sub><sup>+</sup>, one mole of HCO<sub>3</sub><sup>-</sup> was transported to maintain charge balance in the diluate and concentrate flow channels. Based on the hydration numbers (amount of moles of H<sub>2</sub>O in the first hydration shell per mole of ions) determined in the studies of Brugé et al. (1999) and Leung et al. (2007), H<sub>2</sub>O transfer numbers of four and seven were used for NH<sub>4</sub><sup>+</sup> and HCO<sub>3</sub><sup>-</sup>, respectively, agreeing with the range of four to eight of Strathmann (2004a). The osmotic H<sub>2</sub>O transfer was determined based on the mass balance of H<sub>2</sub>O transfer (Eq. 3-3).

$$\theta_{H_2O,e-o} = \frac{n_{NH_4^+,d} \cdot (T_w^{NH_4^+} + T_w^{HCO_3^-}) \cdot MW_{H_2O}}{V_{d,i} \cdot \rho_{H_2O}} \cdot 100\% \quad \text{Eq. 3-2}$$

Where  $\theta_{H_2O,e-o}$  = electro-osmotic H<sub>2</sub>O transfer (unitless),  $n_{NH_4^+,d}$  = amount of transported diluate NH<sub>4</sub><sup>+</sup> (mol),  $T_w^{NH_4^+}$  and  $T_w^{HCO_3^-}$  = NH<sub>4</sub><sup>+</sup> and HCO<sub>3</sub><sup>-</sup> transfer number of H<sub>2</sub>O, respectively (unitless) and  $MW_{H_2O}$  = molecular weight of H<sub>2</sub>O (in g·mol<sup>-1</sup>,  $MW_{H_2O} = 18 \text{ g}\cdot\text{mol}^{-1}$ ).

$$\theta_{H_2O,o} = \theta_{H_2O,t} - \theta_{H_2O,e-o} \quad \text{Eq. 3-3}$$

Where  $\theta_{H_2O,o}$  = osmotic H<sub>2</sub>O transfer (unitless).

We determined the NH<sub>4</sub><sup>+</sup> current efficiency (Eq. 3-4) by the transported charge as NH<sub>4</sub><sup>+</sup>, relative to the total supplied electrical charge. Finally, the electrical energy consumption to remove and concentrate NH<sub>4</sub><sup>+</sup> (Eq. 3-5) was determined based on the mass of transported NH<sub>4</sub><sup>+</sup> from the diluate and the total used electrical energy to transport NH<sub>4</sub><sup>+</sup>.

$$\eta_{NH_4^+} = \frac{z \cdot F \cdot n_{NH_4^+,d}}{N \cdot \sum_{t=0}^t I_t \cdot \Delta t} \cdot 100\% \quad \text{Eq. 3-4}$$

Where  $\eta_{NH_4^+}$  =  $NH_4^+$  current efficiency (unitless),  $z$  = ion valence (unitless,  $z = 1$  for  $NH_4^+$ ),  $F$  = Faraday constant (in  $C \cdot mol^{-1}$ ,  $F = 96,485 C \cdot mol^{-1}$ ),  $N$  = number of cell pairs (unitless),  $I_t$  = electrical current (in A) and  $\Delta t$  = time interval (in s).

$$E = \frac{\sum_{t=0}^t U_t \cdot I_t \cdot \Delta t}{m_{NH_4^+,d}} \quad \text{Eq. 3-5}$$

Where  $E$  = electrical energy consumption (in  $MJ \cdot kg \cdot N^{-1}$ ),  $U_t$  = electrical potential (in V) and  $m_{NH_4^+,d}$  = amount of transported  $NH_4^+$  from the diluate (in  $kg \cdot N$ ).

### 3.2.3. Methods

To determine the current densities for the application of an FCD and DCD, the relationship between the diluate EC and the LCD was experimentally determined. To this end, various dilutions of the initial diluate (1, 0.9, 0.8, 0.75, 0.6, 0.5, 0.25, 0.05 and 0.01) were prepared. Subsequently, the current density was increased with steps of  $1.5 A \cdot m^{-2}$ , while the electrical current and electrical potential were logged automatically, to subsequently determine the LCD for each dilution following the method of [Cowan and Brown \(1959\)](#).

To avoid  $H_2O$  dissociation in local ion depleted zones, [Strathmann \(2004d\)](#) recommends using a safety factor ( $SF < 1$ ) for the application of LCD. A safety factor for the LCD to apply DCD was determined, representing an optimum between the operational run time and the energy consumption. To find an optimum for these quantities with different units, the operational run time (Eq. 3-6) and energy consumption (Eq. 3-7) were normalised for  $SF = 1$ . Equal weights were assigned to operational run time and energy consumption, while in practice different weights can be assigned, to determine an economical (cost-based) optimum safety factor ([Strathmann, 2004d](#)). Safety factors of 0.5, 0.75 and 1 were used to experimentally determine the safety factor that represents an optimum between the operational run time and energy consumption.

According to theory, the operational run time to transport a fixed amount of charge as ions is minimal for  $SF = 1$  and increases reciprocally for lower safety factors (see the Supporting Information of the paper of [van Linden et al. \(2019a\)](#)). The normalised operational run time as a function of the safety factor is therefore described by  $\alpha = SF^{-1} - 1$ . Contrarily, the energy consumption to transport a certain amount of charge as ions has a maximum at  $s = 1$  and decreases linearly for lower safety factors (see the Supporting Information of the paper of [van Linden et al. \(2019a\)](#)). Therefore, the normalised energy consumption as a function of the safety factor is described by  $\beta = SF$ .

$$\alpha = \frac{t_{SF} - t_{SF=1}}{t_{SF=1}} \quad \text{Eq. 3-6}$$

$$\beta = \frac{E_{SF}}{E_{SF=1}} \quad \text{Eq. 3-7}$$

Where  $\alpha$  = normalised operational run time (unitless) and  $\beta$  = normalised energy consumption (unitless).

To dynamically set the electrical current, a Python script was developed, which calculated the electrical current based on the real-time diluate EC, the used safety factor and the determined relationship between the diluate EC and the LCD. The diluate EC measurements were logged on a laptop every five seconds and subsequently, the laptop controlled the power supply automatically to apply the electrical current. Electrical current and electrical potential data were logged every five seconds on the laptop. The data of the concentrate EC was stored on a multimeter and the pH of all solutions was manually measured before and after each run. For the three chosen safety factors, duplicate runs with fresh solutions were conducted, in which the diluate EC was always decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$ .

Finally, sequencing batch experiments (SBEs) were conducted in duplicate, to assess the  $\text{H}_2\text{O}$  transfer and  $\text{NH}_4^+$  current efficiency and study the effect of the current density (an FCD and DCD) on the concentration factor and the energy consumption. For the first batch, fresh diluate, concentrate and electrode rinse solutions were used and the  $\text{NH}_4^+$  concentrations and volumes of all solutions were measured. After that, the diluate EC was again decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$  and the  $\text{NH}_4^+$  concentration and volume of all solutions were measured to make  $\text{H}_2\text{O}$  and  $\text{NH}_4^+$  balances. For the subsequent nine batches, the diluate was replaced for a fresh diluate solution, and the concentrate and electrode rinse solutions of the previous batch were reused. The electrical current during the DCD SBE was again applied using the automated control based on the Python script.

### 3.3. Results

#### 3.3.1. Determination of current densities

We found a linear ( $R^2 = 0.92$ ) relationship between the diluate EC and the LCD at a cross-flow velocity of  $2 \text{ cm}\cdot\text{s}^{-1}$  (Figure 3-3A), which was used to determine the current densities for the application of an FCD and DCD in the SBEs. Subsequently, an optimum between the operational run time and the energy consumption was determined by using a safety factor of 0.5, 0.75 and 1 for the LCD. Figure 3-3B depicts the experimentally determined  $\alpha$  and  $\beta$  as a function of the safety factor. The experimentally determined  $\alpha$  had a minimum at  $\text{SF} = 1$  and increased for lower safety factors. On the contrary, the experimentally determined  $\beta$  had a maximum at  $\text{SF} = 1$  and decreased for lower safety factors. By means of fitting trend lines for the experimentally determined  $\alpha$  and  $\beta$ , an optimum for the safety factor at 0.62 was found.

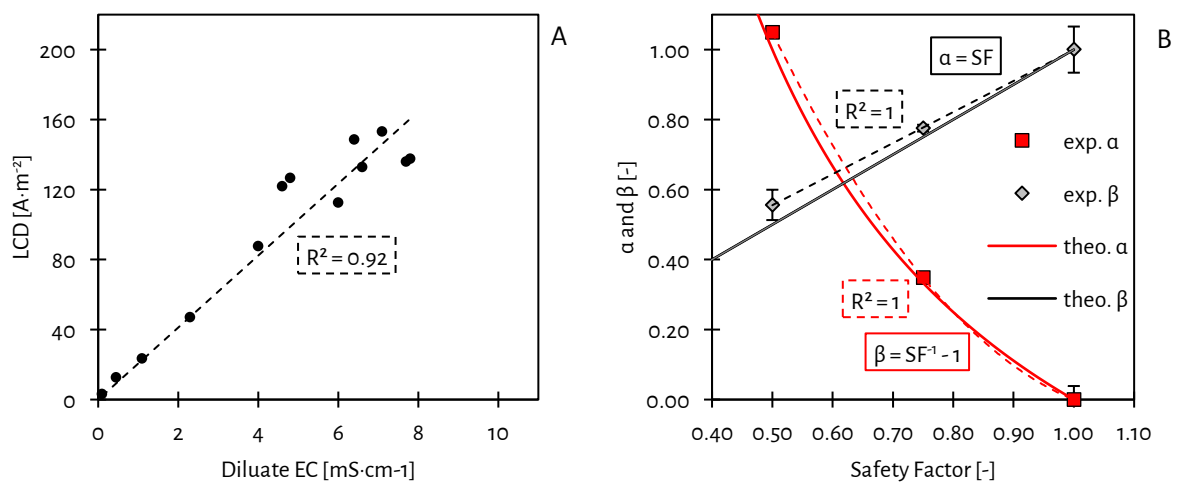


Figure 3-3 - The linear relationship between the diluate EC and the LCD (A). The theoretical (solid lines) and experimental (data points with error bars, representing the averages  $\pm$  minimum and maximum values for duplicate experiments, dashed lines representing the trend lines)  $\alpha$  and  $\beta$  as a function of the safety factor for the LCD (B). An optimum was found at a safety factor of 0.62, representing an optimum between the operational run time and energy consumption.

#### 3.3.2. SBE at an FCD

For the FCD SBE, a current density of  $16 \text{ A}\cdot\text{m}^{-2}$  was applied, based on the LCD of the final diluate EC ( $1 \text{ mS}\cdot\text{cm}^{-1}$ ) and a safety factor of 0.62. Figure 3-4A presents the diluate and concentrate EC over the cumulative amount of consumed energy during the FCD SBE. The operational run time to decrease the diluate EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$  increased by 58% over the number of batches, from 158 minutes for the first batch to 250 minutes for the tenth batch. Because the concentrate was recirculated during the SBE, the concentrate EC increased but reached a plateau at  $32 \text{ mS}\cdot\text{cm}^{-1}$ .

From the  $\text{NH}_4^+$  concentrations during the FCD SBE experiment (Figure 3-4B), it follows that  $91 \pm 1\%$  (AVG  $\pm$  STD) of the  $\text{NH}_4^+$  from the diluate was removed for all batches. The  $\text{NH}_4^+$  concentration in the concentrate reached a plateau at  $6.8 \text{ g}\cdot\text{L}^{-1}$ , corresponding to a concentration factor of 4.5. The difference in concentration

factor between the replicate FCD SBEs was  $< 5\%$ . The increase in  $\text{NH}_4^+$  concentration of the concentrate resulted in an increase in the  $\text{NH}_4^+$  concentration gradient between the diluate and concentrate over the number of batches. The  $\text{NH}_4^+$  concentration gradient was  $2.4 \text{ g}\cdot\text{L}^{-1}$  for the first batch, and increased to  $6.6 \text{ g}\cdot\text{L}^{-1}$  for the tenth batch. In addition to the diluate and concentrate  $\text{NH}_4^+$  concentrations, Figure 3-4B also presents the  $\text{NH}_4^+$  concentration in the electrode rinse, showing that  $21 \pm 3\%$  of the  $\text{NH}_4^+$  transported from each diluate batch was transported to and accumulated in the electrode rinse.

The electrical energy consumption increased for each sequencing batch, from  $3.6 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  for the first batch to  $6.1 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  for the tenth batch.

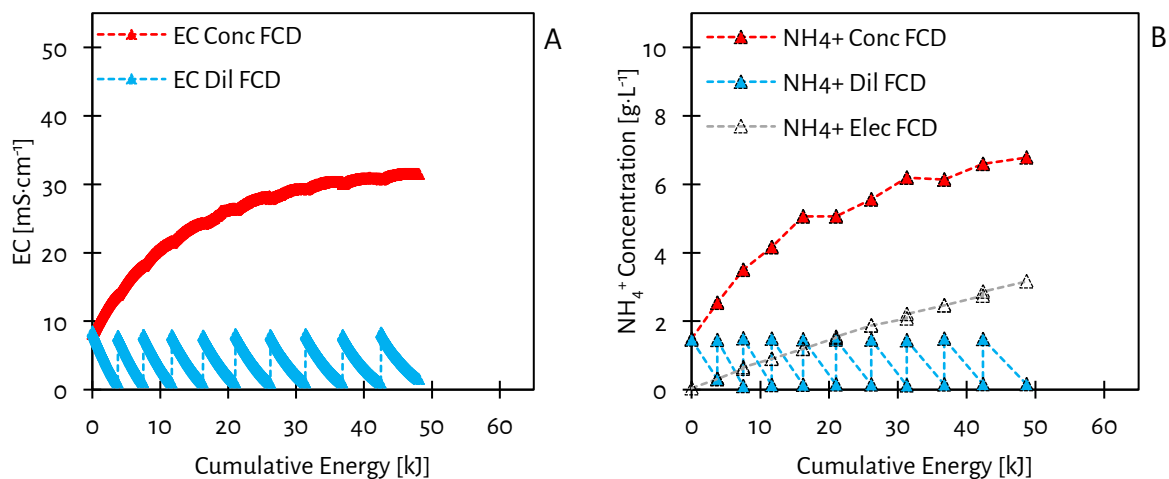


Figure 3-4 - The evolution of the EC (A) and  $\text{NH}_4^+$  concentration (B) over the cumulative spent energy during the FCD SBE. The diluate EC was decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$  for every sequencing batch, corresponding to 91% (on average) removal of  $\text{NH}_4^+$  from the diluate. The concentrate reached a plateau at  $32 \text{ mS}\cdot\text{cm}^{-1}$ , corresponding to an  $\text{NH}_4^+$  concentration of  $6.6 \text{ g}\cdot\text{L}^{-1}$  and a concentration factor of 4.5. Besides transport of  $\text{NH}_4^+$  from the diluate to the concentrate, 21% (on average) of the  $\text{NH}_4^+$  was transported to and accumulated in the electrode rinse.

### 3.3.3. SBE at DCD

For the DCD SBE, a safety factor of 0.62 was used for the LCD as current density. Figure 3-5A presents the diluate and concentrate EC over the cumulative amount of consumed energy during the DCD SBE. Similar to the FCD SBE, the operational run time increased over the number of batches. However, the operational run time increased only by 29%, from 49 min for the first batch to 63 min for the tenth batch. The application of DCD resulted in a reduction of 69 - 75% of the operational run time, with respect to the application of an FCD, which can be translated to a decrease in the required membrane area. In addition, the concentrate EC did not reach a plateau and reached  $40 \text{ mS}\cdot\text{cm}^{-1}$  after ten batches.

During the DCD SBE,  $90 \pm 1\%$  of the  $\text{NH}_4^+$  from the diluate was removed for each sequencing batch, as follows from Figure 3-5B. However, in contrast to the FCD SBE, the concentration of  $\text{NH}_4^+$  in the concentrate did not reach a plateau, but increased linearly to  $10 \text{ g}\cdot\text{L}^{-1}$  after ten batches, corresponding to a concentration factor of 6.7. The difference in concentration factor between the replicate DCD SBEs was negligible:  $< 1\%$ . The  $\text{NH}_4^+$

concentration gradient increased from  $2.4 \text{ g}\cdot\text{L}^{-1}$  for the first batch to  $9.8 \text{ g}\cdot\text{L}^{-1}$  for the final batch. Similar to the FCD SBE,  $24 \pm 7\%$  of  $\text{NH}_4^+$  that was transported from the diluate accumulated in the electrode rinse during the DCD SBE.

In contrast to the increasing electrical energy consumption during the FCD SBE, the electrical energy consumption during the DCD SBE remained stable at  $5.4 \pm 0.4 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . The electrical energy consumption of the tenth batch was lower for the application of DCD ( $5.9 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ) than for the application of an FCD ( $6.1 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ), while the  $\text{NH}_4^+$  concentration gradient was actually higher for the application of DCD ( $6.6 \text{ g}\cdot\text{L}^{-1}$ ) than an FCD ( $9.8 \text{ g}\cdot\text{L}^{-1}$ ).

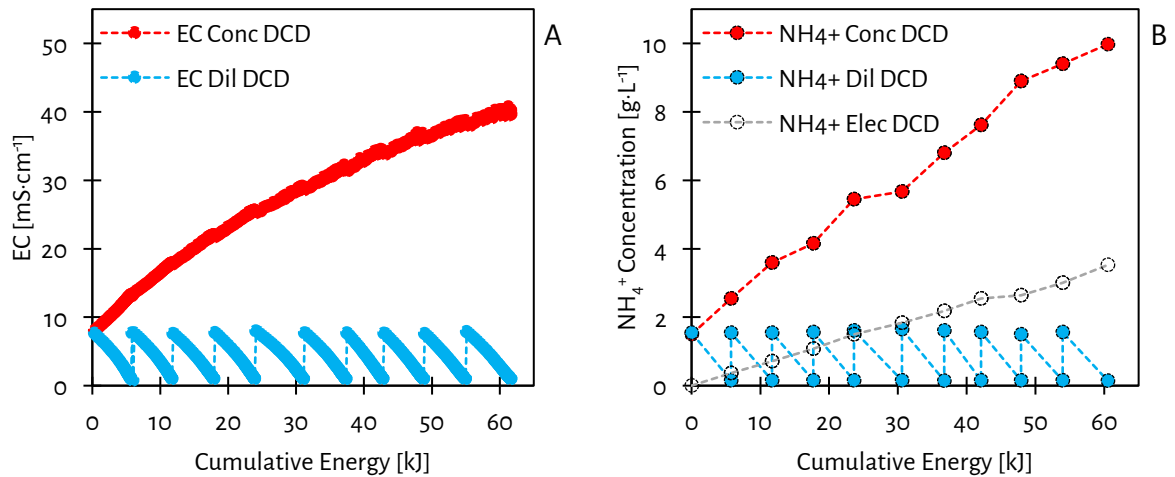


Figure 3-5 - The evolution of the EC (A) and  $\text{NH}_4^+$  concentration (B) over the cumulative spent energy during the DCD SBE. The diluate EC was again decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$  for every sequencing batch, corresponding to 90% (on average) removal of  $\text{NH}_4^+$  from the diluate. The EC and  $\text{NH}_4^+$  concentration in the concentrate did not reach a plateau, but increased to  $40 \text{ mS}\cdot\text{cm}^{-1}$  and  $10 \text{ g}\cdot\text{L}^{-1}$  (concentration factor = 6.7), respectively.

For the DCD SBE, 24% (on average) of the  $\text{NH}_4^+$  accumulated in the electrode rinse.

3.4. Discussion3.4.1. Determination of current densities

The found linear relationship between the diluate EC and the LCD corresponds with [Strathmann \(2004c\)](#), who reported that the LCD is linearly related to the diluate ion concentration for a specific flow channel geometry and cross-flow velocity.

In addition, an optimum between the operational run time and the energy consumption was experimentally found at a safety factor of 0.62. Figure 3-5B also presents the theoretical  $\alpha$  and  $\beta$ . Similar to the experimentally determined  $\alpha$  and  $\beta$ , a theoretical optimum was found at a safety factor of 0.62, by equating the theoretical expressions for  $\alpha$  and  $\beta$ .

3.4.2. SBE at an FCD

The plateau of the  $\text{NH}_4^+$  concentration in the concentrate, and thus the limitation of the concentration factor, was caused by  $\text{H}_2\text{O}$  transfer from the diluate to the concentrate. Figure 3-6A shows how much  $\text{H}_2\text{O}$  was transported during each batch by electro-osmosis and osmosis, as a function of the  $\text{NH}_4^+$  concentration gradient. For the FCD SBE, osmosis was the dominant mechanism of  $\text{H}_2\text{O}$  transfer. The electro-osmotic  $\text{H}_2\text{O}$  transfer remained constant at 1.5% of the diluate throughout the SBE, because always the same amount of  $\text{NH}_4^+$  was removed from the diluate ( $1.34 \pm 0.02 \text{ g}$ ). The removal of  $\text{NH}_4^+$  was constant because the diluate EC of the fresh solutions was always decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$ . The osmotic  $\text{H}_2\text{O}$  transfer increased from 2.5% at an  $\text{NH}_4^+$  concentration gradient of  $2.4 \text{ g}\cdot\text{L}^{-1}$  to 10.5% at an  $\text{NH}_4^+$  concentration gradient of  $6.6 \text{ g}\cdot\text{L}^{-1}$ . The increase in osmotic  $\text{H}_2\text{O}$  transfer was caused by two factors: as the  $\text{NH}_4^+$  concentration gradient increased, the driving force for osmosis was higher and as the operational run time increased, more time was available to allow osmosis to take place.

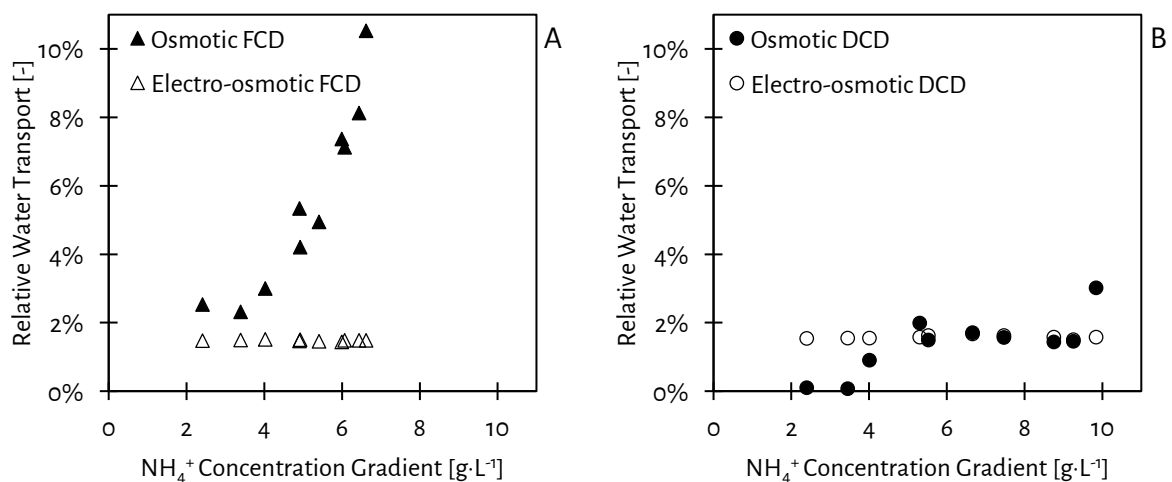


Figure 3-6 - The  $\text{H}_2\text{O}$  transfer during the FCD SBE (A) and the DCD SBE (B). During both SBEs, the electro-osmotic  $\text{H}_2\text{O}$  transfer was stable at 1.5–1.6% and the osmotic  $\text{H}_2\text{O}$  transfer for both SBEs increased over the  $\text{NH}_4^+$  concentration gradient as both the driving force for osmosis and the operational run time increased.



$\text{NH}_4^+$  accumulation in the electrode rinse was caused by transport of  $\text{NH}_4^+$  from the diluate through a cation exchange (end) membrane, ending up in the electrode rinse at the cathode side of the membrane stack. At the anode side of the membrane stack, an equivalent amount of charge migrated as cations from the electrode rinse to the concentrate. However, because the electrode rinse consisted of 1 M  $\text{NaNO}_3$ , the transported charge not only consisted of  $\text{NH}_4^+$ , but also of  $\text{Na}^+$ . This phenomenon is schematically presented in Figure 3-2. By taking into account the accumulated  $\text{NH}_4^+$  in the electrode rinse solution, the  $\text{NH}_4^+$  mass balances fitted within 5%, while previous researchers assigned a 17 - 28%  $\text{NH}_4^+$  loss to volatilisation of ammonia ( $\text{NH}_3$ ) from the diluate, concentrate and electrode rinse (Mondor et al., 2008b; Ward et al., 2018). Figure 3-7A presents the  $\text{NH}_4^+$  current efficiency over the  $\text{NH}_4^+$  concentration gradient during the FCD SBE. The  $\text{NH}_4^+$  current efficiency was 76% at an  $\text{NH}_4^+$  concentration gradient of  $2.4 \text{ g}\cdot\text{L}^{-1}$  and decreased to 48% at an  $\text{NH}_4^+$  concentration gradient of  $6.6 \text{ g}\cdot\text{L}^{-1}$ . In general, current efficiency in ED is mainly affected by  $\text{H}_2\text{O}$  dissociation at current densities higher than the LCD, the transport of other ions than the target ion and back-diffusion (Strathmann, 2004b; Pronk et al., 2006a). Because during the FCD SBE, the LCD was never exceeded due to the application of the safety factor, the effect of  $\text{H}_2\text{O}$  dissociation on the  $\text{NH}_4^+$  current efficiency was negligible. Besides, the pH ranged between 7.8 – 8.8 throughout the entire SBE. At  $\text{pH} = 7.8$ ,  $\text{H}^+$  represented only  $1.5\cdot 10^{-3} \text{ C}$ , while  $\text{NH}_4^+$  in the initial diluate represented approximately 7,500 C. In addition,  $\text{Na}^+$  is transported from the electrode rinse solution to the concentrate and is therefore assumed not to be relevant for the assessment of the  $\text{NH}_4^+$  current efficiency. Therefore, also the effect of the transport of other cations such as  $\text{H}^+$  and  $\text{Na}^+$  on the  $\text{NH}_4^+$  current efficiency was negligible. According to Rottiers et al. (2014), the ion concentration gradient and back-diffusion are linearly related. Because during the FCD SBE the  $\text{NH}_4^+$  current efficiency decreased over the increasing  $\text{NH}_4^+$  concentration gradient, the decrease in the  $\text{NH}_4^+$  current efficiency is assigned to back-diffusion, also in line with Pronk et al. (2006a). During the FCD SBE, the  $\text{NH}_4^+$  concentration gradient increased, resulting in a higher driving force for back-diffusion for each sequencing batch. Because back-diffusion took place from the concentrate to the diluate,  $\text{NH}_4^+$  needed to be transported back and forth to decrease the diluate EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$ , resulting in an increase in the operational run time. The transport of back-diffused  $\text{NH}_4^+$  was at the expense of more supplied electrical charge, which led to a decrease in the  $\text{NH}_4^+$  current efficiency. Because for each batch more back-diffusion took place over the number of batches, more electrical energy was required to transport  $\text{NH}_4^+$  to decrease the diluate EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$ . The electrical energy consumption increased from  $3.6 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  to  $6.1 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  when the  $\text{NH}_4^+$  concentration gradient increased from  $2.4 \text{ g}\cdot\text{L}^{-1}$  to  $6.6 \text{ g}\cdot\text{L}^{-1}$ , as presented in Figure 3-7B.

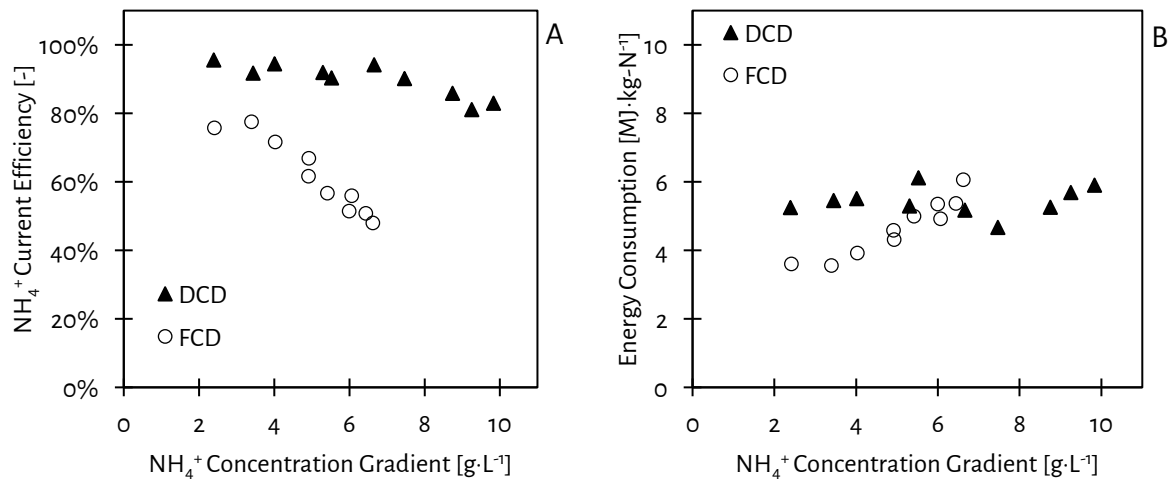


Figure 3-7 - The  $\text{NH}_4^+$  current efficiency (A) and the electrical energy consumption (B) over the  $\text{NH}_4^+$  concentration gradient during the SBEs. The  $\text{NH}_4^+$  current efficiency decreased during both SBEs, but the  $\text{NH}_4^+$  current efficiency during the DCD SBE was always higher than during the FCD SBE. The electrical energy consumption during the FCD SBE increased because the driving force for back-diffusion and the operational run time increased, while on the other, the electrical energy consumption during the DCD SBE remained stable at  $5.4 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .

#### 3.4.3. SBE at DCD

Figure 3-6B depicts the  $\text{H}_2\text{O}$  transfer during the DCD SBE. For the first nine batches, electro-osmosis was dominant and only for the last batch osmosis was the dominant  $\text{H}_2\text{O}$  transfer mechanism. The electro-osmotic  $\text{H}_2\text{O}$  transfer of 1.6% was constant during the DCD SBE and was similar to the electro-osmotic  $\text{H}_2\text{O}$  transfer during the FCD SBE (1.5%). The osmotic  $\text{H}_2\text{O}$  transfer was only 0.1% at an  $\text{NH}_4^+$  concentration gradient of  $2.4 \text{ g}\cdot\text{L}^{-1}$  and increased to 3% at an  $\text{NH}_4^+$  concentration gradient of  $9.8 \text{ g}\cdot\text{L}^{-1}$ . Since the osmotic driving force was higher during the DCD SBE than during FCD SBE, the decrease in osmotic  $\text{H}_2\text{O}$  transfer is caused by the decreased operational run time, due to the application of DCD. Results indicate that due to the decrease in the operational run time by means of the application of DCD, less osmosis took place, resulting in a higher concentration factor, with respect to an FCD.

Figure 3-7A presents the  $\text{NH}_4^+$  current efficiency over the  $\text{NH}_4^+$  concentration gradient for the DCD SBE. If  $\text{Na}^+$  from the electrolyte ended up in the diluate and was transported to the concentrate, it would account for a 24% loss in the  $\text{NH}_4^+$  current efficiency. However, the  $\text{NH}_4^+$  current efficiency for the first batch was 96% at an  $\text{NH}_4^+$  concentration gradient of  $2.4 \text{ g}\cdot\text{L}^{-1}$ . This high  $\text{NH}_4^+$  current efficiency supports the claim that the  $\text{NH}_4^+$  current efficiency was not affected by the transport of other ions than  $\text{NH}_4^+$ , such as  $\text{H}^+$  and  $\text{Na}^+$ . Throughout the SBE, the  $\text{NH}_4^+$  current efficiency decreased to 83% in the tenth batch at an  $\text{NH}_4^+$  concentration gradient of  $9.8 \text{ g}\cdot\text{L}^{-1}$ . Similar to the FCD SBE, more back-diffusion took place due to the increase in  $\text{NH}_4^+$  concentration gradient and the increase in operational run time. However, the effect of back-diffusion on the  $\text{NH}_4^+$  current efficiency only caused a decrease in  $\text{NH}_4^+$  current efficiency of 13% during the DCD SBE, in comparison to a decrease in  $\text{NH}_4^+$  current efficiency of 28% during the FCD SBE. Since the  $\text{NH}_4^+$  concentration gradient was

even higher for the DCD SBE than for the FCD SBE, the higher current efficiencies and the lower decrease in  $\text{NH}_4^+$  current efficiency are assigned to the decreased operational run times during the DCD SBE. Apparently, decreasing the operational run time by the application of DCD, results in less back-diffusion compared to an FCD, leading to a higher  $\text{NH}_4^+$  current efficiency.

The increase in operational run time and  $\text{NH}_4^+$  concentration gradient did not affect the electrical energy consumption for the application of DCD ( $5.4 \pm 0.4 \text{ MJ} \cdot \text{kg}^{-1} \cdot \text{N}^{-1}$ ), in contrast to an FCD. The increase in electrical energy consumption due to back-diffusion was countered by the decrease of the electrical resistance, because the EC of the concentrate increased.

### 3.5. Conclusions

The experimental work to optimise the operation of ED in terms of concentration factor and energy consumption while achieving 90%  $\text{NH}_4^+$  removal resulted in the following conclusions:

- Concentrating  $\text{NH}_4^+$  by ED resulted in an  $\text{NH}_4^+$  concentration gradient between the diluate and the concentrate stream. The increasing gradient subsequently resulted in increased mass transfer by osmosis and back-diffusion;
- The increased back-diffusion of  $\text{NH}_4^+$  decreased the  $\text{NH}_4^+$  current efficiency from 76% to 48% when applying an FCD and the electrical energy consumption for the removal of 90%  $\text{NH}_4^+$  increased from  $3.6 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  to  $6.1 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ;
- When a DCD was applied, the operational run time for removing 90%  $\text{NH}_4^+$  decreased by 75%, which can be translated to a decrease in the required membrane area;
- The application of DCD resulted in a decrease in osmotic  $\text{H}_2\text{O}$  transfer, compared to an FCD, leading to an increased concentration factor of 6.7;
- When applying a DCD, the  $\text{NH}_4^+$  current efficiency decreased over the  $\text{NH}_4^+$  concentration gradient from 96% to 83% and eventually 90%  $\text{NH}_4^+$  was removed at the expense of a stable electrical energy consumption of  $5.4 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ;
- The results show that the application of DCD allows for a lower operational run time, a higher concentration factor and a lower electrical energy consumption to concentrate  $\text{NH}_4^+$  by ED, compared to an FCD.

3.6. References

- Brugé, F., Bernasconi, M., & Parrinello, M. (1999). Ab Initio Simulation of Rotational Dynamics of Solvated Ammonium Ion in Water. *Journal of the American Chemical Society*, *121*(47), 10883-10888. doi:10.1021/ja990520y
- Cowan, D. A., & Brown, J. H. (1959). Effect of Turbulence on Limiting Current in Electrodialysis Cells. *Industrial & Engineering Chemistry*, *51*(12), 1445-1448. doi:10.1021/ie50600a026
- Ippersiel, D., Mondor, M., Lamarche, F., Tremblay, F., Dubreuil, J., & Masse, L. (2012). Nitrogen potential recovery and concentration of ammonia from swine manure using electrodialysis coupled with air stripping. *Journal of Environmental Management*, *95*, S165-S169. doi:<http://dx.doi.org/10.1016/j.jenvman.2011.05.026>
- Leung, K., Nielsen, I. M. B., & Kurtz, I. (2007). Ab Initio Molecular Dynamics Study of Carbon Dioxide and Bicarbonate Hydration and the Nucleophilic Attack of Hydroxide on CO<sub>2</sub>. *The Journal of Physical Chemistry B*, *111*(17), 4453-4459. doi:10.1021/jp068475l
- Mondor, M., Masse, L., Ippersiel, D., Lamarche, F., & Massé, D. I. (2008b). Use of electrodialysis and reverse osmosis for the recovery and concentration of ammonia from swine manure. *Bioresource Technology*, *99*(15), 7363-7368. doi:<http://dx.doi.org/10.1016/j.biortech.2006.12.039>
- PCA. (2016b). PCA Ion Exchange Membranes: Technical Data Sheet. Retrieved from <https://www.pca-gmbh.com/publi/PCAMembranes.pdf>
- Pronk, W., Biebow, M., & Boller, M. (2006a). Electrodialysis for Recovering Salts from a Urine Solution Containing Micropollutants. *Environmental Science & Technology*, *40*(7), 2414-2420. doi:10.1021/es051921i
- Rottiers, T., Ghyselbrecht, K., Meesschaert, B., Van der Bruggen, B., & Pinoy, L. (2014). Influence of the type of anion membrane on solvent flux and back diffusion in electrodialysis of concentrated NaCl solutions. *Chemical Engineering Science*, *113*, 95-100. doi:<https://doi.org/10.1016/j.ces.2014.04.008>
- Strathmann, H. (2004a). Chapter 2 - Electrochemical and Thermodynamic Fundamentals. In *Ion-Exchange Membrane Separation Processes* (9 ed., pp. 23-88): Elsevier.
- Strathmann, H. (2004b). Chapter 3 - Preparation and Characterization of Ion-Exchange Membranes. In *Ion-Exchange Membrane Separation Processes* (9 ed., pp. 89-146): Elsevier.
- Strathmann, H. (2004c). Chapter 4 - Operating Principle of Electrodialysis and Related Processes. In *Ion-Exchange Membrane Separation Processes* (9 ed., pp. 147-225): Elsevier.
- Strathmann, H. (2004d). Chapter 5 - Ion-Exchange Membrane Process and Equipment Design. In *Ion-Exchange Membrane Separation Processes* (9 ed., pp. 227-286): Elsevier.
- Strathmann, H. (2010). Electrodialysis, a mature technology with a multitude of new applications. *Desalination*, *264*(3), 268-288. doi:<https://doi.org/10.1016/j.desal.2010.04.069>

- van Linden, N., Spanjers, H., & van Lier, J. B. (2019a). Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electrodialysis. *Water Research*, 114856. doi:<https://doi.org/10.1016/j.watres.2019.114856>
- Wang, X., Zhang, X., Wang, Y., Du, Y., Feng, H., & Xu, T. (2015). Simultaneous recovery of ammonium and phosphorus via the integration of electrodialysis with struvite reactor. *Journal of Membrane Science*, 490, 65-71. doi:<https://doi.org/10.1016/j.memsci.2015.04.034>
- Ward, A. J., Arola, K., Thompson Brewster, E., Mehta, C. M., & Batstone, D. J. (2018). Nutrient recovery from wastewater through pilot scale electrodialysis. *Water Research*, 135, 57-65. doi:<https://doi.org/10.1016/j.watres.2018.02.021>



## Chapter 4.

# Bipolar membrane electro dialysis for ammonium removal and producing concentrated dissolved ammonia solutions

Based on: Bipolar membrane electro dialysis for energetically competitive ammonium removal and dissolved ammonia production

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Abstract

Bipolar membrane electro dialysis (BPMED) can be used to convert salt solutions to acid and base solutions without the use of chemicals. This chapter focuses on the application of BPMED to remove total ammoniacal nitrogen (TAN) from water and to simultaneously produce concentrated dissolved  $\text{NH}_3$  solutions. The current efficiency and electrical energy consumption to transport ammonium ( $\text{NH}_4^+$ ) from the diluate (the feed water) were assessed throughout sequencing batch experiments.

The  $\text{NH}_4^+$  removal efficiency for BPMED ranged between 85 and 91% and the electrical energy consumption was stable at  $19 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , taking both electrochemical and pumping energy into account. The base pH increased from 7.8 to 9.8 and the TAN concentration increased from  $1.5$  to  $7.3 \text{ g}\cdot\text{L}^{-1}$ , corresponding to a final  $\text{NH}_3$  concentration of  $4.5 \text{ g}\cdot\text{L}^{-1}$  in the base. Only 48% of the TAN transported from the diluate ended up in the base as  $\text{NH}_3$  due to accumulation of TAN in the electrode rinse and diffusion of  $\text{NH}_3$  from the base to the acid and back to the dilute. Furthermore, leakage of hydroxide ( $\text{OH}^-$ ) and diffusion of dissolved  $\text{NH}_3$  and ions (such as  $\text{NH}_4^+$  and bicarbonate ( $\text{HCO}_3^-$ )) from the base to the diluate all contributed to a loss in  $\text{NH}_4^+$  current efficiency. Due to the increase in operational run time and concentration gradients throughout the sequencing batch experiments, the  $\text{NH}_4^+$  current efficiency decreased from 69 to 54%.

BPMED proved to be able to simultaneously remove TAN from water and produce concentrated dissolved  $\text{NH}_3$  while avoiding the use of chemicals. The energy consumption was competitive with that of the combination of electro dialysis and the addition of chemicals ( $22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ).

Keywords

water treatment; ammonia recovery; water dissociation; current efficiency; energy consumption;



#### 4.1. Introduction

Chapter 1 of this thesis identifies bipolar membrane electro dialysis (BPMED) as a suitable technology to produce concentrated  $\text{NH}_3$  solutions. Subsequently, a literature review presented in Chapter 2 of this thesis confirms that BPMED is a suitable technology for the production of  $\text{NH}_3$  solutions, but that there is a lack of information on the fate of TAN during the operation and on the energy consumption to achieve  $\text{NH}_4^+$  removal and produce  $\text{NH}_3$  solutions.

##### 4.1.1. Chemical addition to convert $\text{NH}_4^+$ to dissolved $\text{NH}_3$

The amount of added chemicals to increase the solution pH at standard temperature and pressure conditions ( $T = 25\text{ }^\circ\text{C}$  and  $p = 101,325\text{ Pa}$ ) to a certain value depends on the buffer capacity and the ionic strength of the solution. Various nitrogen-loaded (N-loaded) residual waters, such as urine, reject water and industrial condensates contain buffering anions, such as bicarbonate ( $\text{HCO}_3^-$ ). Figure 4-1A depicts the effect of the buffer capacity on the required addition of sodium hydroxide ( $\text{NaOH}$ ) to increase the solution pH from 7.8 to 10 for solutions with various TAN concentrations. Because  $\text{HCO}_3^-$  reacts with hydroxide ( $\text{OH}^-$ ) to form carbonate ( $\text{CO}_3^{2-}$ ), less  $\text{OH}^-$  is available to effectively increase the pH. Therefore, double the amount of  $\text{NaOH}$  is required to increase the pH in buffered solutions ( $\text{NH}_4\text{HCO}_3$ ), compared to non-buffered solutions ( $\text{NH}_4\text{Cl}$ ). Besides, the ammoniacal nitrogen equilibrium pH ( $\text{pK}_a$ ) increases when the ionic strength of the solution increases. Figure 4-1B shows the distribution of  $\text{NH}_4^+$  and  $\text{NH}_3$  at standard conditions as a function of the pH for solutions with various TAN (as  $\text{NH}_4\text{HCO}_3$ ) concentrations. The  $\text{pK}_a$  for a solution with a TAN concentration of  $1.5\text{ g}\cdot\text{L}^{-1}$  is 9.4, while for  $10\text{ g}\cdot\text{L}^{-1}$  the  $\text{pK}_a$  is 9.6, meaning that the pH must be further increased for solutions with TAN concentrations of  $1.5\text{ g}\cdot\text{L}^{-1}$  to have the same amount of  $\text{NH}_4^+$  and  $\text{NH}_3$ , compared to solutions with TAN concentrations of  $10\text{ g}\cdot\text{L}^{-1}$ .

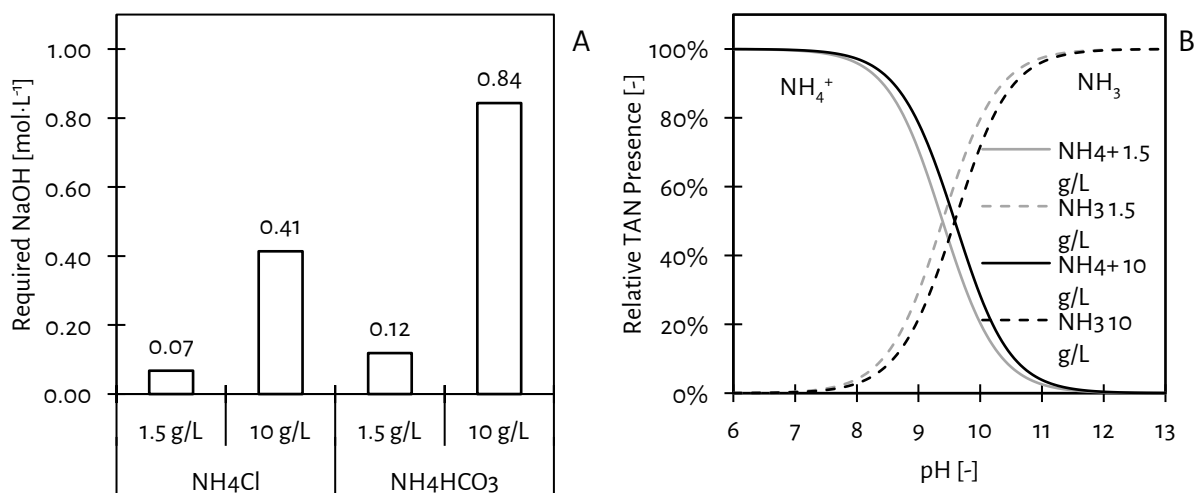


Figure 4-1 - The required  $\text{NaOH}$  addition to increase the pH from 7.8 to 10 for solutions containing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{HCO}_3$  (A). The ammoniacal nitrogen equilibrium pH shifts for TAN concentrations of 1.5 and  $10\text{ g}\cdot\text{L}^{-1}$  (as  $\text{NH}_4\text{HCO}_3$ ) from 9.4 to 9.6, respectively, as a result of an increase in ionic strength (B). Both graphs are derived from PHREEQC software simulations using the phreeqc.dat database.

#### 4.1.2. Bipolar membrane electro dialysis for $\text{NH}_4^+$ removal from N-loaded residual waters

To avoid the addition of chemicals, bipolar membrane electro dialysis (BPMED) can be used to change the solution pH in situ by only using electrical energy (Mani, 1991; Tongwen, 2002). BPMED can be used to remove ions from a feed stream (the diluate) and simultaneously concentrate cations in a base stream (the base) and anions in an acid stream (the acid). The cations in the base are combined with hydroxide ions ( $\text{OH}^-$ ), while the anions are combined with protons ( $\text{H}^+$ ), which are produced in the bipolar membranes by dissociating water when an electric current is applied.

Previous studies showed that BPMED can be applied for the treatment of N-loaded residual waters containing TAN mainly as  $\text{NH}_4^+$ . Various studies assessed the application of BPMED to produce dissolved  $\text{NH}_3$  and acids such as HCl and  $\text{HNO}_3$  from industrial N-loaded residual waters containing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{NO}_3$ , respectively (Graillon et al., 1996; Ali et al., 2004; Li et al., 2016; Lv et al., 2018). In addition, Pronk et al. (2006d) and Shi et al. (2018) used BPMED for the recovery of nitrogen and phosphorus from source-separated urine and pig manure hydrolysate, respectively. Finally, Shuangchen et al. (2015) applied BPMED to recover  $\text{CO}_2$  from spent  $\text{NH}_3$ -based carbon capture solutions ( $\text{NH}_4\text{HCO}_3$ ).

#### 4.1.3. Problem description

In previous research, the efficiency of BPMED to use supplied electric charge (current efficiency) to produce acid and base was mainly limited by leakage of  $\text{H}^+$ , while also diffusion of  $\text{NH}_3$  and leakage of  $\text{OH}^-$  through the (imperfect) membranes comprised the current efficiency (Graillon et al., 1996; Ali et al., 2004). However, these studies were conducted with high concentrations of  $\text{NH}_4^+$  in the diluate (ranging 2 - 4  $\text{mol}\cdot\text{L}^{-1}$   $\text{NH}_4^+$ ), at high current densities (ranging 480 – 900  $\text{A}\cdot\text{m}^{-2}$ ) and in the absence of buffering anions, such as  $\text{HCO}_3^-$  (Ali et al., 2004; Li et al., 2016; Lv et al., 2018). These feed water compositions and operational conditions are not representative for the application of BPMED on N-loaded residual waters such as (sludge) reject water and industrial condensates, which have a typical  $\text{NH}_4^+$  concentration ranging from 0.5 to 2.5  $\text{g}\cdot\text{L}^{-1}$  (Gonzalez-Martinez et al., 2018). Besides, the previously conducted studies merely focused on the current efficiency of acid and base production, rather than on the current efficiency to transport  $\text{NH}_4^+$  ( $\text{NH}_4^+$  current efficiency) from the diluate (Ali et al., 2004; Shuangchen et al., 2015; Li et al., 2016). Finally, there are no studies available that assess the energy consumption to remove  $\text{NH}_4^+$  from water by BPMED.

#### 4.1.4. Research objective

This chapter presents the assessment of the current efficiency and energy consumption to remove TAN from feed water by BPMED, while simultaneously producing concentrated dissolved  $\text{NH}_3$ . This chapter focuses on the fate and concentrations of TAN throughout BPMED operation and the processes affecting the  $\text{NH}_4^+$  current efficiency and energy consumption. Furthermore, the energy consumption of BPMED and of ED in combination with the addition of chemicals to remove TAN from water and produce concentrated dissolved  $\text{NH}_3$  were compared.

## 4.2. Materials and methods

### 4.2.1. Materials

We used a bench-scale PC-Cell 64004 ED cell, consisting of a Pt/Ir-MMO coated and Ti-stretched metal anode and a stainless-steel cathode, both with a surface area of  $8 \times 8 \text{ cm}^2$ . The cell contained a BPMED membrane stack consisting of ten cell triplets. Each cell triplet consisted of a cation exchange membrane (CEM), an anion exchange membrane (AEM) and a bipolar membrane (BPM), as depicted in Figure 4-2. Two PCA SC cation exchange end membranes (CEEM) were placed next to the electrodes, similar to the studies conducted by [Graillon et al. \(1996\)](#) and [Pronk et al. \(2006d\)](#) on BPMED and similar to the study of [Ward et al. \(2018\)](#) and the study of [van Linden et al. \(2019a\)](#) on  $\text{NH}_4^+$  removal by ED. The rest of the BPMED membrane stack consisted of ten PCA Acid-60 AEMs, nine PCA SK CEMs and ten PCA BPMs. Specific membrane characteristics can be found through the supplier ([PCA, 2016a](#)). The membranes and electrodes were separated by 0.5 mm thick wire mesh spacers made from silicon/polyethylene sulfone to form diluate, acid and base (flow) cells and electrode rinse compartments.

The electric current was applied by a Tenma 72-2535 power supply, having an electric current and potential range of 0.001 – 3.000 A and 0.01 – 30.00 V, respectively.

The diluate, acid, base and electrode rinse solutions were stored in 1 L borosilicate bottles and were continuously mixed by magnetic stirrers on a mixing plate. The solutions were recirculated through the BPMED membrane stack by a calibrated peristaltic Watson-Marlow 520S pump with separate Watson-Marlow 313 pump heads for each solution. The pump was set at a flow rate of  $19 \text{ L}\cdot\text{h}^{-1}$ , corresponding to a cross-flow velocity of  $2 \text{ cm}\cdot\text{s}^{-1}$  in the diluate, acid and base cells. The diluate, acid and base pH were measured in the respective bottles, using three calibrated IDS SenTix 940 pH sensors and a WTW Multi 3630 IDS multimeter. The acid and base EC were also measured in the respective bottles, using two calibrated TetraCon 925 EC-sensors and a separate multimeter. The diluate EC was measured with a separate EC-sensor and multimeter. Figure 4-3 presents a schematic representation of the complete experimental BPMED set-up.

TAN concentrations were measured with Machery-Nagel NANOCOLOR Ammonium 200 (range:  $0.04 - 0.2 \text{ g}\cdot\text{L}^{-1}$ ) and 2,000 (range:  $0.4 - 2.0 \text{ g}\cdot\text{L}^{-1}$ ) test kits. Calibrated volumetric cylinders were used to determine the solution volumes. The initial diluate, acid and base solutions contained  $6.6 \text{ g}\cdot\text{L}^{-1} \text{ NH}_4\text{HCO}_3$ , corresponding to an  $\text{NH}_4^+$  concentration of  $1.5 \text{ g}\cdot\text{L}^{-1}$ , which is a representative concentration of N-loaded residual waters such as (sludge) reject water and certain industrial condensates. The initial electrode rinse solutions consisted of 1 M  $\text{NaNO}_3$ . It must be noted that due to BPMED membrane stack configuration (equipped with CEEMs) and the use of  $\text{NaNO}_3$  in the initial electrode rinse solution,  $\text{NH}_4^+$  can be transported to the electrode rinse at the cathode, while sodium ( $\text{Na}^+$ ) can be washed-out from the electrode rinse at the anode, as depicted in Figure 4-2. Furthermore, for the  $\text{NH}_3$  diffusion experiment, Acros Organics 25%  $\text{NH}_4\text{OH}$  and NaCl were used. All salts were of analytical grade (Sigma Aldrich Reagent Plus,  $\geq 99\%$ ) and were added to 1 L of demi-water. All experiments were conducted at a temperature of  $24 \pm 2 \text{ }^\circ\text{C}$  (AVG  $\pm$  STD,  $n = 20$ ).

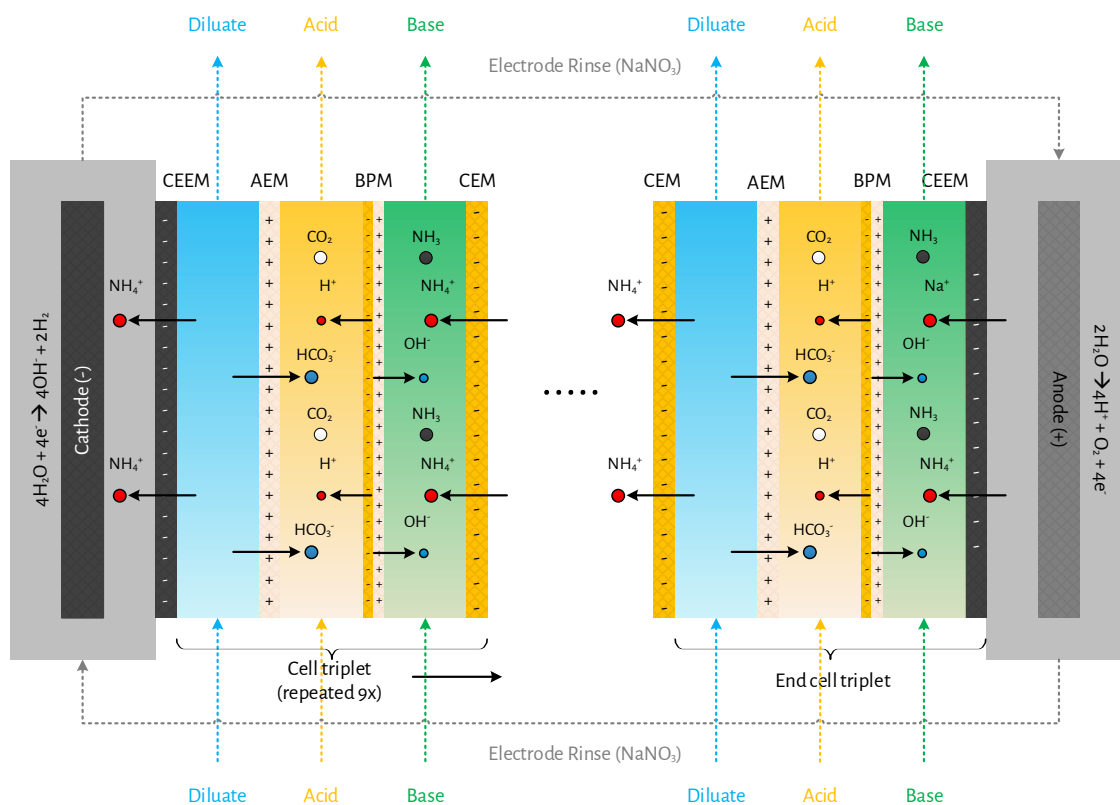


Figure 4-2 - The membrane and (flow) cell sequence in the BPMED membrane stack and the intended ion transport (electro-migration and water dissociation) as a result of the applied current. In the acid, H<sup>+</sup> and HCO<sub>3</sub><sup>-</sup> are combined and react to CO<sub>2</sub>, while in the base OH<sup>-</sup> and NH<sub>4</sub><sup>+</sup> are combined and react to NH<sub>3</sub>. At the cathode, NH<sub>4</sub><sup>+</sup> is transported to the electrode rinse, while at the anode, both Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> are transported to the base, resulting in the accumulation of NH<sub>4</sub><sup>+</sup> in the electrode rinse and the wash-out of Na<sup>+</sup> to the base.

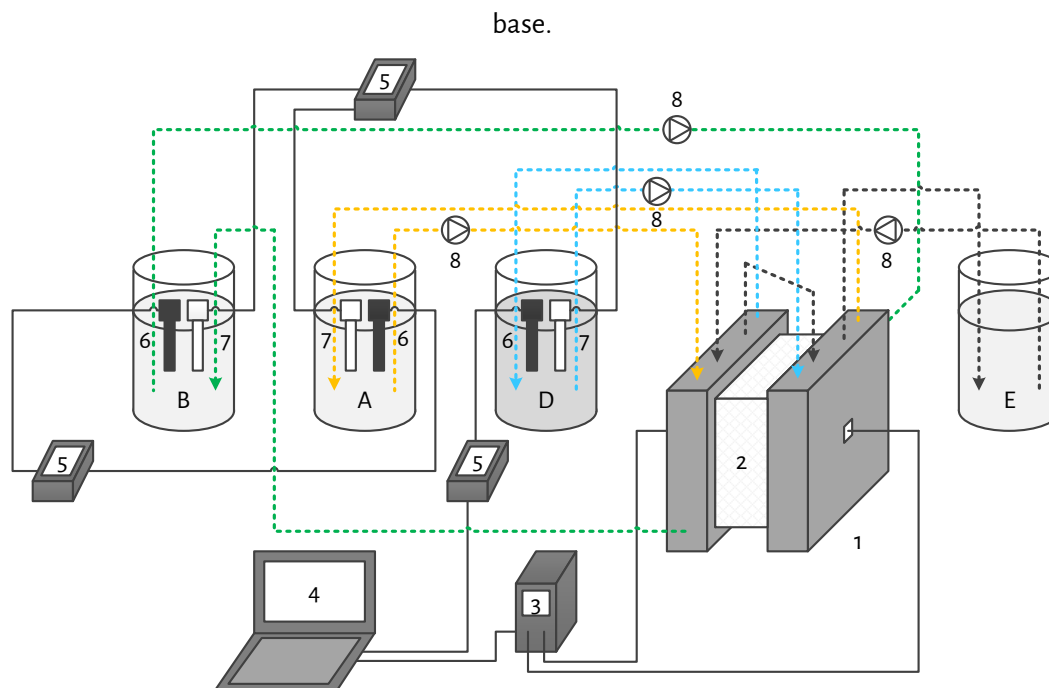


Figure 4-3 - The used experimental set-up, including the cell (1), the BPMED membrane stack (2), power supply (3), laptop (4), multimeters (5), EC-sensors (6), pH-sensors (7), peristaltic pumps (8) and the diluate (D), acid (A), base (B) and electrode rinse (E) bottles and solutions.

#### 4.2.2. Methods

##### 4.2.2.1. Removal of $\text{NH}_4^+$ and production of concentrated dissolved $\text{NH}_3$

To assess the current efficiency and electrical energy consumption to remove  $\text{NH}_4^+$  from water by BPMED, while simultaneously producing concentrated dissolved  $\text{NH}_3$ , duplicate sequencing batch experiments (SBEs) were performed. For the first batch of the SBEs, new diluate, acid, base and electrode rinse solutions were used. The diluate EC of each consecutive batch was decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$  by applying dynamic current density, as described in the study of van Linden et al. (2019a), which shows that the decrease of the diluate EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$  corresponds to 90% removal of  $\text{NH}_4^+$  from the new diluate solutions. The removal of  $\text{NH}_4^+$  by 90% is comparable to state-of-the-art  $\text{NH}_4^+$  removal technologies such as anammox and air stripping. In both ED and BPMED, the diluate is determining for the limiting current density. Because the same diluate solution, spacer geometry and cross-flow velocity were used, the same procedure of dynamic current density application was followed, using a safety factor of 0.62 (van Linden et al. (2019a)). When the diluate EC was decreased from 8 to  $1 \text{ mS}\cdot\text{cm}^{-1}$ , the treated diluate batch was replaced by a new diluate batch, while the acid, base and electrode rinse batches were recycled. Solution volumes and TAN concentrations were measured at the beginning and end of each batch to assess the TAN mass balance. In addition, the electric current and electric potential were automatically logged every five seconds on a laptop. Finally, the EC and pH of the diluate, acid and base were also logged automatically every five seconds, while the EC and pH of the electrode rinse were manually measured at the beginning and end of each batch.

##### 4.2.2.2. Diffusion of $\text{NH}_3$ through the BPMED membrane stack

Additionally, a diffusion experiment to study the diffusion of  $\text{NH}_3$  was performed. During this experiment, a 1 L base solution containing  $\text{NH}_3$  (as  $\text{NH}_4\text{OH}$ ) in demi water was recirculated through the BPMED cell containing the same BPMED membrane stack as was used in the SBEs. In addition, 1 L diluate and acid solutions without  $\text{NH}_3$  (demi water) were also recirculated through the ED cell. NaCl was added to the diluate, acid and base, to obtain equal ionic strengths (corresponding to an EC of  $8 \text{ mS}\cdot\text{cm}^{-1}$ ), to minimise osmotic water transport. A 1 L solution consisting of 1 M  $\text{NaNO}_3$  was again used as electrode rinse. The same hydraulic conditions were used for the diffusion experiment as during the SBEs, but no electric current was applied. TAN concentrations were measured in all solutions every hour and the diluate, acid, base and electrode rinse pH and EC were measured and logged automatically every five minutes. Finally, initial and final solution volumes were determined to assess the TAN mass balance.

##### 4.2.2.3. Avoiding accumulation of TAN in the electrode rinse

Additional experiments aimed to avoid any accumulation of TAN in the electrode rinse. To this end, a BPMED membrane stack equipped with AEMs was constructed, by replacing the CEEMs of the original BPMED membrane stack by additional identical AEMs already used in the original BPMED membrane stack. The membrane sequence was adjusted in such a way that again ten cell triplets were formed. A schematisation with the membrane configuration of the BPMED membrane stacks equipped with CEEMs



and AEEMs can be found in the Supporting Information of the paper of [van Linden et al. \(2020\)](#). Only the first batch of the SBEs with the adjusted BPMED membranes stack was repeated in duplicate, at identical operational conditions and applied settings and used the same analytical procedures.

#### 4.2.3. Performance indicators

As a measure for utilisation of electric current to remove  $\text{NH}_4^+$  from the diluate, the  $\text{NH}_4^+$  current efficiency was assessed. The  $\text{NH}_4^+$  current efficiency represents the efficiency to transport  $\text{NH}_4^+$  by electro-migration through the CEMs. Ideally, the charge transported as  $\text{NH}_4^+$  is equal to the supplied electric charge, but diffusion and leakage processes, and the transport of other cations through the CEM all decrease the  $\text{NH}_4^+$  current efficiency. The  $\text{NH}_4^+$  current efficiency was determined by the ratio between the charge transported as  $\text{NH}_4^+$  and the supplied electric charge (Eq. 4-1).

$$\eta_{\text{NH}_4^+} = \frac{z \cdot F \cdot n_{\text{NH}_4^+,d}}{N \cdot \sum_{t=0}^t I_t \cdot \Delta t} \cdot 100\% \quad \text{Eq. 4-1}$$

Where  $\eta_{\text{NH}_4^+}$  =  $\text{NH}_4^+$  current efficiency (unitless),  $z$  = ion valence (unitless,  $z = 1$  for  $\text{NH}_4^+$ ),  $F$  = Faraday constant (in  $\text{C} \cdot \text{mol}^{-1}$ ,  $F = 96,485 \text{ C} \cdot \text{mol}^{-1}$ ),  $n_{\text{NH}_4^+,d}$  = amount of  $\text{NH}_4^+$  transported from the diluate (in mol),  $N$  = number of cell triplets in the BPMED membrane stack (unitless,  $N = 10$ ),  $I_t$  = average electric current during each time interval (in  $\text{A} = \text{C} \cdot \text{s}^{-1}$ ) and  $\Delta t$  = time interval (in s).

Furthermore, the electrochemical energy consumption to transport  $\text{NH}_4^+$  from the diluate by BPMED was determined based on the consumed electrical energy and the transported  $\text{NH}_4^+$  mass (Eq. 4-2).

$$E_e = \frac{\sum_{t=0}^t U_t \cdot I_t \cdot \Delta t}{m_{\text{NH}_4^+,d}} \quad \text{Eq. 4-2}$$

Where  $E_e$  = electrochemical energy consumption (in  $\text{MJ} \cdot \text{kg} \cdot \text{N}^{-1}$ ),  $U_t$  = average electric potential during each time interval (in V) and  $m_{\text{NH}_4^+,d}$  = amount of transported  $\text{NH}_4^+$  from the diluate (in g-N).

4.3. Results4.3.1. Removal of  $\text{NH}_4^+$  and production of concentrated dissolved  $\text{NH}_3$ 

The presented values represent the average results of the duplicate SBEs unless indicated differently. The deviation (min-max) of the duplicate results was always below 10%. Figure 4-4A presents the diluate, acid and base EC over the cumulative electrochemical energy consumption throughout one SBE. In the Supporting Information of the paper of [van Linden et al. \(2020\)](#), the evolution of the EC and pH throughout the duplicate SBE is presented. The diluate EC for each new batch was decreased from 8 to 1  $\text{mS}\cdot\text{cm}^{-1}$ . For each consecutive diluate batch, more time was needed to decrease the diluate EC to 1  $\text{mS}\cdot\text{cm}^{-1}$ . The operational run time increased from 66 minutes for the first batch to 89 minutes for the tenth batch. However, the increase in operational run time did not result in an increase in electrochemical energy consumption per batch, as for the first batch 18.7 kJ was used and for the tenth batch 18.1 kJ was used. The base EC increased steadily throughout the SBEs and finally reached 18  $\text{mS}\cdot\text{cm}^{-1}$ . The acid EC only increased from 8 to 10  $\text{mS}\cdot\text{cm}^{-1}$  during the first three batches. Subsequently, the increase in acid EC accelerated and the acid EC exceeded the base EC after six batches. The acid EC reached a final value of 25  $\text{mS}\cdot\text{cm}^{-1}$ .

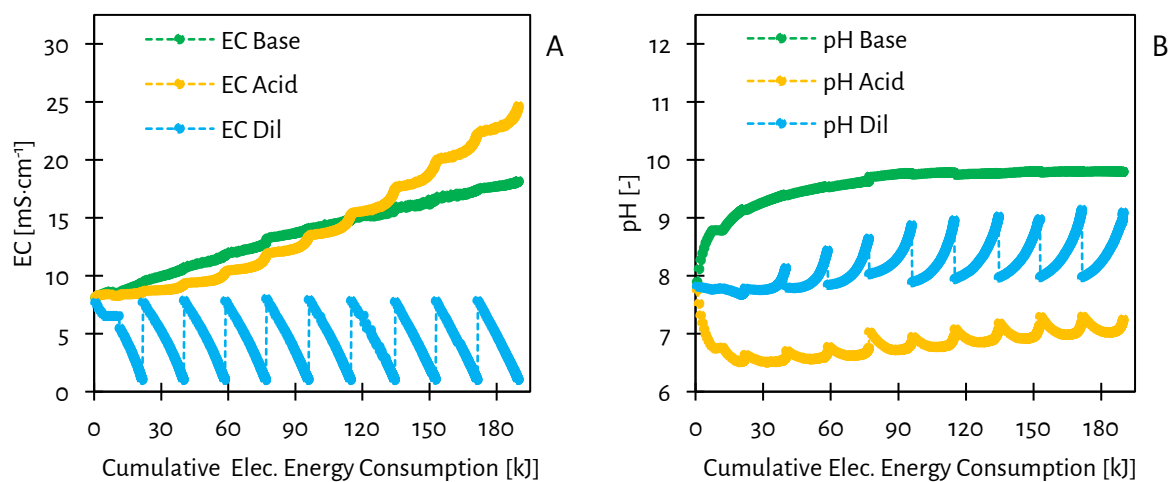


Figure 4-4 - The EC (A) and pH (B) throughout one of the SBE duplicates. The diluate EC decreased to 1  $\text{mS}\cdot\text{cm}^{-1}$  for each batch, while the acid and base EC increased to 25 and 19  $\text{mS}\cdot\text{cm}^{-1}$  throughout the SBE, respectively. The diluate pH increased during each batch and the final diluate pH increased over the consecutive batches from 7.8 to 9.1. The base pH increased throughout the SBEs and reached a plateau at 9.8, while the acid pH initially decreased to 6.5 and subsequently increased each consecutive batch to a final value of 7.3.

Figure 4-4B presents the pH of the diluate, acid and base. The base pH increased during the first five batches and subsequently reached a plateau at a pH of 9.8. The acid pH decreased from 7.8 to 6.5 after the first two batches and subsequently increased for each consecutive batch. The acid pH eventually reached a pH of 7.3 after the tenth batch. The new diluate batches had an average pH of 7.8 and for each batch after the first batch, the diluate pH increased and reached 9.1 for the tenth batch.

According to Figure 4-5A, the decrease in diluate EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$  corresponded to a TAN removal efficiency ranging 85–91%. The amount of transported  $\text{NH}_4^+$  was  $1.3 \pm 0.1 \text{ g}$  (AVG  $\pm$  STD,  $n = 20$ ) for consecutive batches in duplicate. For the first five batches, at least 90% of  $\text{NH}_4^+$  was removed from the diluate, but the TAN removal efficiency decreased to 85% for the tenth batch. The TAN concentration in the base increased from 1.5 to  $7.3 \text{ g}\cdot\text{L}^{-1}$ , corresponding to a concentration factor of 5, but approached a plateau (decelerating increase). Based on the intended ion transport (Figure 4-2), no  $\text{NH}_4^+$  transport should take place to the acid. However, the TAN concentration in the acid increased from 1.5 to  $5.4 \text{ g}\cdot\text{L}^{-1}$  and showed a first-order kinetics trend (accelerating increase). Finally, the TAN concentration also increased in the electrode rinse, from 0 to  $3.4 \text{ g}\cdot\text{L}^{-1}$ . The acid EC reached a final value of  $25 \text{ mS}\cdot\text{cm}^{-1}$ . In the Supporting Information of the paper of [van Linden et al. \(2020\)](#), the evolution of the TAN and  $\text{NH}_3$  concentrations throughout the duplicate SBE is presented. The TAN mass balance of all batches fitted with an average error of 3%.

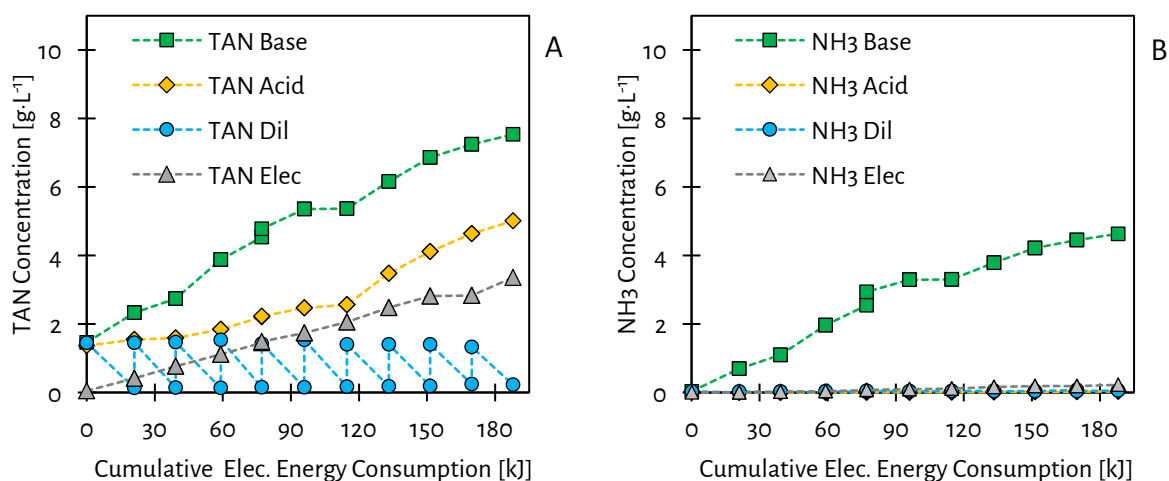


Figure 4-5 - The concentrations of TAN (A) and  $\text{NH}_3$  (B) in the diluate, acid, base and electrode rinse throughout one of the SBE duplicates. The removal efficiency of TAN from the diluate decreased from 91% for the first batch to 85% for the tenth batch. The transported  $\text{NH}_4^+$  partially ended to the base, which had a final pH of 9.8, resulting in a final  $\text{NH}_3$  concentration in the base of  $4.5 \text{ g}\cdot\text{L}^{-1}$ . The residual fraction of the transported  $\text{NH}_4^+$  ended up as  $\text{NH}_4^+$  in the acid and the electrode rinse.

Figure 4-5B presents the actual  $\text{NH}_3$  concentrations throughout the SBEs, as calculated based on the measured TAN concentrations, temperature, pH and ionic strength in the various solutions. The concentration of  $\text{NH}_3$  in the base increased from 0 to  $4.5 \text{ g}\cdot\text{L}^{-1}$  after the tenth batch and, similarly to the TAN concentration in the base, also approached a plateau, indicating a decelerating increase. On the other hand, the  $\text{NH}_3$  concentration in the diluate, acid and electrode rinse throughout the SBE never exceeded  $0.2 \text{ g}\cdot\text{L}^{-1}$ . Due to the accumulation of  $\text{NH}_3$  in the base, an  $\text{NH}_3$  concentration gradient, ranging  $0.7 - 4.5 \text{ g}\cdot\text{L}^{-1}$ , established between the base and diluate and the base and acid.

Figure 4-6A shows that the  $\text{NH}_4^+$  current efficiency decreased from 69% for the first batch to 54% for the tenth batch during the SBEs. Interestingly, according to Figure 4-6B, the electrochemical energy consumption to remove  $\text{NH}_4^+$  by 85 – 91% was stable at  $18 \pm 1 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  (AVG  $\pm$  STD,  $n = 20$ ).

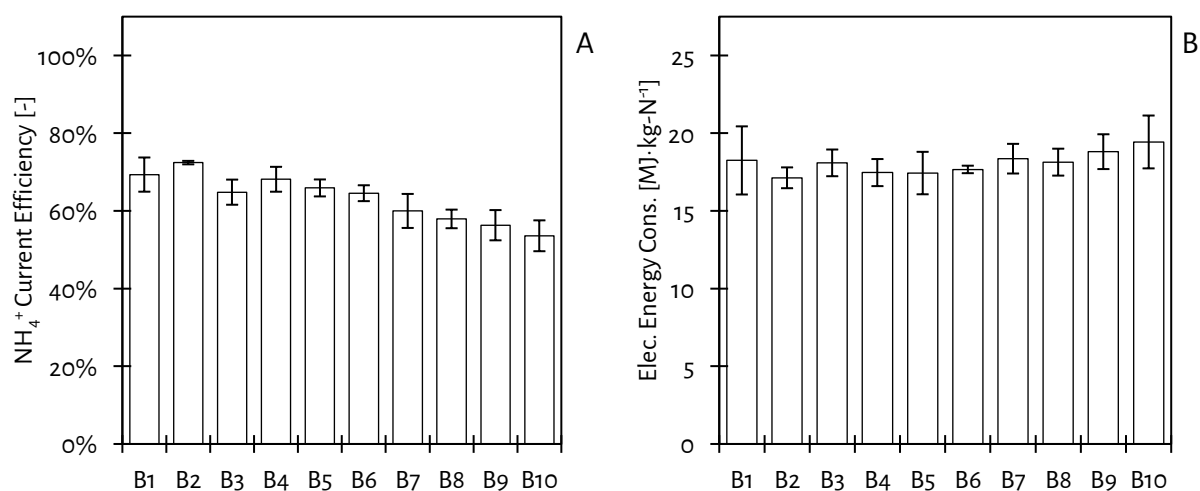


Figure 4-6 - The  $\text{NH}_4^+$  current efficiency (A) decreased over the consecutive batches from 69% to 54%, while the electrochemical energy consumption (B) to remove  $\text{NH}_4^+$  by 85 – 91% remained stable at  $18 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  over the consecutive batches. Average values of the duplicate SBEs are presented, along with the minimum and maximum values (outer values of error bars).

4.3.2. Diffusion of NH<sub>3</sub> through the BPMED membrane stack

Figure 4-7 shows the NH<sub>3</sub> concentrations throughout the additionally conducted diffusion experiment, during which no electric current was applied. The NH<sub>3</sub> concentrations are again calculated based on the measured TAN concentrations, temperature, pH and ionic strength of the solutions. The pH of the diluate, acid and base pH was always higher than 10.3 after the start of the experiment, indicating that TAN was present as NH<sub>3</sub> for at least 90%. The initial NH<sub>3</sub> concentration in the base was 12.5 g·L<sup>-1</sup> and decreased to 6.4 g·L<sup>-1</sup> after 480 minutes, showing a decelerating trend. The NH<sub>3</sub> concentration in the diluate and acid increased, also showing a decelerating trend. The NH<sub>3</sub> in the diluate and the acid increased from 0 to 2.4 and 3.1 g·L<sup>-1</sup>, respectively. The NH<sub>3</sub> concentration in the electrode rinse throughout the diffusion experiment did not exceed 0.1 g·L<sup>-1</sup>. The NH<sub>3</sub> mass balance of the diffusion experiment fitted with an error of 6%, which was probably caused by the volatilisation of NH<sub>3</sub>.

Due to the decrease in NH<sub>3</sub> concentration in the base and increase in NH<sub>3</sub> in the diluate and acid, the NH<sub>3</sub> concentration gradient between the base and acid and the base and diluate, decreased over time, from 12.5 g·L<sup>-1</sup> to 3.3 g·L<sup>-1</sup> and 4.0 g·L<sup>-1</sup>, respectively. The NH<sub>3</sub> concentration gradient between the diluate and acid increased from 0 to only 0.8 g·L<sup>-1</sup>.

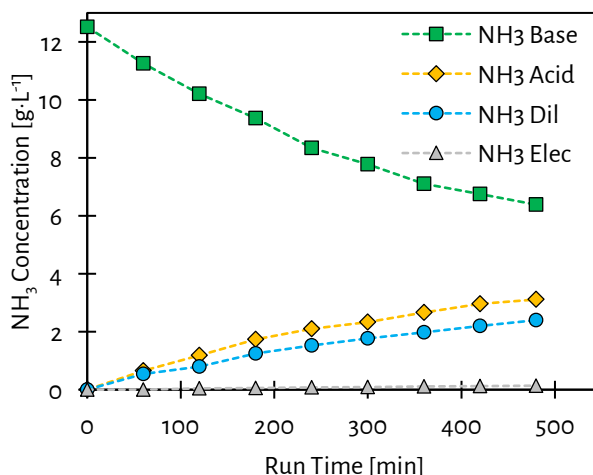


Figure 4-7 - The NH<sub>3</sub> concentration in the base decreased during the diffusion experiment due to NH<sub>3</sub> diffusion from the base to the diluate and the acid.

4.3.3. Avoiding accumulation of TAN in the electrode rinse

During the duplicate SBEs, 27 ± 11% (AVG ± STD, n = 20) of the TAN transported from new diluate batches ended up and accumulated as NH<sub>4</sub><sup>+</sup> in the electrode rinse, resulting in a final TAN concentration in the electrode rinse of 3.4 g·L<sup>-1</sup>. The observed accumulation of TAN in the electrode rinse was similar to the findings in the study of [van Linden et al. \(2019a\)](#), in which ED was to remove TAN as NH<sub>4</sub><sup>+</sup> from the same diluate. Figure 4-8 shows that during the first batch of the duplicate SBEs 26% of the TAN that was transported from the diluate accumulated in the electrode rinse when the BPMED membrane stack was

equipped with CEEMs. Concurrently, only 64% of the TAN transported from the diluate accumulated in the base for the first batches of the duplicate SBEs.

By using a BPMED membrane stack equipped with AEEMs, the accumulation of TAN in the electrode rinse was prevented. During the experiments with a BPMED membrane stack equipped with AEEMs, the fraction of TAN that accumulated in the electrode rinse was negligible, while the fraction of TAN that accumulated in the base increased to 94%.

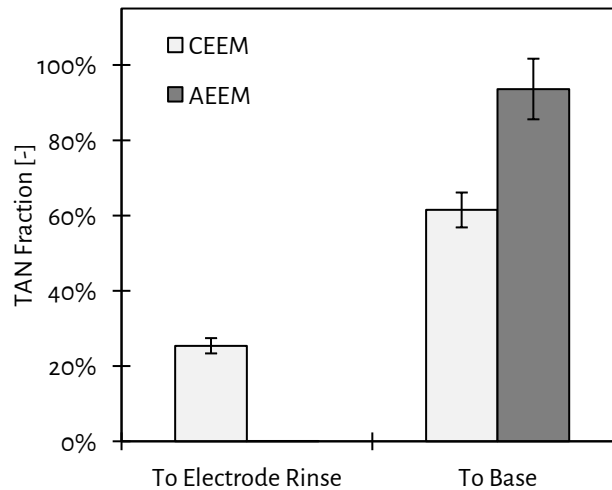


Figure 4-8 - The accumulation of TAN transported from the diluate in the electrode rinse decreased from 26% for the use of CEEMs to 0% for the use of AEEMs in the BPMED membrane stack. In addition, the accumulation of TAN transported from the diluate in the base increased from 64% for the use of CEEMs to 94% for the use of AEEMs. Average values of the duplicate experiments are shown, along with the minimum and maximum values (outer values of the error bars).

#### 4.4. Discussion

##### 4.4.1. Removal of $\text{NH}_4^+$ and production of concentrated dissolved $\text{NH}_3$

##### 4.4.1.1. Evaluation of the diluate

The decrease in diluate EC from 8 to 1  $\text{mS}\cdot\text{cm}^{-1}$  (Figure 4-4A) was the result of the effective removal of  $\text{NH}_4^+$  and  $\text{HCO}_3^-$  from the diluate. The diluate pH increased during the treatment of a new diluate batch (Figure 4-4B), in contrast to multiple previous studies (Li et al., 2016; Shi et al., 2018). Two phenomena probably caused the increase in diluate pH. Firstly, diffusion of  $\text{NH}_3$  from the base, which was validated to take place in the diffusion experiment (section 3.3), resulted in the consumption of  $\text{H}^+$  in the diluate to form  $\text{NH}_4^+$ , leading to the diluate pH increase. Secondly, the diluate pH increased due to leakage of  $\text{OH}^-$  from the base to the diluate.  $\text{OH}^-$  is prone to leak through CEMs due to, amongst others, its high diffusivity (Strathmann, 2010). The effect of  $\text{NH}_3$  diffusion and  $\text{OH}^-$  leakage on the diluate pH became more apparent at the end of each batch (Figure 4-4B), when the concentration gradients were highest and the buffer capacity of the diluate was decreased, due to the removal of  $\text{NH}_4^+$  and  $\text{HCO}_3^-$ . Apparently,  $\text{NH}_3$  diffusion and  $\text{OH}^-$  leakage affected the diluate pH more than any diffusion of  $\text{CO}_2$  or leakage of  $\text{H}^+$  from the acid, which would cause a decrease in the diluate pH. Because the operational run time and the  $\text{NH}_3$  and  $\text{OH}^-$  concentration gradients between the base and diluate increased throughout the SBEs, the final diluate pH increased from 7.7 for the first batch to 9.1 for the tenth batch. The decrease in  $\text{NH}_4^+$  removal efficiency from 91 to 85% over the consecutive batches was also a result of the diluate pH increase throughout each batch. Due to the pH increase, a fraction of the  $\text{NH}_4^+$  was converted to  $\text{NH}_3$  and was therefore not transported by electro-migration.

##### 4.4.1.2. Evaluation of the base

The base pH reached a plateau at  $\text{pH} = 9.8$  (Figure 4-4B), whereas in previous studies pH values higher than 11 were achieved (Li et al., 2016; Shi et al., 2018). One of the causes of the plateauing of the base pH was the consumption of  $\text{OH}^-$  by  $\text{NH}_4^+$ , resulting in the formation of  $\text{NH}_3$  and water. Therefore, a certain fraction of  $\text{OH}^-$  produced by the BPMs was not translated to an increase in base pH. Besides, in contrast to previous studies, the initial base contained  $\text{HCO}_3^-$ , which reacted with the produced  $\text{OH}^-$  to  $\text{CO}_3^{2-}$ . Therefore, not all generated  $\text{OH}^-$  was available to increase the pH effectively. Finally, any diffusion of  $\text{CO}_2$  from the acid also contributed to the plateauing of the base pH. The  $\text{OH}^-$  concentration gradient between the base and diluate increased from  $1.2\cdot 10^{-5}$  to  $4.9\cdot 10^{-5}$   $\text{mol}\cdot\text{L}^{-1}$  throughout the SBEs. At a final base pH of 9.8, a temperature of 24 °C and an EC of 18  $\text{mS}\cdot\text{cm}^{-1}$ , 71% of the TAN was present as  $\text{NH}_3$ . Eventually, only  $48 \pm 21\%$  (AVG  $\pm$  STD,  $n = 20$ ) of the  $\text{NH}_4^+$  that was transported from the diluate accumulated in the base. The residual  $\text{NH}_4^+$  that was transported from the diluate accumulated in the acid and the electrode rinse. The  $\text{NH}_3$  concentration in the base increased from 0 to 4.5  $\text{g}\cdot\text{L}^{-1}$ , while the  $\text{NH}_4^+$  concentration in the acid increased from 1.5 to 2.9  $\text{g}\cdot\text{L}^{-1}$ . As mentioned in section 2.1, the transport of  $\text{NH}_4^+$  to the electrode rinse led to the wash-out of  $\text{Na}^+$  from the electrode rinse, resulting in the accumulation of  $\text{Na}^+$ -species (such as  $\text{NaOH}$ ,  $\text{NaHCO}_3$  and  $\text{Na}_2\text{CO}_3$ ) in the

base.  $\text{NH}_4^+$  and  $\text{Na}^+$  accumulated with the anions  $\text{OH}^-$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  in the base, explaining the increase in base EC (Figure 4-4A). Of these anions,  $\text{OH}^-$  was produced by the BPMs, while  $\text{HCO}_3^-$  either diffused as  $\text{CO}_2$  (as mentioned by [Pronk et al. \(2006d\)](#)) or as  $\text{HCO}_3^-$ -species from the acid and  $\text{CO}_3^{2-}$  was formed by  $\text{OH}^-$  and  $\text{HCO}_3^-$ . The  $\text{NH}_3$  and  $\text{NH}_4^+$  concentration gradients between the base and diluate ranged  $0.04 - 0.27 \text{ mol}\cdot\text{L}^{-1}$  and  $0.08 - 0.15 \text{ mol}\cdot\text{L}^{-1}$ , respectively.

### 4.4.1.3. Evaluation of the acid

The limited increase in acid EC after the first three batches (Figure 4-4A) was a result of the formation of uncharged  $\text{CO}_2$  from the generated  $\text{H}^+$  and the  $\text{HCO}_3^-$  in the acid. Because  $\text{CO}_2$  has a relatively low solubility ( $1.5 \text{ g}\cdot\text{L}^{-1}$  at  $T = 24 \text{ }^\circ\text{C}$ , based on the Henry's constant and thermodynamic data taken from [Sander \(2015\)](#)), it became supersaturated in the acid, indicated by the observation of obvious gas bubbles. The transport of gas bubbles to the headspace of the acid solution bottle indicated spontaneous stripping of  $\text{CO}_2$  from the acid, which prevented the accumulation of  $\text{H}^+$  in the acid. In previous studies  $\text{H}^+$  accumulated in the acid with ions such as  $\text{Cl}^-$ , resulting in  $\text{H}^+$  leakage from the acid to the diluate and ultimately a decrease in diluate pH ([Li et al., 2016](#); [Shi et al., 2018](#)). Because in this study  $\text{HCO}_3^-$  was the main anion, accumulation and leakage of  $\text{H}^+$  from the acid to the diluate was limited. After the sixth batch, the increase in acid EC and also TAN concentration accelerated (Figure 4-4A and Figure 4-5A). Because the operational run time and the  $\text{NH}_3$  concentration gradient between the base and acid both increased throughout the SBEs, more  $\text{NH}_3$  diffusion to the acid took place, causing the accelerated increase in acid EC and TAN concentration. Besides, the acid pH increased each consecutive batch (Figure 4-4B), due to  $\text{NH}_3$  diffusion and  $\text{OH}^-$  leakage from the base.

### 4.4.1.4. Assessment of the $\text{NH}_4^+$ current efficiency

For the treatment of each consecutive diluate batch, a loss in  $\text{NH}_4^+$  current efficiency was observed. The loss in  $\text{NH}_4^+$  current efficiency was caused by the leakage of  $\text{OH}^-$ , the diffusion of dissolved  $\text{NH}_3$  and the diffusion of ionic species. Because a concentration gradient was present, TAN species such as  $\text{NH}_4\text{HCO}_3$  could diffuse from the base back to the diluate. Therefore, to decrease the diluate EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$ ,  $\text{NH}_4^+$  must be transported back and forth, at the expense of additional electric charge. Besides, the accumulated  $\text{Na}^+$ -species could also diffuse from the base to the diluate and therefore contributed to the loss in  $\text{NH}_4^+$  current efficiency, because electric charge was also used to transport  $\text{Na}^+$  from the diluate to decrease the diluate EC. The mentioned  $\text{OH}^-$  leakage, dissolved  $\text{NH}_3$  diffusion and diffusion of TAN-species and  $\text{Na}^+$ -species (the ionic species) all took place from the base, through the CEMs, to the diluate. The contribution of  $\text{H}^+$  leakage in the form of proton or hydronium ( $\text{H}_3\text{O}^+$ ) ions was neglected, because the  $\text{H}^+$  concentration gradient was at least two orders of magnitude lower than the  $\text{NH}_3$ ,  $\text{OH}^-$  and ionic species concentration gradients between the base and the diluate. Also, electro-migration of  $\text{H}^+$  was neglected because the amount of charge in the new diluate batches represented by  $\text{H}^+$  was only  $1\cdot 10^{-3} \text{ C}$ , compared to approximately  $8,000 \text{ C}$  for  $\text{NH}_4^+$  (corresponding to  $1.5 \text{ g NH}_4^+$ ). However, based on the available data, no



conclusions can be drawn on what process ( $\text{OH}^-$  leakage, dissolved  $\text{NH}_3$  diffusion or ionic species diffusion) had the largest contribution to the loss in  $\text{NH}_4^+$  current efficiency.

Because more electric charge needed to be supplied used to transport  $\text{NH}_4^+$ , the operational run time to treat the new diluate batches increased. The  $\text{NH}_4^+$  current efficiency decreased over consecutive batches, as is depicted in Figure 4-6A. Because a fixed amount of TAN mass was transported per batch of new diluate, a fixed amount of charge as  $\text{NH}_4^+$  was transported. Therefore, according to Eq. 4-1, the loss in  $\text{NH}_4^+$  current efficiency was a result of an additionally supplied electric charge. Ultimately, the decrease in  $\text{NH}_4^+$  current efficiency throughout the SBEs was a result of both the increase in operational run time and concentration gradients, which led to more  $\text{OH}^-$  leakage and dissolved  $\text{NH}_3$  diffusion and ionic species diffusion.

#### 4.4.1.5. Assessment of the electrochemical energy consumption

Even though the  $\text{NH}_4^+$  current efficiency decreased over the consecutive batches, the electrochemical energy consumption to remove  $\text{NH}_4^+$  by 85 – 91% was stable at  $18 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  (Figure 4-6B). The decrease in  $\text{NH}_4^+$  current efficiency was compensated by a decrease in electric potential throughout the SBEs. Figure 4-9 shows that the average electric potential throughout a batch decreased over the consecutive batches. The average electric potential was 15.5 V for the first batch and dropped to 12.6 V for the tenth batch. The decrease in electric potential was a result of the increase in acid and base EC throughout the SBEs (Figure 4-4A), which led to a decrease in electrical resistance of the BPMED membrane stack.

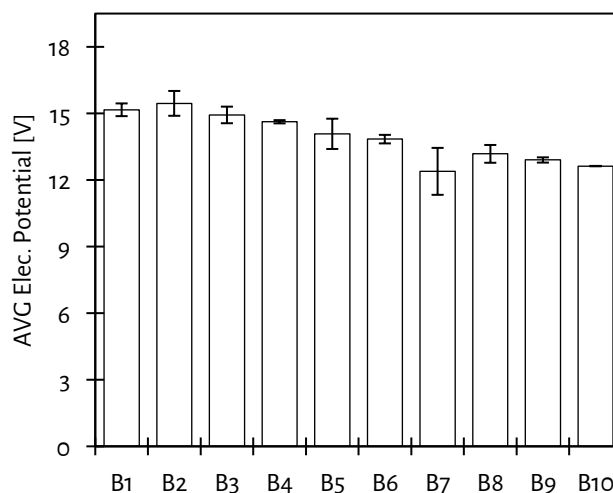


Figure 4-9 - The average electric potentials during each consecutive batch decreased throughout the SBEs due to a decrease in electrical resistance of the BPMED membrane stack as a result of the increase in acid and base EC. Average values of the duplicate experiments are shown, along with the minimum and maximum values (outer values error bars).

#### 4.4.2. Diffusion of NH<sub>3</sub> through the BPMED membrane stack

During the diffusion experiment (Figure 4-7), diffusion of NH<sub>3</sub> took probably place from the base (through the BPMs) to the acid and (through the CEMs) to the diluate, because the NH<sub>3</sub> concentration gradients between the base and acid and the base and diluate (ranging 3.3 to 12.5 g·L<sup>-1</sup>) were at least four times higher than the NH<sub>3</sub> concentration gradient that between the diluate and acid (ranging 0.0 – 0.8 g·L<sup>-1</sup>). Furthermore, the decelerated changes (first-order kinetics) in NH<sub>3</sub> concentrations in the base, acid and diluate during the diffusion experiment were caused by the decrease in NH<sub>3</sub> concentration gradients, which is typical for diffusion experiments. The NH<sub>3</sub> concentration in the acid was always higher than in the diluate, suggesting that NH<sub>3</sub> diffused more easily from the base, through the BPMs, to the acid than from the base, through the CEMs, to the diluate. While the diffusion of NH<sub>3</sub> through CEMs and BPMs was also observed by (Ali et al., 2004), drawing firm conclusions on what membranes are more susceptible to NH<sub>3</sub> diffusion requires the determination of membrane permeability constants.

#### 4.4.3. Avoiding accumulation of TAN in the electrode rinse

According to the results of the diffusion experiment in section 3.3, the transport of TAN to the electrode rinse by diffusion of NH<sub>3</sub> from the base was negligible. Therefore, the main mechanism responsible for the transport of TAN to the electrode rinse was electro-migration of NH<sub>4</sub><sup>+</sup>, even though TAN-species can also diffuse from the electrode rinse to the adjacent diluate and base cells. During the SBEs, NH<sub>4</sub><sup>+</sup> was transported by electro-migration from the diluate, through the CEEM at the cathode, to the electrode rinse. Because the electrode rinse consisted of NaNO<sub>3</sub>, both Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> were transported from the electrode rinse, through the CEEM at the anode, to the base (Figure 4-2), resulting in the accumulation of NH<sub>4</sub><sup>+</sup> in the electrode rinse and the wash-out of Na<sup>+</sup>.

By replacing CEEMs by AEEMs in the BPMED membrane stack, electro-migration to the electrode rinse was prevented and the transport of TAN to the base increased (Figure 4-8), suggesting that higher TAN and NH<sub>3</sub> concentrations potentially can be achieved in the base when the same amount of diluate is treated. Furthermore, the use of AEEMs also resulted in an increase in NH<sub>4</sub><sup>+</sup> current efficiency from 69 to 78% and a decrease in electrochemical energy consumption from 18 to 16 MJ·kg-N<sup>-1</sup>. The observed increase in NH<sub>4</sub><sup>+</sup> current efficiency and decrease in energy consumption may be explained by the avoided diffusion of Na<sup>+</sup>-species from the base to the diluate, as wash-out of Na<sup>+</sup> was avoided.

The results show that the use of AEEMs instead of CEEMs in the BPMED membrane stack effectively prevented the accumulation of NH<sub>4</sub><sup>+</sup> in the electrode rinse, without notable negative side-effects. However, it is expected that HCO<sub>3</sub><sup>-</sup> accumulated in the electrode rinse, at the expense of the anion initially present in the electrode rinse (NO<sub>3</sub><sup>-</sup>). To avoid the loss of NO<sub>3</sub><sup>-</sup> from the electrode rinse, it could be considered to use HCO<sub>3</sub><sup>-</sup> as an anion in the initial electrode rinse, to avoid any accumulation and wash-out of ions. Another option is to equip the BPMED membrane stack with CEEMs and use NH<sub>4</sub><sup>+</sup> as the cation for the initial electrode rinse. The latter would not require an adjustment in the initially used BPMED membrane stack configuration containing CEEMs.

#### 4.4.4. Energetic evaluation of BPMED and ED in combination with the addition of chemicals

The electrochemical energy consumption to transport  $\text{NH}_4^+$  by BPMED was three times as much compared to the  $5.4 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  reported for ED in the study of [van Linden et al. \(2019a\)](#). The difference in electrochemical energy consumption is partially explained by the lower  $\text{NH}_4^+$  current efficiency of BPMED, compared to ED. The  $\text{NH}_4^+$  current efficiency of BPMED ranged 54 – 69%, whereas the  $\text{NH}_4^+$  current efficiency of ED ranged 83 – 96%. Thus, for BPMED more electric charge was required to transport the same amount of  $\text{NH}_4^+$ . In addition, the average electric potential during a batch for BPMED (ranging 12.6 – 15.2 V) was higher than for ED (ranging 5.7 – 7.0 V). The higher electric potential for BPMED was a result of the presence of additional cells and the presence of BPMs. While ED contains cell pairs (diluate and concentrate), BPMED contains cell triplets (diluate, acid and base). The addition of extra cells introduces additional electrical resistance of the liquids and the spacers. Besides, BPMED makes use of BPMs, which introduce an electrical resistance and an additional electric potential for the dissociation of water, depending on the pH gradient between the acid and base ([Mani, 1991](#)). For BPMED, 30% more electric charge was required, whereas the electric potential was 130% higher than for ED. Together, the extra electric charge and the higher electric potential explain the higher electrochemical energy consumption of BPMED to transport  $\text{NH}_4^+$ .

Besides the energy to drive the electrochemical processes, energy is required to pump the solutions through the ED cell. The pumping energy was determined based on additional hydraulic pressure measurements over the membrane stack and the respective hydraulic flow rates. The hydraulic pressure loss at a flow rate of  $19 \text{ L}\cdot\text{h}^{-1}$  was 9.3 kPa for the diluate, acid and base, having ten cells each. In addition, the hydraulic pressure loss for the electrode rinse was 8.4 kPa. With a maximum operational run time of 89 minutes for BPMED and 66 minutes for ED, the pumping energy was 1.0 kJ and 0.5 kJ, respectively. More information on the determination of the pumping energy is presented in the Supporting Information of the paper of [van Linden et al. \(2020\)](#).

In the study [van Linden et al. \(2019a\)](#), a concentrate solution with a TAN concentration of  $10 \text{ g}\cdot\text{L}^{-1}$  was produced, which was present as  $\text{NH}_4\text{HCO}_3$ . To compare the energy consumption of BPMED and ED for the removal of  $\text{NH}_4^+$  and simultaneous production of  $\text{NH}_3$ , an equal  $\text{NH}_3$  concentration should be taken as a reference point. In this chapter, after ten batches, a base solution with a TAN concentration of  $7.3 \text{ g}\cdot\text{L}^{-1}$  at a pH of 9.8 was produced, corresponding to an  $\text{NH}_3$  concentration of  $4.5 \text{ g}\cdot\text{L}^{-1}$ . To achieve this, in total 13 grams of TAN was transported as  $\text{NH}_4^+$  from the diluate by BPMED. For ED, seven identical diluate batches (1 L solutions containing  $1.5 \text{ g}\cdot\text{L}^{-1}$  TAN as  $\text{NH}_4\text{HCO}_3$ ) were treated the same way (reduction of EC to  $1 \text{ mS}\cdot\text{cm}^{-1}$ ) to produce a concentrate solution with a TAN concentration of  $7.3 \text{ g}\cdot\text{L}^{-1}$ , corresponding to the transport of 10 grams of TAN as  $\text{NH}_4^+$  from the diluate. However, the final pH of the ED concentrate only reached 8.8. The amount of NaOH addition to increase the pH to 9.8 was obtained from the results of PHREEQC software simulations, in order to subsequently calculate how much energy is associated with the industrial production of NaOH. According to the study of [Hong et al. \(2014\)](#) on the life cycle analysis of NaOH

production, 2,176 kWh of electricity is consumed to produce one ton of NaOH by electrolysis, which corresponds to  $7.8 \text{ kJ}\cdot\text{g}\cdot\text{NaOH}^{-1}$ .

Table 4-1 presents the amount of required NaOH to increase the pH from 8.8 to 9.8 of the ED concentrate. When the energy consumption for driving the electrochemical processes, pumping and chemical production is considered, BPMED appears to be energetically competitive to ED in combination with the addition of chemicals. The energy consumption to produce  $4.5 \text{ g}\cdot\text{L}^{-1} \text{ NH}_3$  by BPMED and ED with the addition of chemicals was 19 and  $22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , respectively.

Table 4-1 - The energetic evaluation of the production of a solution with an  $\text{NH}_3$  concentration of  $4.5 \text{ g}\cdot\text{L}^{-1}$  by BPMED and ED, including on the energy input to drive the electrochemical processes, the pumping energy to recirculate the solutions and the energy to produce chemicals.

		Unit	BPMED Base	ED Concentrate
Solution Conditions	Final TAN	$\text{g}\cdot\text{L}^{-1}$	7.3	7.3
	Final pH	-	9.8	8.8
Chemical Addition	NaOH	g	-	16.5
Energy Consumed	Electrochemical	kJ	$18\cdot 10 = 180$	$5.4\cdot 7 = 38$
	Pumping	kJ	$1.0\cdot 10 = 10$	$0.5\cdot 7 = 3.5$
	NaOH	kJ	-	129
Mass Transported	TAN	g	13	10
Energy Consumption		$\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$	19	22

#### 4.5. Conclusions

The experimental study to assess the feasibility and energy consumption of BPMED to produce concentrated  $\text{NH}_3$  solutions resulted in the following conclusions:

- BPMED proved to be able to remove 85 – 91% of the  $\text{NH}_4^+$  from feed water with an initial  $\text{NH}_4^+$  concentration of  $1.5 \text{ g}\cdot\text{L}^{-1}$  as  $\text{NH}_4\text{HCO}_3$ .
- The pH in the base was effectively increased from 7.8 to 9.8 and the  $\text{NH}_3$  concentration was increased from 0 to  $4.5 \text{ g}\cdot\text{L}^{-1}$ .
- Only 48% of the  $\text{NH}_4^+$  transported from the diluate ended up in the base as  $\text{NH}_3$  due to accumulation of  $\text{NH}_4^+$  in the electrode rinse and diffusion of  $\text{NH}_3$  from the base to the acid and back to the dilute;
- Replacing the CEEMs by AEEMs in the BPMED membrane stack prevented the transport of the  $\text{NH}_4^+$  to the electrode rinse and therewith the accumulation of  $\text{NH}_4^+$  in the electrode rinse.
- The electrical energy consumption for BPMED remained stable at  $19 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , comprising the required energy for the transport of  $\text{NH}_4^+$  from the diluate, the dissociation of water for the production of  $\text{H}^+$  and  $\text{OH}^-$  and the pumping energy to recirculate the solutions.
- The losses in  $\text{NH}_4^+$  current efficiency were caused by the leakage of  $\text{OH}^-$ , the diffusion of dissolved  $\text{NH}_3$  and the diffusion of ionic species (such as  $\text{NH}_4\text{HCO}_3$ ) from the base to the diluate.
- The electrochemical energy consumption eventually remained stable because the decrease in  $\text{NH}_4^+$  current efficiency was compensated by a decrease in electric potential, caused by a decrease in the electrical resistance of the BPMED membrane stack as a result of an increase in the acid and base EC.
- An energetic evaluation showed that the energy consumption of BPMED to remove  $\text{NH}_4^+$  and simultaneously produce concentrated dissolved  $\text{NH}_3$  was competitive to the combination of ED and the addition of chemicals ( $22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ).

#### 4.6. References

- Ali, M. A. B., Rakib, M., Laborie, S., Viers, P., & Durand, G. (2004). Coupling of bipolar membrane electrodialysis and ammonia stripping for direct treatment of wastewaters containing ammonium nitrate. *Journal of Membrane Science*, *244*(1-2), 89-96. doi:10.1016/j.memsci.2004.07.007
- Gonzalez-Martinez, A., Muñoz-Palazon, B., Rodriguez-Sanchez, A., & Gonzalez-Lopez, J. (2018). New concepts in anammox processes for wastewater nitrogen removal: recent advances and future prospects. *FEMS Microbiology Letters*, *365*(6). doi:10.1093/femsle/fny031
- Graillon, S., Persin, F., Pourcelly, G., & Gavach, C. (1996). Development of electrodialysis with bipolar membrane for the treatment of concentrated nitrate effluents. *Desalination*, *107*(2), 159-169. doi:[http://dx.doi.org/10.1016/S0011-9164\(96\)00155-5](http://dx.doi.org/10.1016/S0011-9164(96)00155-5)
- Hong, J., Chen, W., Wang, Y., Xu, C., & Xu, X. (2014). Life cycle assessment of caustic soda production: a case study in China. *Journal of Cleaner Production*, *66*, 113-120. doi:<https://doi.org/10.1016/j.jclepro.2013.10.009>
- Li, Y., Shi, S., Cao, H., Wu, X., Zhao, Z., & Wang, L. (2016). Bipolar membrane electrodialysis for generation of hydrochloric acid and ammonia from simulated ammonium chloride wastewater. *Water Research*, *89*(Supplement C), 201-209. doi:<https://doi.org/10.1016/j.watres.2015.11.038>
- Lv, Y., Yan, H., Yang, B., Wu, C., Zhang, X., & Wang, X. (2018). Bipolar membrane electrodialysis for the recycling of ammonium chloride wastewater: Membrane selection and process optimization. *Chemical Engineering Research and Design*, *138*, 105-115. doi:<https://doi.org/10.1016/j.cherd.2018.08.014>
- Mani, K. N. (1991). Electrodialysis water splitting technology. *Journal of Membrane Science*, *58*(2), 117-138. doi:[https://doi.org/10.1016/S0376-7388\(00\)82450-3](https://doi.org/10.1016/S0376-7388(00)82450-3)
- PCA. (2016a). PCA Ion Exchange Membranes: Technical Data Sheet. In: Heusweiler: PCA GmbH.
- Pronk, W., Biebow, M., & Boller, M. (2006d). Treatment of source-separated urine by a combination of bipolar electrodialysis and a gas transfer membrane. *Water Sci Technol*, *53*(3), 139-146.
- Sander, R. (2015). Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmos. Chem. Phys.*, *15*(8), 4399-4981. doi:10.5194/acp-15-4399-2015
- Shi, L., Hu, Y., Xie, S., Wu, G., Hu, Z., & Zhan, X. (2018). Recovery of nutrients and volatile fatty acids from pig manure hydrolysate using two-stage bipolar membrane electrodialysis. *Chemical Engineering Journal*, *334*, 134-142. doi:<https://doi.org/10.1016/j.cej.2017.10.010>
- Shuangchen, M., Tingting, H., Lan, M., Jingxiang, M., Gongda, C., & Jing, Y. (2015). Experimental study on desorption of simulated solution after ammonia carbon capture using bipolar membrane electrodialysis. *International Journal of Greenhouse Gas Control*, *42*, 690-698. doi:<https://doi.org/10.1016/j.ijggc.2015.09.020>
- Strathmann, H. (2010). Electrodialysis, a mature technology with a multitude of new applications. *Desalination*, *264*(3), 268-288. doi:<https://doi.org/10.1016/j.desal.2010.04.069>

Tongwen, X. (2002). Electro dialysis processes with bipolar membranes (EDBM) in environmental protection—a review. *Resources, Conservation and Recycling*, 37(1), 1-22.

doi:[https://doi.org/10.1016/S0921-3449\(02\)00032-0](https://doi.org/10.1016/S0921-3449(02)00032-0)

van Linden, N., Bandinu, G. L., Vermaas, D. A., Spanjers, H., & van Lier, J. B. (2020). Bipolar membrane electro dialysis for energetically competitive ammonium removal and dissolved ammonia production. *Journal of Cleaner Production*, 120788.

doi:<https://doi.org/10.1016/j.jclepro.2020.120788>

van Linden, N., Spanjers, H., & van Lier, J. B. (2019a). Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electro dialysis. *Water Research*, 114856. doi:<https://doi.org/10.1016/j.watres.2019.114856>

Ward, A. J., Arola, K., Thompson Brewster, E., Mehta, C. M., & Batstone, D. J. (2018). Nutrient recovery from wastewater through pilot scale electro dialysis. *Water Research*, 135, 57-65.

doi:<https://doi.org/10.1016/j.watres.2018.02.021>







## Chapter 5.

# Recovery of ammonia-water mixtures by vacuum membrane stripping

Based on: Selectivity of vacuum ammonia stripping using porous gas-permeable and dense pervaporation membranes under various hydraulic conditions and feed water compositions

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### Abstract

Simultaneous evaporation of water (H<sub>2</sub>O) during ammonia (NH<sub>3</sub>) stripping under vacuum dilutes the recovered NH<sub>3</sub> gas. Whereas porous gas-permeable membranes are already used for vacuum NH<sub>3</sub> stripping, the use of non-porous silica-based pervaporation (PV) membranes showed promising results in recent literature, with respect to more selective transfer of NH<sub>3</sub> compared to H<sub>2</sub>O. This chapter presents the assessment of the selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer ( $S_{\text{NH}_3/\text{H}_2\text{O}}$ ) for different types of membranes under various hydraulic conditions and for feed water compositions. The three following membranes were tested: a porous gas-permeable polytetrafluoroethylene (PTFE) membrane, a hydrophilic (Hybrid Silica PV) membrane and a hydrophobic polydimethylsiloxane PV (PDMS PV) membrane.

For all tested membranes,  $S_{\text{NH}_3/\text{H}_2\text{O}}$  ranged between 0.1 and 0.4, indicating that the transfer of NH<sub>3</sub> was consistently less preferred over the transfer of H<sub>2</sub>O. The preference for H<sub>2</sub>O over NH<sub>3</sub> transfer through the membranes at various hydraulic conditions and feed water compositions can be assigned to the similarity in polarity and kinetic diameter of NH<sub>3</sub> and H<sub>2</sub>O and the low relative concentration of NH<sub>3</sub> in the used feed waters (approximately 0.1 – 1.0 wt%). The PDMS PV membrane showed negligible NH<sub>3</sub> transfer and deteriorated rapidly during the NH<sub>3</sub> stripping experiments. The  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of both gas-permeable and PV membranes was higher for unsteady than for steady hydraulic conditions. Furthermore, the  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of the both PTFE and the Hybrid Silica decreased when the ionic strength of the feed water increased from 0.0 to 0.8 mol·L<sup>-1</sup> and when the NH<sub>3</sub> feed water concentration increased from 1 to 10 g·L<sup>-1</sup>. According to the results, the used PV membranes did not show selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer. In fact, the used PV membranes consistently had a lower  $S_{\text{NH}_3/\text{H}_2\text{O}}$  than the PTFE membrane. Hence, the dense silica-based PV membranes do not offer opportunities to recover gaseous NH<sub>3</sub> from water while decreasing the content of H<sub>2</sub>O in the recovered gas, compared to porous PTFE membranes.

### Keywords

ammonia; water vapour; stripping; selectivity; mass transfer coefficient; pervaporation;



## 5.1. Introduction

Chapter 1 of this thesis identifies vacuum membrane stripping (VMS) as a suitable technology to recover gaseous  $\text{NH}_3$  solutions. Subsequently, a literature review presented in Chapter 2 of this thesis confirms that VMS is a suitable technology for the production of  $\text{NH}_3$  solutions, but that water transfer due to evaporation leads to dilution of the recovered  $\text{NH}_3$  gas.

### 5.1.1. Evaporation of $\text{H}_2\text{O}$ during recovery of gaseous $\text{NH}_3$ from water

During  $\text{NH}_3$  recovery by vacuum stripping processes, such as vacuum membrane stripping (VMS) using porous gas-permeable membranes, stripping of  $\text{NH}_3$  is accompanied by the evaporation of  $\text{H}_2\text{O}$ , which dilutes the obtained gaseous  $\text{NH}_3$  (Ding et al., 2006; El-Bourawi et al., 2007; van Linden et al., 2022a). To obtain more concentrated  $\text{NH}_3$  gas, the concentration of  $\text{NH}_3$  in the feed water can be increased (He et al., 2018; Scheepers et al., 2020; van Linden et al., 2022a). Moreover, according to the study of van Linden et al. (2022a), increasing the feed water temperature at an  $\text{NH}_3$  feed concentration of  $10 \text{ g}\cdot\text{L}^{-1}$  from 25 to 35 °C results in an increase in  $\text{NH}_3$  concentration in the permeate from 8 to 11 wt%. However, a further increase in the feed water temperature to 45 and 55 °C leads to dilution of  $\text{NH}_3$  in the gaseous permeate to 5 and 4 wt%, respectively. To obtain more concentrated  $\text{NH}_3$  by VMS, the evaporation of  $\text{H}_2\text{O}$  must be minimised. To this end, a physical barrier for the transfer of  $\text{H}_2\text{O}$  that does not negatively affect the  $\text{NH}_3$  transfer may be introduced. Porous gas-permeable membranes are not considered to be effective barriers, because the pore size of about  $0.1 \mu\text{m}$  is at least two orders of magnitude larger than the kinetic diameter of transferred gases such as  $\text{NH}_3$  ( $< 1 \text{ nm}$ ). To recover more concentrated  $\text{NH}_3$  by vacuum stripping processes, the use of dense pervaporation (PV) membranes to more selectively transfer  $\text{NH}_3$  through the membrane was initially proposed by Yang et al. (2014).

### 5.1.2. Selectivity of $\text{NH}_3$ transfer through PV membranes

For PV, selectivity ( $S$ ) is defined as the ratio of the permeances of the respective gases permeating through the membrane, whereas the permeance describes the normalised transfer rate: the mass flux normalised for the driving force (Baker et al., 2010). Hence, selectivity ( $S_{i/j}$ ) describes the normalised transfer rate of gas 'i' with respect to another gas 'j'. In this view, selective transfer of 'i' over 'j' is considered when  $S_{i/j} > 1$ . Selective permeation of  $\text{NH}_3$  over hydrogen ( $\text{H}_2$ ) and  $\text{N}_2$  by using PV membranes proved to be feasible for gas separation, for the recovery of  $\text{NH}_3$  from gas mixtures consisting of the respective gases (Camus et al., 2006; Kanezashi et al., 2010):  $S_{\text{NH}_3/\text{H}_2}$  and  $S_{\text{NH}_3/\text{N}_2} > 1$ . Camus et al. (2006) showed that silica-based PV membranes had a seven and fourteen times higher  $\text{NH}_3$  permeance compared to the permeance of  $\text{H}_2$  and  $\text{N}_2$  when using mixtures of  $\text{NH}_3\text{-H}_2$  and  $\text{NH}_3\text{-N}_2$  gas as a feed at a temperature of 80 °C. Subsequently, Kanezashi et al. (2010) reported  $\text{H}_2$  permeances up to twenty times higher than the  $\text{NH}_3$  permeances for silica-based PV membranes when pure  $\text{H}_2$  and  $\text{NH}_3$  gas were used as the feed at a temperature of 50 °C. However, when mixtures of  $\text{NH}_3/\text{H}_2$  gas were used as feed at the same temperature, selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  took place ( $S_{\text{NH}_3/\text{H}_2}$  of 29), in agreement with Camus et al. (2006). Both Camus et al. (2006) and Kanezashi et al. (2010) attributed

the selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  to the adsorption of  $\text{NH}_3$  to the membrane material, which contained silica groups. According to [Kanezashi et al. \(2010\)](#),  $\text{NH}_3$  and  $\text{H}_2$  have a kinetic diameter of 0.33 and 0.26 nm, respectively. Hence, for pure gases, transfer of  $\text{H}_2$  is faster than the transfer of  $\text{NH}_3$  based on the higher reported permeances, but when gaseous  $\text{NH}_3$ - $\text{H}_2$  mixtures are present in the feed,  $\text{NH}_3$  adsorbs on the membrane interface and hinders the adsorption and permeation of  $\text{H}_2$ , resulting in selective transfer of  $\text{NH}_3$  over  $\text{H}_2$  ([Camus et al., 2006](#); [Kanezashi et al., 2010](#)).

### 5.1.3. Recovery of gaseous $\text{NH}_3$ from feed waters using PV membranes

In addition to the application to obtain more enriched permeate streams from gas mixtures by gas separation, PV membranes can also be used to remove and/or recover gases from a liquid feed such as water. According to the review of [Jyoti et al. \(2015\)](#), different types of PV membranes are used to allow for either selective transfer of water ( $\text{H}_2\text{O}$ ) or volatile organics from liquid  $\text{H}_2\text{O}$ -organics mixtures. For the selective transfer of  $\text{H}_2\text{O}$  from liquid  $\text{H}_2\text{O}$ -organics mixtures, hydrophilic PV membranes are used, whereas hydrophobic PV membranes are used for selective transfer of volatile organics, such as alcohols or volatile fatty acids.

Research of [Yang et al. \(2014\)](#) focused on the recovery of gaseous  $\text{NH}_3$  from liquid feed water, using silica-based PV membranes that were hydrothermally-treated by addition of iron and cobalt in the membrane material. [Yang et al. \(2014\)](#) did not report on the transfer selectivity of the PV membranes according to the proposed definition of [Baker et al. \(2010\)](#), but did report concentration factors up to 63 for a PV membrane for an  $\text{NH}_3$  feed concentration of  $0.8 \text{ g}\cdot\text{L}^{-1}$  at feed temperatures ranging between 45 and 50 °C. Because the concentration factor represents the ratio of the  $\text{NH}_3$  concentration in the permeate and the feed, the relatively high concentration factors suggest high transfer rates of  $\text{NH}_3$  compared to  $\text{H}_2\text{O}$ . In a follow-up study, [Yang et al. \(2016\)](#) stripped  $\text{NH}_3$  from liquid water using a PV membrane that contained a combination of silica and organic groups for hydrothermal stability in the selective layer and was further referred to as hybrid-silica. For an  $\text{NH}_3$  feed concentration of  $50 \text{ mg}\cdot\text{L}^{-1}$  and at a feed temperature of 45 °C, the authors reported a concentration factor of 12 and an  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of 0.5, indicating selective transfer of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  for the used PV membranes. Finally, [Yang et al. \(2018\)](#) assessed the effect of cobalt content in the selective layer of silica-based PV membranes on the transfer of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  and observed again selective transfer of  $\text{H}_2\text{O}$  over  $\text{NH}_3$  ( $S_{\text{NH}_3/\text{H}_2\text{O}} < 1$ ).

Hence, in currently available literature, there is no consensus on whether selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  can be achieved by using silica-based PV membranes. The differences in transfer selectivity observed in previous studies may be explained by the differences in applied experimental conditions, as [Yang et al. \(2014\)](#) and [Yang et al. \(2018\)](#) used configurations in which the membranes were submerged in the feed water, whereas [Yang et al. \(2016\)](#) used a cross-flow configuration. The mentioned studies did not describe the location of the selective layer on the membranes. The location of the selective layer of the membrane and the used configuration are key to control the hydraulic conditions, which affect polarisation effects at the membrane interface, which in their turn affect the mass transfer rates through the membrane ([Oliveira](#)

et al., 2001). Furthermore, the contradicting results on the transfer selectivity of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  also may be explained by differences in tested feed characteristics, such as feed temperature and  $\text{NH}_3$  feed concentration.

#### 5.1.4. Research objective

Currently available literature showed that silica-based PV membranes allow for selective transfer of  $\text{NH}_3$  over  $\text{N}_2$  and  $\text{H}_2$  when treating gas mixtures, but it remains unclear whether also selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  can be achieved when stripping  $\text{NH}_3$  from liquid water. Silica-based PV membranes are considered to be hydrophilic, indicating that these membranes allow for the transfer of  $\text{H}_2\text{O}$ . Currently, it is unknown whether hydrophobic silica-based PV membranes allow for selective transfer of  $\text{NH}_3$  when stripping  $\text{NH}_3$  from water. Furthermore, according to available literature, there is no clarity whether PV membranes have higher  $S_{\text{NH}_3/\text{H}_2\text{O}}$  compared to conventional porous gas-permeable membranes. Therefore, this chapter presents the assessment of the mass transfer rates and  $S_{\text{NH}_3/\text{H}_2\text{O}}$  of a porous gas-permeable membrane and dense hydrophilic and hydrophobic PV membranes while stripping  $\text{NH}_3$  from water, using the hydraulic conditions and the feed composition, in terms of  $\text{NH}_3$  feed concentration and ionic strength as variable operational conditions.



5.2. Materials and methods

5.2.1. Materials

For the porous gas-permeable membrane experiments, the same equipment and spacer-filled flat sheet membrane configuration as described in the study of [van Linden et al. \(2022a\)](#) was used. For the experiments with the PV membranes, again the same experimental set-up was used, except a stainless-steel membrane housing was used for the tubular PV membranes, including rubber rings at the ends of the PV membranes to ensure liquid and gas tightness. Figure 5-1 presents the experimental setup, including the membrane housings for the porous gas-permeable and PV membranes. The porous gas-permeable membrane was a Sterlitech polytetrafluoroethylene membrane (hereafter PTFE membrane) and the PV membranes were a hydrophilic Pervatech Hybrid Silica (hereafter Hybrid Silica PV membrane) and a hydrophobic Pervatech polydimethylsiloxane membrane (hereafter PDMS PV membrane). Table 5-1 presents an overview of the specific characteristics and measured dimensions of the used membranes.

The feed waters were prepared by the addition of Acros Organics 25 wt% ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) stock solution, or Sigma Aldrich ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) salt and Merck 1M sodium hydroxide ( $\text{NaOH}$ ) solution to demineralised water. The used  $\text{NH}_4\text{OH}$  solution,  $\text{NH}_4\text{HCO}_3$  salt and  $\text{NaOH}$  solution were all analytical grade. The prepared feed waters consisted of  $\text{NH}_4\text{HCO}_3$  because bicarbonate ( $\text{HCO}_3^-$ ) is often the main anion in nitrogen-loaded (N-loaded) residual streams, such as reject waters, urine and industrial condensates. All experimental runs were conducted in at least triplicate.

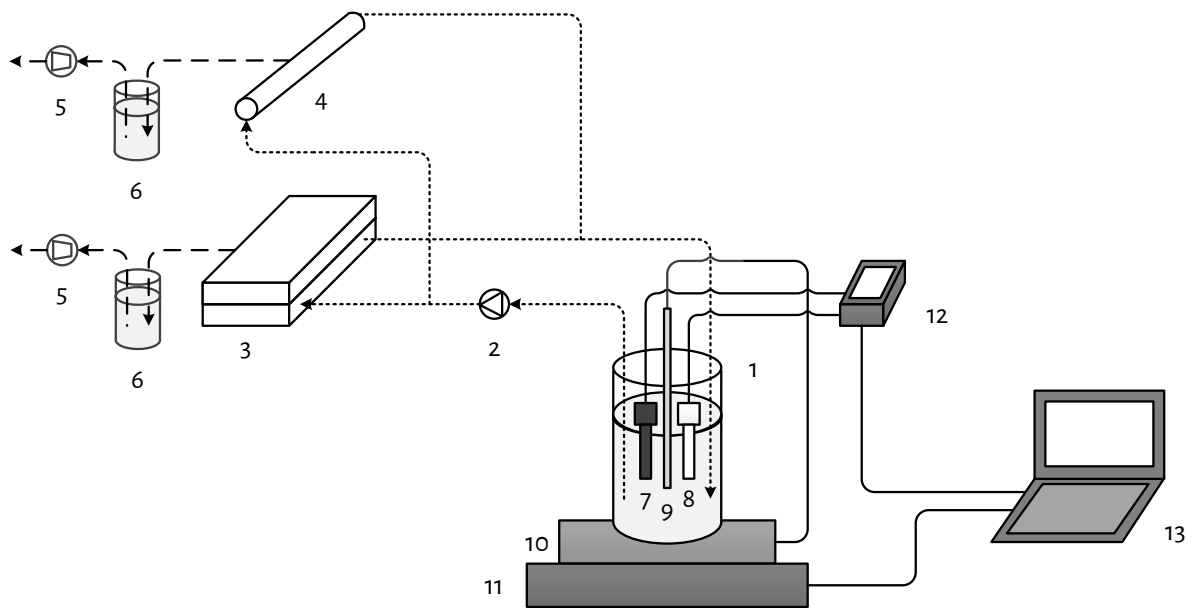


Figure 5-1 - Schematic representation of the used experimental set-up including feed water bottle (1), peristaltic pump (2), gas-permeable membrane housing including membrane (3), PV membrane housing including membrane (4), vacuum pump (5), pressure sensor (6), cooled permeate scrubber (7), EC-sensor (8), pH-sensor (9), temperature sensor (10), integrated heating and mixing plate (11), balance (12), multimeter (13) and laptop (14).

Table 5-1 - Key characteristics of the membranes used for the NH<sub>3</sub> stripping experiments.

	Unit	Porous gas-permeable (PTFE) membrane	Hydrophilic (Hybrid Silica) PV membrane	Hydrophobic (PDMS) PV membrane
Channel height	mm	2.3	-	-
Channel width	mm	39	-	-
Internal diameter	mm	-	7	7
Membrane thickness	mm	0.2	1.5	1.5
Membrane length	mm	87	250	250
Effective membrane area	m <sup>2</sup>	0.0034	0.0055	0.0055
Pore size <sup>5</sup>	nm	100	0.5 <sup>6</sup>	-
Selective membrane layer	-	PTFE <sup>1</sup>	Hybrid Silica – AR <sup>3</sup>	PDMS <sup>4</sup>
Membrane material	-	PTFE – PP <sup>2</sup>	α-Al <sub>2</sub> O <sub>3</sub>	α-Al <sub>2</sub> O <sub>3</sub>
Maximum temperature <sup>5</sup>	°C	82	150	70
pH range <sup>5</sup>		1 - 14	0.5 – 8.5	1 - 12

<sup>1</sup>PTFE = polytetrafluoroethylene, <sup>2</sup>PP = polypropylene, <sup>3</sup>Hybrid Silica – AR = organic (methyl and ethanol) groups and silica (Yang et al., 2016), <sup>4</sup>PDMS = polydimethylsiloxane, <sup>5</sup>according to the supplier, <sup>6</sup>(van Veen et al., 2011)

5.2.2. Performance indicators

For the assessment of the  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , the overall mass transfer coefficient ( $K_o$ ) for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  was determined. The  $K_o$  normalises the mass flux with respect to the respective driving force for the transfer of gases, which for  $\text{NH}_3$  and  $\text{H}_2\text{O}$  is the vapour pressure difference between the liquid feed water and the gaseous permeate.  $K_o$  is usually described by a series-resistance model, consisting of three separate components: the mass transfer coefficients for the liquid feed water ( $K_f$ ), the membrane ( $K_m$ ) and the gaseous permeate ( $K_p$ ) as described in Eq. 5-1.

$$\frac{1}{K_o} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_p} \quad \text{Eq. 5-1}$$

Where,  $K_o$ ,  $K_f$ ,  $K_m$  and  $K_p$  = the overall, the liquid feed water, the membrane, and the gaseous permeate mass transfer coefficient (in  $\text{s}\cdot\text{m}^{-1}$ ), respectively.

$K_p$  is negligible for vacuum stripping applications due to the low absolute pressure of the gaseous permeate, according to the studies of [Bandini et al. \(1992\)](#), [Lawson and Lloyd \(1997\)](#) and [Jyoti et al. \(2015\)](#).

$K_f$  can be determined as a function of the hydraulic conditions and the diffusion characteristics of the dissolved gases in the feed water ([Oliveira et al., 2001](#); [Chiam & Sarbatly, 2013](#)), but this is only applicable for uniform hydraulic conditions of the feed water. At the interface of the feed water and the membrane, the hydraulic conditions are different from those in the bulk phase, due to polarisation phenomena. For stripping of gases from water in vacuum configurations, three polarisation phenomena are relevant:

1. Temperature polarisation;
2. Ion accumulation concentration polarisation;
3. Gas depletion concentration polarisation;

Firstly, temperature polarisation, which is the decrease in temperature of the feed water at the membrane interface as a result of heat transport due to the evaporation of  $\text{H}_2\text{O}$  ([Lawson & Lloyd, 1997](#); [Martínez-Díez & Vázquez-González, 1999](#)). Secondly, accumulation concentration polarisation, describing the increase in concentration of non-volatile solutes such as ions at the membrane interface as a result of the evaporation of  $\text{H}_2\text{O}$  ([Lawson & Lloyd, 1997](#); [Martínez-Díez & Vázquez-González, 1999](#)). Thirdly, gas depletion concentration polarisation, which is the decrease in concentration of volatile solutes such as dissolved gases at the membrane interface, caused by a faster transfer rate of the respective gas through the membrane than the transfer rate from bulk-phase of the feed liquid to the membrane interface ([Bandini et al., 1992](#); [Wijmans et al., 1996](#)).

Finally,  $K_m$  depends on the type of membrane. For porous gas-permeable membranes, the main mass transfer mechanism is Knudsen diffusion because the ratio of the kinetic diameter of the gas molecule and pore size is smaller than 0.05 ([Lawson & Lloyd, 1997](#); [Khayet & Matsuura, 2004](#); [El-Bourawi et al., 2007](#)), whereas PV membranes are dense membranes for which the main mass transfer mechanisms rely on sorption/dissolution and diffusion ([Jyoti et al., 2015](#)). In general, for both types of membranes,  $K_m$  is a function of the specific membrane characteristics, such as thickness, and the temperature of the membranes

(Lawson & Lloyd, 1997; Jyoti et al., 2015). However, due to temperature polarisation, the actual temperature of the membrane is different from the temperature of the bulk phase of the liquid feed.

The mentioned three polarisation phenomena occur simultaneously during vacuum stripping of gases such as NH<sub>3</sub> from water and do not only affect the mass transfer coefficients K<sub>f</sub> and K<sub>m</sub>. The polarisation phenomena also affect the driving force of NH<sub>3</sub> and H<sub>2</sub>O transfer, because the local accumulation of ions, the local depletion of dissolved NH<sub>3</sub> and the lower temperature at the membrane interface compared to the bulk feed water temperature affect the vapour pressures of NH<sub>3</sub> and H<sub>2</sub>O at the liquid side of the membrane. Understanding the mass transfer in vacuum membrane stripping processes, including all three polarisation phenomena and their interdependency is lacking in current literature. Therefore, this chapter does not present specific results on the investigation of the respective contribution of K<sub>f</sub> and K<sub>m</sub> separately, but only K<sub>o</sub>.

To calculate the K<sub>o</sub> of NH<sub>3</sub> (K<sub>o,NH<sub>3</sub></sub>), various studies used the logarithmic decrease in NH<sub>3</sub> concentration over time, in combination with the initial feed volume (El-Bourawi et al., 2007; He et al., 2018). However, this method of determining the K<sub>o</sub> only applies to the transfer of the solute (NH<sub>3</sub>) and not to the solvent (H<sub>2</sub>O). Moreover, this method assumes a fixed feed volume, whereas the feed water volumes decrease due to the evaporation of H<sub>2</sub>O during the stripping process. Therefore, the K<sub>o</sub> for NH<sub>3</sub> and H<sub>2</sub>O were determined using the measured fluxes and the calculated vapour pressure difference, in line with the study of (Jyoti et al., 2015). The NH<sub>3</sub> (Eq. 5-2) and H<sub>2</sub>O (Eq. 5-3) fluxes were determined using the mass changes in the feed water over time. The vapour pressures of NH<sub>3</sub> and H<sub>2</sub>O in the liquid feed were obtained by simulations using chemical equilibrium simulation software named PHREEQC, whereas the vapour pressures of NH<sub>3</sub> (Eq. 5-4) and H<sub>2</sub>O (Eq. 5-5) in the gaseous permeate were calculated using the ratio of the fluxes and the absolute pressure of the permeate. More details on the determination of the fluxes can be found in the study of van Linden et al. (2022a). Based on the NH<sub>3</sub> and H<sub>2</sub>O fluxes and vapour pressures, the K<sub>o,NH<sub>3</sub></sub> and K<sub>o,H<sub>2</sub>O</sub> were determined using Eq. 5-6 and Eq. 5-7, respectively. Finally, S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> was determined using Eq. 5-8, as the ratio of K<sub>o,NH<sub>3</sub></sub> and K<sub>o,H<sub>2</sub>O</sub>, in line with Camus et al. (2006) and Baker et al. (2010).

$$J_{NH_3} = \frac{-(m_{NH_3,i+1} - m_{NH_3,i})}{A_m \cdot (t_{i+1} - t_i)} \quad \text{Eq. 5-2}$$

$$J_{H_2O} = \frac{-(m_{H_2O,i+1} - m_{H_2O,i})}{A_m \cdot (t_{i+1} - t_i)} \quad \text{Eq. 5-3}$$

Where, J<sub>NH<sub>3</sub></sub> and J<sub>H<sub>2</sub>O</sub> = NH<sub>3</sub> and H<sub>2</sub>O flux (in kg·m<sup>-2</sup>·s<sup>-1</sup>), m<sub>NH<sub>3</sub>,i</sub> and m<sub>H<sub>2</sub>O,i</sub> = NH<sub>3</sub> and H<sub>2</sub>O mass at time instant 'i', respectively (in kg), A<sub>m</sub> = membrane area (in m<sup>2</sup>) and t<sub>i</sub> = time instant 'i' (in s).

$$p_{p,NH_3} = \frac{J_{NH_3}}{J_{NH_3} + J_{H_2O}} \cdot p_p \quad \text{Eq. 5-4}$$

$$p_{p,H_2O} = \frac{J_{H_2O}}{J_{NH_3} + J_{H_2O}} \cdot p_p \quad \text{Eq. 5-5}$$

Where,  $p_{p,NH_3}$  and  $p_{p,H_2O}$  = vapour pressure of  $NH_3$  and  $H_2O$  in the gaseous permeate, respectively (in Pa =  $kg \cdot m^{-2} \cdot s^{-1}$ ) and  $p_p$  = permeate pressure (in Pa =  $kg \cdot m^{-2} \cdot s^{-1}$ ,  $p_p = 1,500$  Pa).

$$K_{o,NH_3} = \frac{J_{NH_3}}{p_{f,NH_3} - p_{p,NH_3}} \quad \text{Eq. 5-6}$$

$$K_{o,H_2O} = \frac{J_{H_2O}}{p_{f,H_2O} - p_{p,H_2O}} \quad \text{Eq. 5-7}$$

Where  $K_{o,NH_3}$  and  $K_{o,H_2O}$  = mass transfer coefficient of  $NH_3$  and  $H_2O$ , respectively (in  $s \cdot m^{-1}$ ) and  $p_{f,NH_3}$  and  $p_{f,H_2O}$  = vapour pressure of  $NH_3$  and  $H_2O$  in the liquid feed water (in Pa =  $kg \cdot m^{-2} \cdot s^{-1}$ ).

$$S_{NH_3/H_2O} = \frac{K_{NH_3}}{K_{H_2O}} \quad \text{Eq. 5-8}$$

Where  $S_{NH_3/H_2O}$  = selectivity of  $NH_3$  over  $H_2O$  transfer (no unit).

### 5.2.3. Experimental conditions

For all conducted experiments in this chapter, the vacuum pressure at the permeate side was fixed at 1,500 Pa by a vacuum pump, while unsteady hydraulic flow conditions were maintained unless stated otherwise. Moreover, the temperature of the feed water was 35 °C, unless stated differently, as in the study of [van Linden et al. \(2022a\)](#), stripping  $NH_3$  at 35 °C resulted in the most concentrated  $NH_3$  in the vapour permeate. Initially, the transfer of  $H_2O$  through the various membranes was assessed at three different feed water temperatures: 25, 35 and 45 °C. Subsequently, unless stated differently, feed waters with a feed water concentration of 1 g·L<sup>-1</sup> of  $NH_3$  as  $NH_4OH$  were used to assess the  $S_{NH_3/H_2O}$  for the various membranes, similar to [Yang et al. \(2014\)](#) and [Yang et al. \(2016\)](#).

#### 5.2.3.1. Hydraulic conditions

We assessed the effect of the hydraulic conditions on the  $S_{NH_3/H_2O}$ , by using various Reynolds numbers, corresponding to steady (poorly mixed, or laminar) or unsteady (well-mixed, or transition/turbulent) hydraulic conditions. Unsteady flow conditions refer to the hydraulic flow conditions with good mixing properties. The unsteady flow conditions cover the range between laminar and turbulent hydraulic conditions. The Reynolds number is a function of the feed water properties, the cross-flow velocity and the hydraulic diameter of the flow channel (Eq. 5-9). According to the study of [Oliveira et al. \(2001\)](#), the hydraulic flow conditions are unsteady at a Reynolds number of 2,300 in tubular channels, whereas according to [Mojab et al. \(2014\)](#) unsteady hydraulic conditions in spacer-filled channels correspond to a Reynolds number of 500. By taking the feed water properties into account, the Reynolds numbers were set by controlling the cross-flow velocity through the flow channels using the peristaltic pump.

$$Re = \frac{\rho_f \cdot u \cdot d_h}{\mu_f} \quad \text{Eq. 5-9}$$

Where  $\rho_f$  = feed water density (in  $\text{kg}\cdot\text{m}^{-3}$ ),  $u$  = average cross-flow velocity (in  $\text{m}\cdot\text{s}^{-1}$ ),  $d_h$  = hydraulic diameter (in m),  $\mu_w$  = dynamic viscosity of feed water (in  $\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$ ).

The hydraulic diameter relates the surface tension and the shear stress of a liquid flowing through a channel. For circular open channels (for the tubular PV membranes), the hydraulic diameter is equal to the diameter of the respective channel. For spacer-filled channels (for the flat-sheet PTFE membrane), the determination of the hydraulic diameter is more elaborate, as the liquid is in contact with both the spacer and the perimeter of the flow channel. To this end, [Schock and Miquel \(1987\)](#) proposed a general expression for the hydraulic diameter in spacer-filled channels (Eq. 5-10), as a function of the void volume and the wetted surface area of the flow channel.

$$d_h = \frac{4 \cdot V_v}{A_w} \quad \text{Eq. 5-10}$$

Where,  $V_v$  = void volume (in  $\text{m}^3$ ) and  $A_w$  = wetted surface area (in  $\text{m}^2$ ).

The determination of the void volume and the wetted surface area of the flow channels as a function of the specific channel geometries are described in detail in the Supporting Information of the paper of [van Linden et al. \(2022b\)](#). The hydraulic diameters were 2.3 and 7.0 mm for the PTFE and PV membranes, respectively. For the PTFE membrane, the range of the cross-flow velocity was  $8 - 20 \text{ cm}\cdot\text{s}^{-1}$  and  $14 - 36 \text{ cm}\cdot\text{s}^{-1}$  for the PV membranes. The cross-flow velocities for the PTFE membrane to achieve unsteady hydraulic conditions are lower compared to the PV membranes, because the PTFE membrane is in contact with a spacer (to enhance mixing), while the PV membranes are open tubular channels.

#### 5.2.3.2. NH<sub>3</sub> feed water concentration and ionic strength of the feed water

Current literature mainly reports on the transfer of NH<sub>3</sub> from feed water through membranes, in which the NH<sub>3</sub> is only present as NH<sub>4</sub>OH. Only the study of [He et al. \(2018\)](#) and the study of [van Linden et al. \(2022a\)](#) did not use NH<sub>4</sub>OH solutions as feed water, but used pre-treated biogas slurry and NH<sub>4</sub>HCO<sub>3</sub> solutions at a pH of 10, respectively. Whereas  $1 \text{ g}\cdot\text{L}^{-1}$  is a representative concentration of NH<sub>3</sub> in N-loaded residual waters,  $10 \text{ g}\cdot\text{L}^{-1}$  represents the concentration of NH<sub>3</sub> in pre-concentrated streams ([Deng et al., 2021](#)). Obtaining NH<sub>3</sub> concentrations up to  $10 \text{ g}\cdot\text{L}^{-1}$  can be achieved by using electrodialysis to concentrate NH<sub>4</sub><sup>+</sup> from  $1.5$  to  $10 \text{ g}\cdot\text{L}^{-1}$  ([van Linden et al., 2019a](#)), followed by the addition of chemicals to increase the solution pH, or by using bipolar membrane electrodialysis to directly obtain concentrated NH<sub>3</sub> without chemical addition ([van Linden et al., 2020](#)). Because various N-loaded residual waters, typically contain NH<sub>4</sub><sup>+</sup> in combination with HCO<sub>3</sub><sup>-</sup> as the main anion, the addition of NaOH to obtain concentrated NH<sub>3</sub> from feed water with high NH<sub>4</sub><sup>+</sup> concentrations results in a high ionic strength, as a result of the presence of Na<sup>+</sup>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>. The presence of ions affects the vapour pressure of NH<sub>3</sub> in two ways. On the one hand, when the ionic strength increases, the equilibrium between NH<sub>4</sub><sup>+</sup> and NH<sub>3</sub> shifts towards NH<sub>4</sub><sup>+</sup>, according to chemical equilibrium simulations performed with PHREEQC software. On the other hand, the solubility of gases decreases when the ionic strength increases, which is called the salting-out effect, increasing the vapour pressure. According to Figure 5-2, the vapour pressure of NH<sub>3</sub> increases linearly when the ionic strength of the feed water

increases, indicating that the salting-out effect is stronger than the effect of the ionic strength on the equilibrium between  $\text{NH}_3$  and  $\text{NH}_4^+$ . Furthermore, an increase in ionic strength results in a linear decrease in  $\text{H}_2\text{O}$  vapour pressure according to Raoult's Law. Hence, by increasing the ionic strength of the feed water, the  $\text{NH}_3$  vapour pressure increases, while the  $\text{H}_2\text{O}$  vapour pressure decreases. The effect of the ionic strength on the vapour pressure of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  is similar for feed waters with  $\text{NH}_3$  concentrations of 1 and 10  $\text{g}\cdot\text{L}^{-1}$ . However, in addition to the effect of the ionic strength on the vapour pressures, the ionic strength also affects the resistance to mass transfer of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ . Due to the evaporation of  $\text{H}_2\text{O}$ , ions accumulate at the membrane interface (ion accumulation concentration polarisation), which can hinder the transfer of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , particularly under steady hydraulic conditions.

We assessed the effect of ionic strength on  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , because the presence of ions affects both the vapour pressure of dissolved gases (salting-out effect) and the mass transfer coefficient (ion accumulation concentration polarisation). To assess the effect of the  $\text{NH}_3$  feed concentration and ionic strength on  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , various feed waters containing dissolved  $\text{NH}_3$  were prepared, with initial concentrations of 1 and 10  $\text{g}\cdot\text{L}^{-1}$  as  $\text{NH}_4\text{OH}$  and  $\text{NH}_4\text{HCO}_3$  (at a pH of 10 by addition of  $\text{NaOH}$ ). According to chemical equilibrium simulations, the ionic strength of feed water consisting of  $\text{NH}_4\text{OH}$  is negligible, whereas feed waters consisting of  $\text{NH}_4\text{HCO}_3$  at a pH of 10 have an ionic strength of 0.1 and 0.8  $\text{mol}\cdot\text{L}^{-1}$  at  $\text{NH}_3$  feed water concentration of 1 and 10  $\text{g}\cdot\text{L}^{-1}$ , respectively. For these calculations, the contribution of both  $\text{NH}_4\text{HCO}_3$  and  $\text{NaOH}$  to the ionic strength were taken into account.

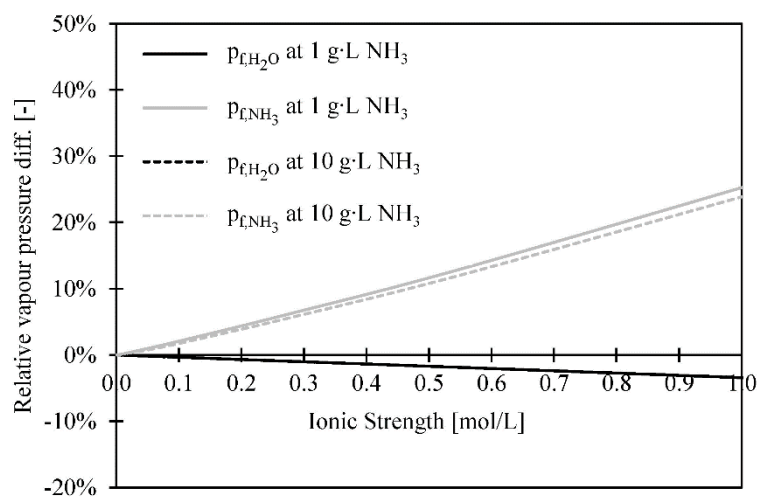


Figure 5-2 - The calculated vapour pressures of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in water with an  $\text{NH}_3$  feed water concentration of 1 and 10  $\text{g}\cdot\text{L}^{-1}$ , as a function of the ionic strength of the feed water. The vapour pressures were calculated using PHREEQC simulation software, using the phreeqc.dat database.

### 5.3. Results and discussion

#### 5.3.1. H<sub>2</sub>O transfer through the various membranes as a function of the feed temperature

Initially, the transfer rate of H<sub>2</sub>O as the H<sub>2</sub>O flux and the  $K_{o,H_2O}$  through the membranes was assessed at various temperatures, using water as a feed without dissolved gaseous and ions, at unsteady hydraulic conditions. Figure 5-3A presents the H<sub>2</sub>O fluxes as a function of the feed water temperature for the PTFE, Hybrid Silica PV and PDMS PV membrane. The reported values represent averages of at least triplicate experimental runs. At a feed water temperature of 25 °C, the H<sub>2</sub>O flux for the PTFE membrane was 12.0 kg·m<sup>-2</sup>·h<sup>-1</sup>, compared to 2.3 and 0.4 kg·m<sup>-2</sup>·h<sup>-1</sup> for the Hybrid Silica PV and PDMS PV membrane, respectively. By increasing the feed water temperature to 45 °C, the H<sub>2</sub>O fluxes increased to 24.5, 6.3 and 0.7 kg·m<sup>-2</sup>·h<sup>-1</sup> for the PTFE, Hybrid Silica PV and PDMS PV membranes, respectively, because the vapour pressure of H<sub>2</sub>O and thus the driving force increased as a function of temperature. The H<sub>2</sub>O flux for the PTFE membrane was at least four times higher than the H<sub>2</sub>O flux for the Hybrid Silica PV membrane, which in its turn was at least five times higher than the H<sub>2</sub>O flux of the PDMS PV membrane.

Because the same feed water temperature range and same vacuum pressure were applied for the experiments, the higher H<sub>2</sub>O fluxes of the PTFE membrane compared to the PV membranes are explained by the higher  $K_{o,H_2O}$  of the PTFE membrane (ranging between  $1 \cdot 10^{-6}$  and  $2 \cdot 10^{-6}$  s·m<sup>-1</sup>) compared to the  $K_{o,H_2O}$  of the Hybrid Silica PV (ranging between  $2 \cdot 10^{-7}$  and  $4 \cdot 10^{-7}$  s·m<sup>-1</sup>) and the PDMS PV membrane (ranging between  $7 \cdot 10^{-8}$  and  $2 \cdot 10^{-7}$  s·m<sup>-1</sup>), as presented in Figure 5-3B. The difference in  $K_{o,H_2O}$  between the PTFE membrane and the PV membranes can be assigned to the differences in selective layers of the membranes. The PTFE membrane had pores of 0.1 μm, whereas the Hybrid Silica PV and PDMS PV membranes were dense membranes, resulting in lower transfer rates of H<sub>2</sub>O than compared to the porous PTFE membrane. The difference in  $K_{o,H_2O}$  between the Hybrid Silica PV and the PDMS PV membrane can be explained by the functional groups present in the selective layers of the respective membranes. The selective layer of the Hybrid Silica PV membrane was hydrophilic and contained polar organosilica groups, allowing for the permeation of polar H<sub>2</sub>O molecules. On the contrary, the selective layer of the PDMS PV membrane was hydrophobic, which hindered the dissolution of H<sub>2</sub>O in the membrane and the subsequent diffusion of H<sub>2</sub>O through the membrane.

According to Figure 5-3B, the  $K_{o,H_2O}$  of all three membranes decreased when the feed water temperature increased. The decrease of  $K_{o,H_2O}$  as a function of the increasing feed water temperature can be assigned to a stronger effect of temperature polarisation (Martínez-Díez & Vázquez-González, 1999), as no ions or dissolved gases were present in the feed water. For the PTFE membrane, the decrease in  $K_{o,H_2O}$  as a function of the feed water temperature can be assigned to the decrease in  $K_m$ , which decreases as a function of the temperature according to Knudsen diffusion. In addition, for the PV membranes, the mass transfer through the membranes can be described by sorption-diffusion models. When the temperature increases, diffusion increases, while sorption decreases. Therefore, the decrease in  $K_{o,H_2O}$  of the PV membranes as a function of



the increasing feed water temperature may, besides temperature polarisation, also be caused by the effect of the feed water temperature on the sorption and diffusion mechanisms taking place during the transfer of  $H_2O$ . However, because the temperature at the interface of the liquid feed water and the membranes was not determined, it remains unclear which component of the series resistance model for mass transfer (Eq. 5-1) caused the decrease of the  $K_{o,H_2O}$  as a function of the increasing feed water temperature.

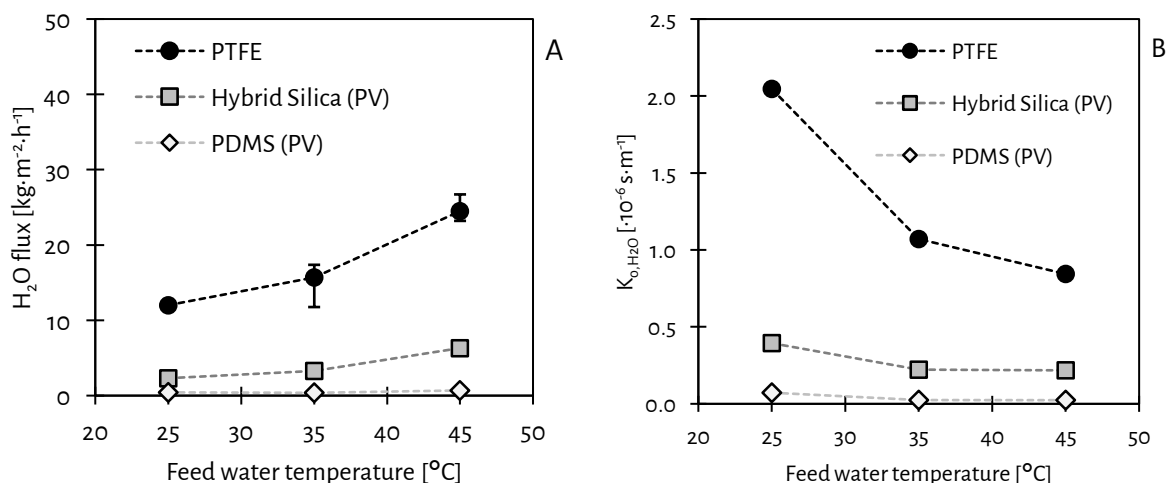


Figure 5-3 - The  $H_2O$  fluxes (A) and the  $K_{o,H_2O}$  (B) of the gas permeable PTFE membrane and the hydrophilic Hybrid Silica PV and hydrophobic PV membrane as a function of the feed water temperature. The reported values and error bars represent the average and the minimum and maximum measurements of at least three replicate experiments.

### 5.3.2. Selectivity of $NH_3$ over $H_2O$ transfer for various membranes

Figure 5-4A presents the fluxes of both  $NH_3$  and  $H_2O$  for the various membranes. The  $H_2O$  and  $NH_3$  fluxes of the PTFE membrane were 11 and 0.11  $kg \cdot m^{-2} \cdot h^{-1}$ , respectively. For the Hybrid Silica PV membrane, the  $H_2O$  flux was 4  $kg \cdot m^{-2} \cdot h^{-1}$  and the  $NH_3$  flux was 0.02  $kg \cdot m^{-2} \cdot h^{-1}$ . Furthermore, the  $H_2O$  flux for the PDMS PV membrane was 1  $kg \cdot m^{-2} \cdot h^{-1}$ , but the  $NH_3$  flux was negligible. Moreover, the selective layer of the PDMS PV membrane deteriorated rapidly during the experiments (see Figure 5-5), indicating that treating alkaline feed waters with an  $NH_3$  concentration of 1  $g \cdot L^{-1}$  was not possible for periods exceeding three hours. Therefore, this chapter does not further report on the applicability of the PDMS PV membrane.

The  $K_{o,H_2O}$  of the Hybrid Silica PV ( $3 \cdot 10^{-8} s \cdot m^{-1}$ ) and PDMS PV ( $7 \cdot 10^{-8} s \cdot m^{-1}$ ) membranes were again (also in 5.3.1.) lower compared to the PTFE membrane  $K_{o,H_2O}$  ( $8 \cdot 10^{-7} s \cdot m^{-1}$ ), caused by the lower resistance of  $H_2O$  transfer through the PTFE membrane. The lower resistance of  $H_2O$  transfer for the PTFE membrane compared to the Hybrid Silica PV membrane, which is expressed as higher  $H_2O$  flux and higher  $K_{o,H_2O}$ , can mainly be assigned to the membrane characteristics. According to Table 5-1, the pore size of the PTFE membrane was orders of magnitude higher compared to the PV membranes, while also the membrane thickness of the PTFE membrane was lower compared to the PV membranes. Hence, both the higher pore size and the lower membrane thickness contributed to the higher  $H_2O$  transfer rates through the PTFE membrane compared

to the PV membranes. Furthermore, the  $K_{o,NH_3}$  of the PTFE membrane ( $3 \cdot 10^{-7} \text{ s} \cdot \text{m}^{-1}$ ) was more than seven times higher than the Hybrid Silica PV ( $4 \cdot 10^{-7} \text{ s} \cdot \text{m}^{-1}$ ). The differences in  $NH_3$  flux and  $K_{o,NH_3}$  between the PTFE membrane and Hybrid Silica PV membrane can again be assigned to the pore size and the thickness of the respective membranes. Due to the negligible  $NH_3$  flux, the  $K_{o,NH_3}$  of the PDMS PV membrane was not determined.

The PTFE membrane showed a preference to permeate  $H_2O$  over  $NH_3$  indicated by the  $S_{NH_3/H_2O}$  of 0.3. The  $S_{NH_3/H_2O}$  of the PTFE membrane was higher than the  $S_{NH_3/H_2O}$  of the Hybrid Silica PV membrane (0.2). Hence, the Hybrid Silica PV did not show an increased preference to permeate  $NH_3$  compared to  $H_2O$ , in contrast to the findings of [Yang et al. \(2014\)](#), but in line with the findings of [Yang et al. \(2016\)](#). The adsorption of  $NH_3$  on the silica groups of the PV membranes, leading to blocking of the  $H_2O$  transfer, as described by [Yang et al. \(2014\)](#), was not present or not strong enough to promote selective  $NH_3$  permeation. This blocking mechanism was responsible for the selective transfer of  $NH_3$  over  $H_2$  in studies conducted by [Camus et al. \(2006\)](#) and [Kanezashi et al. \(2010\)](#). However, in contrast to the non-polar  $H_2$ ,  $NH_3$  (dipole moment of 1.47 D) and  $H_2O$  (dipole moment of 1.85 D) are both polar molecules ([Lide & Haynes, 2011](#)) and both bind with the polar silica groups at the selective layer of the Hybrid Silica PV membrane. In fact,  $H_2O$  is more polar than  $NH_3$  and probably bonded stronger with the selective layer of the Hybrid Silica PV membrane, contributing to the lower  $S_{NH_3/H_2O}$ . Furthermore,  $H_2O$  was more abundantly present in the bulk phase of the feed water than  $NH_3$  (> 99 wt%), as the feed water  $NH_3$  concentration was  $1 \text{ g} \cdot \text{L}^{-1}$ , corresponding to 0.1 wt%. Therefore, also gas depletion concentration polarisation affected the transfer of  $NH_3$ , possibly explaining the preference of  $H_2O$  over  $NH_3$  transfer.

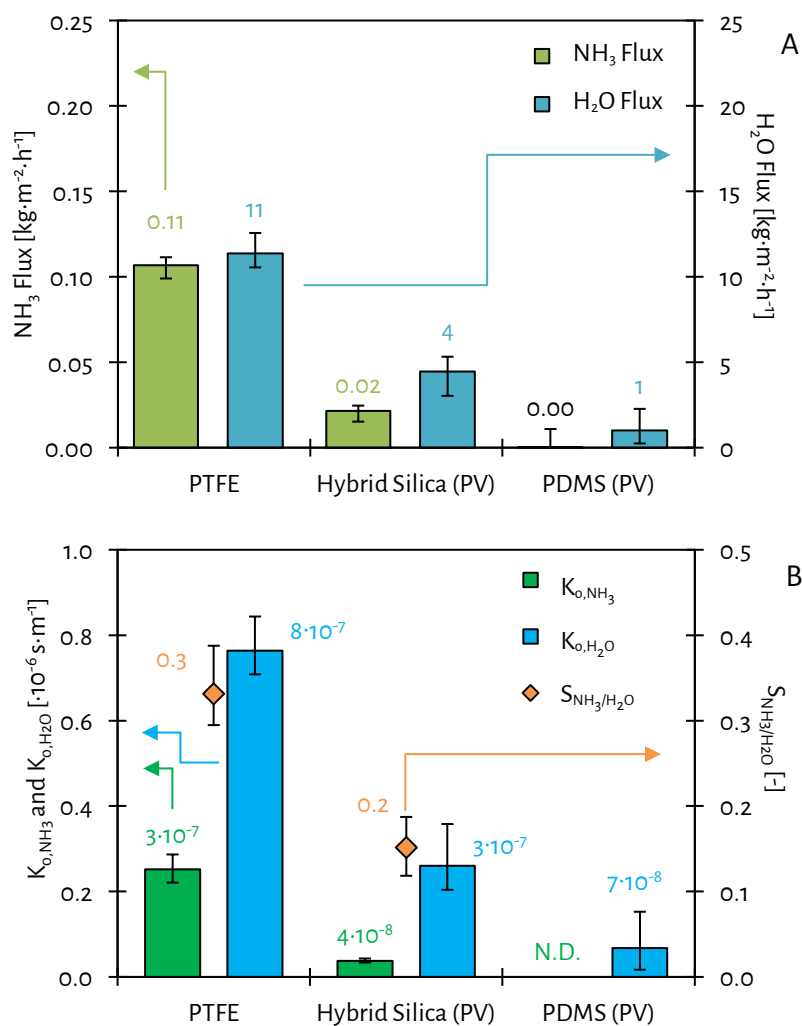


Figure 5-4 - The NH<sub>3</sub> (A) and H<sub>2</sub>O fluxes and the K<sub>0,NH<sub>3</sub></sub>, K<sub>0,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> (B) of the various membranes for stripping NH<sub>3</sub> from feed waters with an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup> (as NH<sub>4</sub>OH) at a feed water temperature of 35 °C at unsteady hydraulic conditions. The reported values and error bars represent the average and the minimum and maximum measurements of at least three replicate experiments. N.D. = not determined (too low flux).

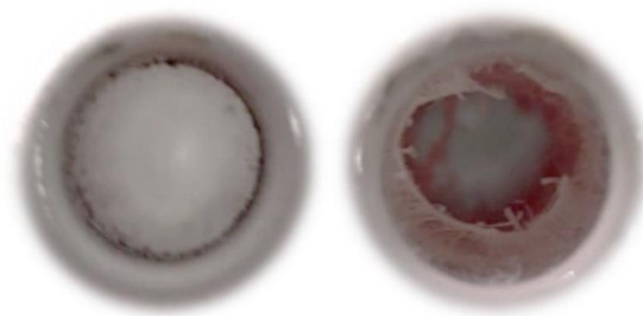


Figure 5-5 - A new PDMS PV membrane (left) and a deteriorated PDMS PV membrane (right) after exposure to feed water of 35 °C with an NH<sub>3</sub> concentration of 1 g·L<sup>-1</sup> for less than six hours.

5.3.3. Selectivity of NH<sub>3</sub> over H<sub>2</sub>O under various hydraulic conditions

5.3.3.1. Identification of hydraulic condition ranges

According to the studies of [Oliveira et al. \(2001\)](#) and [Mojab et al. \(2014\)](#), unsteady flow regions for tubular and spacer-filled channels start at a Reynolds number of 2,300 and 500, respectively. Figure 5-6A and Figure 5-6B present the H<sub>2</sub>O flux as a function of the Reynolds number for the PTFE and the Hybrid Silica PV membrane, respectively, when using demineralised water as feed water. For the PTFE membrane, the H<sub>2</sub>O flux was 11 kg·m<sup>-2</sup>·h<sup>-1</sup> up to a Reynolds number of 300. The H<sub>2</sub>O flux increased to 15 kg·m<sup>-2</sup>·h<sup>-1</sup> when the Reynolds number increased to 400 and remained stable when the Reynolds number further increased to 500 and 600. For the Hybrid Silica PV membrane, the H<sub>2</sub>O flux increased from 3 to 4 kg·m<sup>-2</sup>·h<sup>-1</sup> when the Reynolds number increased from 1,000 to 2,400 and remained 4 kg·m<sup>-2</sup>·h<sup>-1</sup> when the Reynolds number further increased to 3,000, 4,000 and 5,000. Hence, the indicated Reynolds numbers for steady and unsteady hydraulic conditions were in line with the changes in H<sub>2</sub>O flux for both spacer-filled rectangular and open tubular channels ([Oliveira et al., 2001](#); [Mojab et al., 2014](#)).

Because during the H<sub>2</sub>O permeation experiments at various Reynolds numbers the driving force for H<sub>2</sub>O transfer was equal, as the same feed water temperature and vacuum pressure were used, the increase in H<sub>2</sub>O flux due to the shift from steady to unsteady hydraulic conditions was caused by an increase in  $K_{o,H_2O}$ . By shifting from steady to unsteady hydraulic conditions, the effect of temperature polarisation was less apparent, resulting in a higher feed vapour pressure at the membrane interface and thus the actual driving force for H<sub>2</sub>O transfer. Moreover, as the membrane temperature was probably higher at higher Reynolds numbers due to the weaker effect of temperature polarisation, the  $K_m$  for the PTFE decreased, according to mass transfer described Knudsen diffusion. Apparently, the increase in actual H<sub>2</sub>O driving force had a greater impact than the decrease in  $K_m$  on the H<sub>2</sub>O flux. For the Hybrid Silica PV membrane, the increase in Reynolds number probably resulted in an increased actual H<sub>2</sub>O driving force, as well as an increased  $K_m$ , due to the reduced effect of temperature polarisation, ultimately leading to an increase in H<sub>2</sub>O flux.

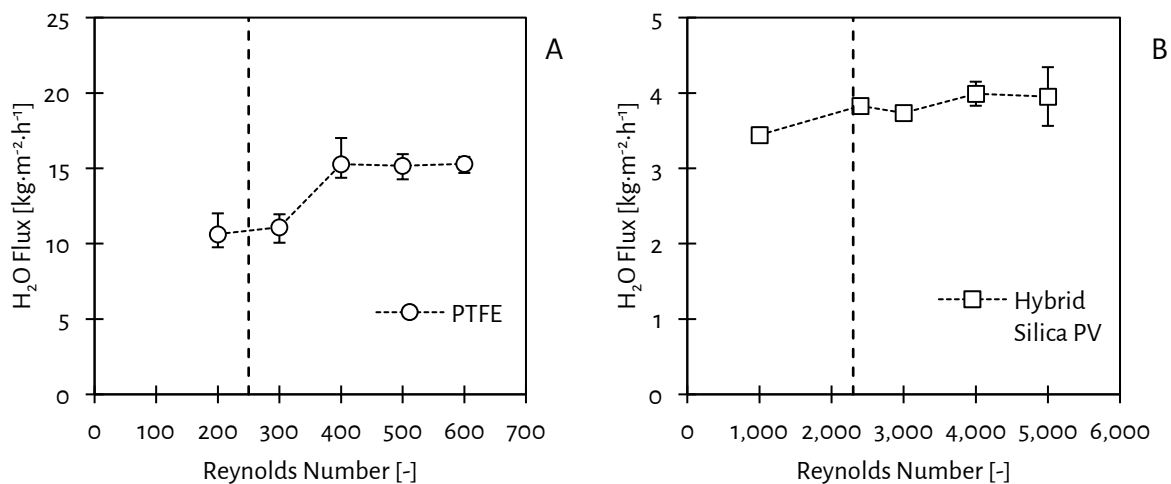


Figure 5-6 - The H<sub>2</sub>O flux of the PTFE (A) and the Hybrid Silica PV (B) membrane at a feed water temperature of 35 °C as a function of the Reynolds numbers. The dotted vertical lines represent the Reynolds numbers at which theoretically the hydraulic conditions become unsteady: 250 for spacer-filled rectangular flow channels and 2,300 for tubular flow channels. The reported values and error bars represent the average and the minimum and maximum measurements of at least three replicate experiments.

### 5.3.3.2. Selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer under steady and unsteady hydraulic conditions

Subsequently, NH<sub>3</sub> transfer was assessed under both steady and unsteady hydraulic conditions for the PTFE and the Hybrid Silica PV membranes. Based on results of H<sub>2</sub>O transfer as a function of the Reynolds number experiments (see 5.3.3.1.), Reynolds numbers of 200 and 500 for the PTFE membrane and 1,000 and 2,400 for the Hybrid Silica PV membrane were used as representative values of steady and unsteady hydraulic conditions, respectively. In line with the findings in 5.3.2., the transfer rates of NH<sub>3</sub> and H<sub>2</sub>O, expressed as flux and  $K_0$  were consistently lower for the Hybrid Silica PV membrane, compared to the PTFE membrane, which can be explained by the membrane thickness and pore size of the respective membranes.

Figure 5-7A shows that the NH<sub>3</sub> flux for the PTFE membrane increased from 0.08 to 0.11 kg·m<sup>-2</sup>·h<sup>-1</sup> when the hydraulic conditions shifted from steady to unsteady, whereas for the Hybrid Silica PV the NH<sub>3</sub> flux increased from 0.01 to 0.02 kg·m<sup>-2</sup>·h<sup>-1</sup>. The H<sub>2</sub>O fluxes for the PTFE and Hybrid Silica PV membrane remained stable at 11 and 3 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively, when the hydraulic conditions shifted from steady to unsteady. The rate of H<sub>2</sub>O transfer during the experiments with demineralised water in 5.3.1. and 5.3.3.1. was consistently higher compared to the experiments using feed waters containing NH<sub>4</sub>OH, indicating that the transfer of NH<sub>3</sub> affected the transfer of H<sub>2</sub>O. Furthermore, the shift from steady to unsteady hydraulic conditions had a greater impact on the  $K_{0,NH_3}$  than on the  $K_{0,H_2O}$ . The  $K_{0,NH_3}$  increased from 1·10<sup>-7</sup> to 3·10<sup>-7</sup> s·m<sup>-1</sup> and from 2·10<sup>-8</sup> to 3·10<sup>-8</sup> s·m<sup>-1</sup> for the PTFE and the Hybrid Silica PV membrane, respectively, whereas the  $K_{0,H_2O}$  remained at 7·10<sup>-7</sup> - 8·10<sup>-7</sup> s·m<sup>-1</sup> and 2·10<sup>-7</sup> s·m<sup>-1</sup>, respectively. The increase in NH<sub>3</sub> fluxes and  $K_{0,NH_3}$  by shifting from steady

to unsteady hydraulic conditions can be explained by a decrease in the effect of gas depletion concentration polarisation.

The  $S_{\text{NH}_3/\text{H}_2\text{O}}$  increased when the hydraulic conditions shifted from steady to unsteady conditions, in line with the findings of [Ding et al. \(2006\)](#) and [El-Bourawi et al. \(2007\)](#). For the PTFE membrane,  $S_{\text{NH}_3/\text{H}_2\text{O}}$  increased from 0.2 to 0.3, while  $S_{\text{NH}_3/\text{H}_2\text{O}}$  for the Hybrid Silica PV membrane increased from 0.1 to 0.2, indicating that the PTFE membrane again had a higher selectivity for  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer than the Hybrid Silica PV membrane, in line with the findings described in 5.3.2. The observed increase in  $S_{\text{NH}_3/\text{H}_2\text{O}}$  for the PTFE membrane contradicted the observations of [He et al. \(2018\)](#), who found that  $K_{\text{o,H}_2\text{O}}$  increased more than  $K_{\text{o,NH}_3}$  for higher cross-flow velocities. However, it was unclear whether these experiments were conducted in either steady or unsteady hydraulic conditions as the hydraulic diameter and geometry of the feed channel were not reported. Hence, the results show that stripping  $\text{NH}_3$  at unsteady hydraulic conditions were preferred over operating at steady hydraulic conditions to maximise  $S_{\text{NH}_3/\text{H}_2\text{O}}$ , irrespective of the used type of membrane, also in line with the findings of [Scheepers et al. \(2020\)](#).

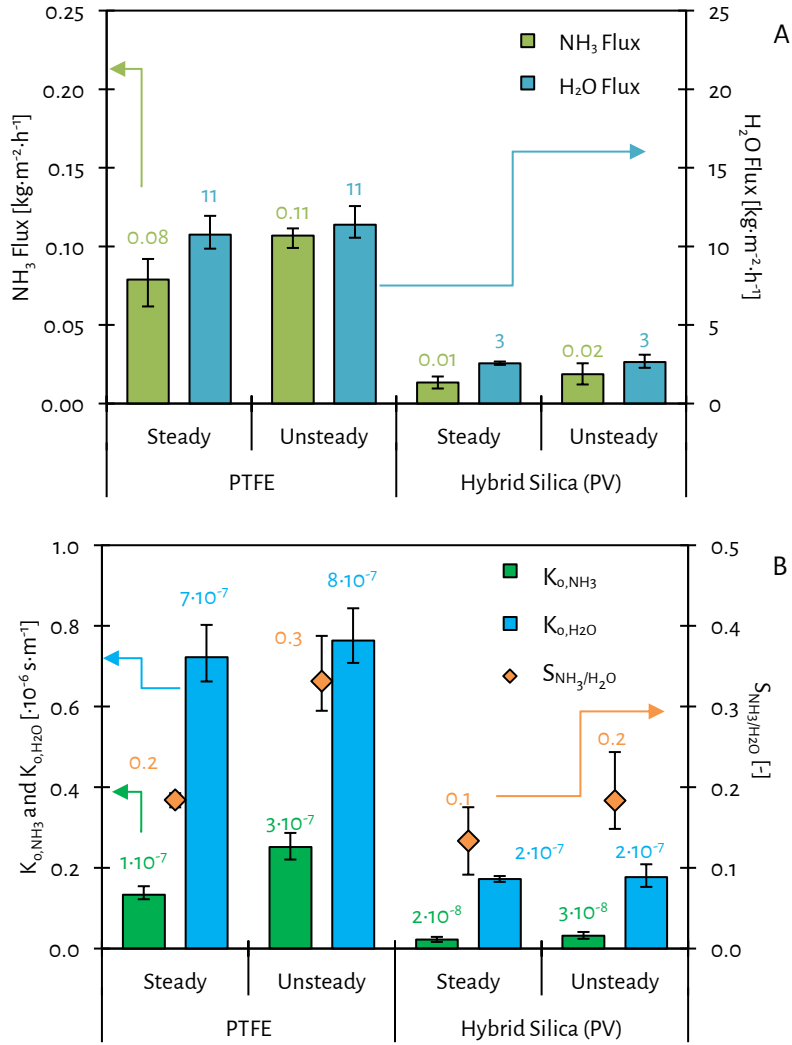


Figure 5-7 - The NH<sub>3</sub> and H<sub>2</sub>O fluxes (A) and the K<sub>o,NH<sub>3</sub></sub>, K<sub>o,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> (B) of the PTFE and the hydrophilic Hybrid Silica PV membrane for stripping NH<sub>3</sub> for steady and unsteady hydraulic conditions, from feed waters with an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup> (as NH<sub>4</sub>OH) at a feed water temperature of 35 °C at both steady and unsteady hydraulic conditions. The reported values and error bars represent the average and the minimum and maximum measurements of at least three replicate experiments.

5.3.4. Selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer for various membranes and feed water compositions5.3.4.1. NH<sub>3</sub> feed water concentration of 1 g·L<sup>-1</sup> at various ionic strengths

Figure 5-8A shows that the fluxes of NH<sub>3</sub> for the PTFE membrane were 0.11 and 0.14 kg·m<sup>-2</sup>·h<sup>-1</sup> when feed waters had a negligible ionic strength (NH<sub>4</sub>OH) and an ionic strength of 0.1 mol·L<sup>-1</sup> (NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10), respectively. The H<sub>2</sub>O flux of the PTFE membrane ranged between 11 and 12 kg·m<sup>-2</sup>·h<sup>-1</sup> for the feed waters with negligible and 0.1 mol·L<sup>-1</sup> ionic strengths, respectively, while the  $K_{o,H_2O}$  was 8·10<sup>-7</sup> s·m<sup>-1</sup> (see Figure 5-8B). Based on the ratio of the NH<sub>3</sub> and H<sub>2</sub>O fluxes (0.01), the electrical energy consumption can be derived, based on the study of [van Linden et al. \(2022a\)](#). The electrical energy consumption for stripping NH<sub>3</sub> at an NH<sub>3</sub> feed water concentration of 1 g·L<sup>-1</sup> was approximately 100 MJ·kg-N<sup>-1</sup>. According to Figure 5-8B, the  $K_{o,NH_3}$  was 3·10<sup>-7</sup> s·m<sup>-1</sup> for both feed waters, indicating that the effect of the difference in ionic strength of 0.1 mol·L<sup>-1</sup> was negligible on the NH<sub>3</sub> transfer. The  $S_{NH_3/H_2O}$  for the PTFE membrane for these experiments ranged between 0.3 and 0.4, which indicates the transfer of H<sub>2</sub>O was again preferential over NH<sub>3</sub> (similar as in 5.3.2. and 5.3.3.), independent of the difference in ionic strength. In addition, in line with the findings in 5.3.2. and 5.3.3., the transfer rates of NH<sub>3</sub> and H<sub>2</sub>O, expressed as flux and  $K_o$  were consistently lower for the Hybrid Silica PV membrane, compared to the PTFE membrane, which can be explained by the membrane thickness and pore size of the respective membranes.

For the Hybrid Silica PV membrane, the NH<sub>3</sub> and H<sub>2</sub>O fluxes were 0.02 and 3 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively, when using feed water with a negligible and 0.1 mol·L<sup>-1</sup> ionic strength at an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup>. The  $K_{o,H_2O}$  of the Hybrid Silica PV membrane for the feed water with different ionic strengths was 2·10<sup>-7</sup> s·m<sup>-1</sup> and the  $K_{o,NH_3}$  was 3·10<sup>-8</sup> s·m<sup>-1</sup>. The  $S_{NH_3/H_2O}$  of the Hybrid Silica PV membrane for both feed waters was 0.2, suggesting that the increase in ionic strength of 0.1 mol·L<sup>-1</sup> did not affect the selectivity of NH<sub>3</sub> over H<sub>2</sub>O transfer, which is in agreement with the findings for the PTFE membrane.

5.3.4.2. NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> at various ionic strengths

At last, the  $S_{NH_3/H_2O}$  was assessed for the PTFE and Hybrid Silica PV membrane using feed waters with an NH<sub>3</sub> feed concentration of 10 g·L<sup>-1</sup> with a negligible ionic strength (NH<sub>4</sub>OH) and an ionic strength of 0.8 mol·L<sup>-1</sup> (NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10). The NH<sub>3</sub> fluxes for the PTFE membrane were 1.00 and 0.74 kg·m<sup>-2</sup>·h<sup>-1</sup> for the feed waters with a negligible and 0.8 mol·L<sup>-1</sup> ionic strength, respectively, whereas the H<sub>2</sub>O fluxes were 14 and 11 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively (see Figure 5-9A). Hence, the fluxes of both NH<sub>3</sub> and H<sub>2</sub>O decreased when the ionic strength of the feed water increased from 0.0 to 0.8 mol·L<sup>-1</sup>. With a ratio of the NH<sub>3</sub> flux and the total flux of 0.06, the electrical energy consumption for stripping NH<sub>3</sub> at an NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> was approximately 10 MJ·kg-N<sup>-1</sup>, based on ([van Linden et al., 2022a](#)). For the Hybrid Silica PV membrane, the NH<sub>3</sub> flux was 0.12 and 0.05 kg·m<sup>-2</sup>·h<sup>-1</sup> for feed waters with a negligible and 0.8 mol·L<sup>-1</sup> ionic strength, respectively, while the H<sub>2</sub>O flux was stable for both feed waters at 3 kg·m<sup>-2</sup>·h<sup>-1</sup>. In line with the findings on the PTFE membrane, the NH<sub>3</sub> flux also decreased for the Hybrid Silica PV membrane when the ionic strength increased from 0.0 to 0.8 mol·L<sup>-1</sup> for feed water with an NH<sub>3</sub> feed concentration of 10 g·L<sup>-1</sup>.



According to Figure 5-9B, the  $K_{o,NH_3}$  ( $2 \cdot 10^{-7} \text{ s} \cdot \text{m}^{-1}$ ) for the PTFE membrane did not change when the ionic strength increased from 0.0 to 0.8 mol·L<sup>-1</sup>, suggesting that the additional presence of ions did not affect the NH<sub>3</sub> transfer. In addition, the increase in ionic strength also did not affect the transfer of H<sub>2</sub>O for the PTFE membrane, as the  $K_{o,H_2O}$  ( $8 \cdot 10^{-7} - 9 \cdot 10^{-7} \text{ s} \cdot \text{m}^{-1}$ ) was similar for a negligible and 0.8 mol·L<sup>-1</sup> ionic strength. Eventually, the  $S_{NH_3/H_2O}$  was 0.2 for feed water with an NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> with both a negligible and 0.8 mol·L<sup>-1</sup> ionic strength, indicating that the selectivity of NH<sub>3</sub> transfer was not affected by the increase in ionic strength for the PTFE membrane. For the Hybrid Silica PV membrane, the  $K_{o,NH_3}$  decreased from  $2 \cdot 10^{-8}$  to  $1 \cdot 10^{-8} \text{ s} \cdot \text{m}^{-1}$  when the ionic strength increased from 0.0 to 0.8 mol·L<sup>-1</sup>, while  $K_{o,H_2O}$  for the Hybrid Silica PV membrane was stable at  $2 \cdot 10^{-7} \text{ s} \cdot \text{m}^{-1}$ . Hence, the increase in ionic strength of 0.8 mol·L<sup>-1</sup> affected only the transfer of NH<sub>3</sub>, which can be assigned to the increased effect of gas depletion concentration polarisation. Eventually, the  $S_{NH_3/H_2O}$  for the Hybrid Silica was 0.1 for an NH<sub>3</sub> feed water concentration of 10 g·L<sup>-1</sup> with both a negligible and 0.8 g·L<sup>-1</sup> ionic strength.

By increasing the NH<sub>3</sub> feed concentration from 1 to 10 g·L<sup>-1</sup>, the NH<sub>3</sub> flux increased for the PTFE membrane from 0.08 – 0.11 to 0.74 – 1.00 kg·m<sup>-2</sup>·h<sup>-1</sup>, in line with the study of [Scheepers et al. \(2020\)](#). However, the  $K_{o,NH_3}$  of the PTFE membrane decreased when increasing the NH<sub>3</sub> feed water concentration, while the  $K_{o,H_2O}$  remained equal, resulting in a decrease in  $S_{NH_3/H_2O}$  from 0.3 – 0.4 to 0.2. In line with the findings for the PTFE membrane, also the  $S_{NH_3/H_2O}$  for the Hybrid Silica decreased when the NH<sub>3</sub> feed water concentration increased from 1 to 10 g·L<sup>-1</sup>, from 0.2 to 0.1, respectively. Hence, the increases in NH<sub>3</sub> flux for both the PTFE and Hybrid Silica PV membrane when the NH<sub>3</sub> feed water concentration increased from 1 to 10 g·L<sup>-1</sup> was caused by the higher driving force as a result of the higher NH<sub>3</sub> vapour pressure in the feed water. Moreover, the selectivity of NH<sub>3</sub> transfer over H<sub>2</sub>O decreased further for both membranes when the NH<sub>3</sub> feed water concentration increased. Apparently, even at a ten-fold higher NH<sub>3</sub> feed concentration, the relative presence of NH<sub>3</sub> was low (approximately 1 wt%) compared to H<sub>2</sub>O, explaining partially the preferential transfer of H<sub>2</sub>O over NH<sub>3</sub> for both membranes, under all various feed water compositions.

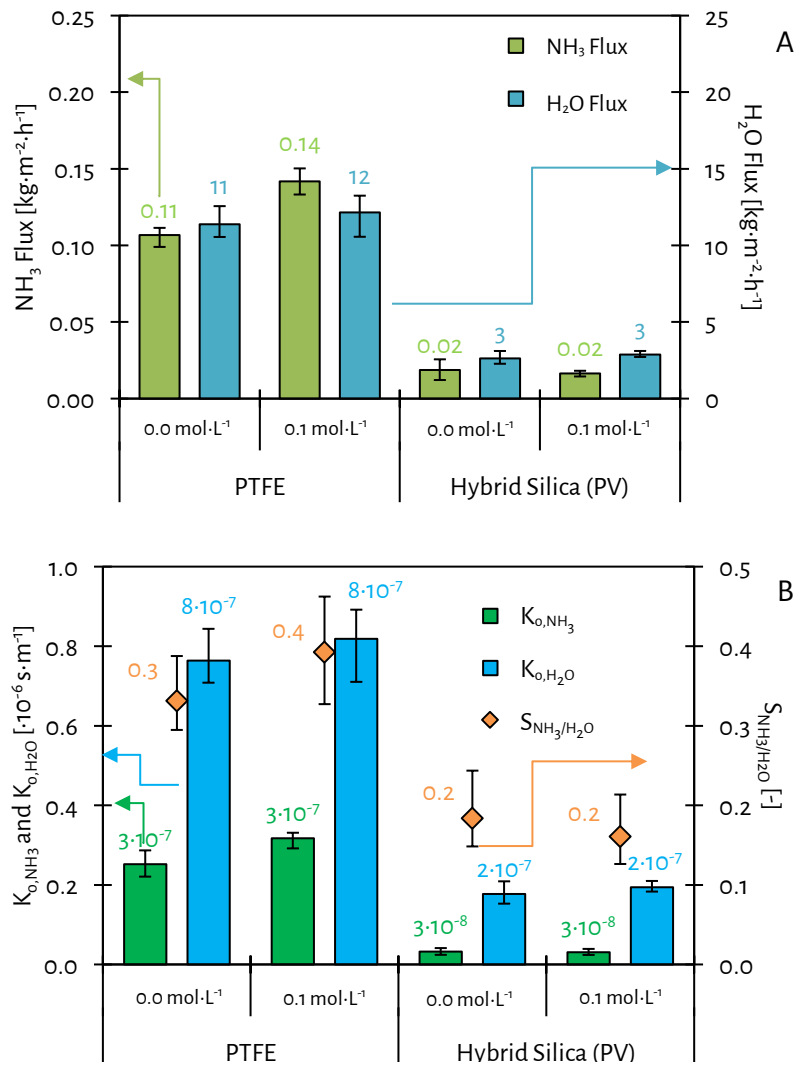


Figure 5-8 - The NH<sub>3</sub> and H<sub>2</sub>O fluxes (A) and the K<sub>o,NH<sub>3</sub></sub>, K<sub>o,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> (B) of the PTFE and the Hybrid Silica PV membrane for stripping NH<sub>3</sub> from feed waters with an NH<sub>3</sub> feed concentration of 1 g·L<sup>-1</sup> having a negligible (as NH<sub>4</sub>OH) and 0.1 mol·L<sup>-1</sup> (as NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10) ionic strength at a feed water temperature of 35 °C at unsteady hydraulic conditions. The reported values and error bars represent the average and the minimum and maximum measurements of at least three replicate experiments.

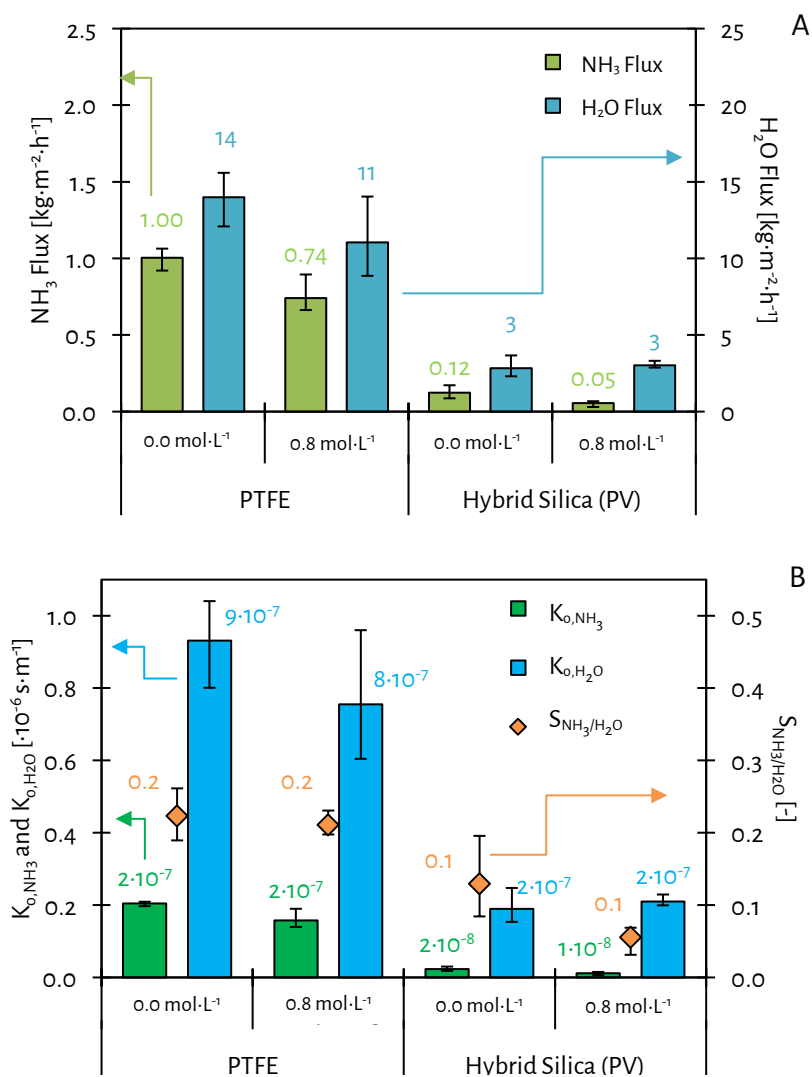


Figure 5-9 - The NH<sub>3</sub> and H<sub>2</sub>O fluxes (A) and the K<sub>o,NH<sub>3</sub></sub>, K<sub>o,H<sub>2</sub>O</sub> and S<sub>NH<sub>3</sub>/H<sub>2</sub>O</sub> (B) of the PTFE and the Hybrid Silica PV membrane for stripping NH<sub>3</sub> from feed waters with an NH<sub>3</sub> feed concentration of 10 g·L<sup>-1</sup> having a negligible (as NH<sub>4</sub>OH) and 0.8 mol·L<sup>-1</sup> (as NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10) ionic strength at a feed water temperature of 35 °C at unsteady hydraulic conditions. The reported values and error bars represent the average and the minimum and maximum measurements of at least three replicate experiments.

#### 5.4. Conclusions

The experimental study to assess the selectivity of NH<sub>3</sub> and water transfer during the stripping of NH<sub>3</sub> under vacuum using various membranes resulted in the following conclusions:

- The transfer rate of H<sub>2</sub>O (as H<sub>2</sub>O flux and  $K_{o,H_2O}$ ) through the used dense hydrophilic Hybrid Silica PV membrane is lower than the transfer rate of H<sub>2</sub>O of the used porous gas-permeable PTFE membrane;
- The transfer rate of H<sub>2</sub>O through the used dense hydrophobic PDMS PV membrane is lower than the transfer rate of H<sub>2</sub>O of the Hybrid Silica PV and the PTFE membrane;
- The transfer of NH<sub>3</sub> through the PMDS PV membrane is negligible and the membrane deteriorates rapidly when using feed waters containing NH<sub>3</sub>;
- The used PTFE membrane and Hybrid Silica PV membranes show selectivity for transfer of H<sub>2</sub>O over NH<sub>3</sub> for all tested hydraulic conditions and feed water compositions;
- The  $S_{NH_3/H_2O}$  of the Hybrid Silica PV membrane (0.1 – 0.2) is consistently lower than the  $S_{NH_3/H_2O}$  of the used PTFE membrane (0.2 – 0.4);
- Unsteady hydraulic conditions result in a higher  $S_{NH_3/H_2O}$  compared to steady hydraulic conditions for both the PTFE and the Hybrid Silica PV membrane;
- An increase in ionic strength of the feed water from 0.0 to 0.8 mol·L<sup>-1</sup> decreases the  $S_{NH_3/H_2O}$  of both the PTFE and the Hybrid Silica PV membranes;
- An increase in NH<sub>3</sub> feed concentration from 1 to 10 g·L<sup>-1</sup> leads to a decrease in  $S_{NH_3/H_2O}$  for both the PTFE and the Hybrid Silica PV membrane;

5.5. References

- Baker, R. W., Wijmans, J. G., & Huang, Y. (2010). Permeability, permance and selectivity: A preferred way of reporting pervaporation performance data. *Journal of Membrane Science*, 348(1), 346-352. doi:<https://doi.org/10.1016/j.memsci.2009.11.022>
- Bandini, S., Gostoli, C., & Sarti, G. C. (1992). Separation efficiency in vacuum membrane distillation. *Journal of Membrane Science*, 73(2), 217-229. doi:[https://doi.org/10.1016/0376-7388\(92\)80131-3](https://doi.org/10.1016/0376-7388(92)80131-3)
- Camus, O., Perera, S., Crittenden, B., van Delft, Y. C., Meyer, D. F., P. A. C. Pex, P., Kumakiri, I., Miachon, S., Dalmon, J.-A., Tennison, S., Chanaud, P., Groensmit, E., & Nobel, W. (2006). Ceramic membranes for ammonia recovery. *AIChE Journal*, 52(6), 2055-2065. doi:10.1002/aic.10800
- Chiam, C.-K., & Sarbatly, R. (2013). Vacuum membrane distillation processes for aqueous solution treatment—A review. *Chemical Engineering and Processing: Process Intensification*, 74, 27-54. doi:<https://doi.org/10.1016/j.cep.2013.10.002>
- Deng, Z., van Linden, N., Guillen, E., Spanjers, H., & van Lier, J. B. (2021). Recovery and applications of ammoniacal nitrogen from nitrogen-loaded residual streams: A review. *Journal of Environmental Management*, 295, 113096. doi:<https://doi.org/10.1016/j.jenvman.2021.113096>
- Ding, Z., Liu, L., Li, Z., Ma, R., & Yang, Z. (2006). Experimental study of ammonia removal from water by membrane distillation (MD): The comparison of three configurations. *Journal of Membrane Science*, 286(1-2), 93-103. doi:10.1016/j.memsci.2006.09.015
- El-Bourawi, M. S., Khayet, M., Ma, R., Ding, Z., Li, Z., & Zhang, X. (2007). Application of vacuum membrane distillation for ammonia removal. *Journal of Membrane Science*, 301(1-2), 200-209. doi:10.1016/j.memsci.2007.06.021
- He, Q., Tu, T., Yan, S., Yang, X., Duke, M., Zhang, Y., & Zhao, S. (2018). Relating water vapor transfer to ammonia recovery from biogas slurry by vacuum membrane distillation. *Separation and Purification Technology*, 191(Supplement C), 182-191. doi:<https://doi.org/10.1016/j.seppur.2017.09.030>
- Jyoti, G., Keshav, A., & Anandkumar, J. (2015). Review on Pervaporation: Theory, Membrane Performance, and Application to Intensification of Esterification Reaction. *Journal of Engineering*, 2015, 24. doi:10.1155/2015/927068
- Kanezashi, M., Yamamoto, A., Yoshioka, T., & Tsuru, T. (2010). Characteristics of ammonia permeation through porous silica membranes. *AIChE Journal*, 56(5), 1204-1212. doi:10.1002/aic.12059
- Khayet, M., & Matsuura, T. (2004). Pervaporation and vacuum membrane distillation processes: Modeling and experiments. *AIChE Journal*, 50(8), 1697-1712. doi:10.1002/aic.10161
- Lawson, K. W., & Lloyd, D. R. (1997). Membrane distillation. *Journal of Membrane Science*, 124(1), 1-25. doi:[https://doi.org/10.1016/S0376-7388\(96\)00236-0](https://doi.org/10.1016/S0376-7388(96)00236-0)
- Lide, D. R., & Haynes, W. M. (2011). *CRC handbook of chemistry and physics : a ready-reference book of chemical and physical data*. Boca Raton, Fla.: CRC Press.

- Martínez-Díez, L., & Vázquez-González, M. I. (1999). Temperature and concentration polarization in membrane distillation of aqueous salt solutions. *Journal of Membrane Science*, *156*(2), 265-273. doi:[https://doi.org/10.1016/S0376-7388\(98\)00349-4](https://doi.org/10.1016/S0376-7388(98)00349-4)
- Mojab, S. M., Pollard, A., Pharoah, J. G., Beale, S. B., & Hanff, E. S. (2014). Unsteady Laminar to Turbulent Flow in a Spacer-Filled Channel. *Flow, Turbulence and Combustion*, *92*(1), 563-577. doi:10.1007/s10494-013-9514-4
- Oliveira, T. A. C., Cocchini, U., Scarpello, J. T., & Livingston, A. G. (2001). Pervaporation mass transfer with liquid flow in the transition regime. *Journal of Membrane Science*, *183*(1), 119-133. doi:[https://doi.org/10.1016/S0376-7388\(00\)00576-7](https://doi.org/10.1016/S0376-7388(00)00576-7)
- Scheepers, D. M., Tahir, A. J., Brunner, C., & Guillen-Burrieza, E. (2020). Vacuum membrane distillation multi-component numerical model for ammonia recovery from liquid streams. *Journal of Membrane Science*, *614*, 118399. doi:<https://doi.org/10.1016/j.memsci.2020.118399>
- Schock, G., & Miquel, A. (1987). Mass transfer and pressure loss in spiral wound modules. *Desalination*, *64*, 339-352. doi:[http://dx.doi.org/10.1016/0011-9164\(87\)90107-X](http://dx.doi.org/10.1016/0011-9164(87)90107-X)
- van Linden, N., Bandinu, G. L., Vermaas, D. A., Spanjers, H., & van Lier, J. B. (2020). Bipolar membrane electro dialysis for energetically competitive ammonium removal and dissolved ammonia production. *Journal of Cleaner Production*, 120788. doi:<https://doi.org/10.1016/j.jclepro.2020.120788>
- van Linden, N., Spanjers, H., & van Lier, J. B. (2019a). Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electro dialysis. *Water Research*, 114856. doi:<https://doi.org/10.1016/j.watres.2019.114856>
- van Linden, N., Spanjers, H., & van Lier, J. B. (2022a). Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping. *Chemical Engineering Journal*, *428*, 131081. doi:<https://doi.org/10.1016/j.cej.2021.131081>
- van Linden, N., Wang, Y., Sudhölter, E., Spanjers, H., & van Lier, J. B. (2022b). Selectivity of vacuum ammonia stripping using porous gas-permeable and dense pervaporation membranes under various hydraulic conditions and feed water compositions. *Journal of Membrane Science*, *642*, 120005. doi:<https://doi.org/10.1016/j.memsci.2021.120005>
- van Veen, H. M., Rietkerk, M. D. A., Shanahan, D. P., van Tuel, M. M. A., Kreiter, R., Castricum, H. L., ten Elshof, J. E., & Vente, J. F. (2011). Pushing membrane stability boundaries with HybSi<sup>®</sup> pervaporation membranes. *Journal of Membrane Science*, *380*(1), 124-131. doi:<https://doi.org/10.1016/j.memsci.2011.06.040>
- Wijmans, J. G., Athayde, A. L., Daniels, R., Ly, J. H., Kamaruddin, H. D., & Pinnau, I. (1996). The role of boundary layers in the removal of volatile organic compounds from water by pervaporation. *Journal of Membrane Science*, *109*(1), 135-146. doi:[https://doi.org/10.1016/0376-7388\(95\)00194-8](https://doi.org/10.1016/0376-7388(95)00194-8)
- Yang, X., Ding, L., Wolf, M., Velterop, F., Bouwmeester, H. J. M., Smart, S., Diniz da Costa, J. C., Liubinas, A., Li, J.-D., Zhang, J., & Duke, M. (2016). Pervaporation of ammonia solution with  $\gamma$ -alumina

supported organosilica membranes. *Separation and Purification Technology*, 168, 141-151.

doi:<http://dx.doi.org/10.1016/j.seppur.2016.05.017>

Yang, X., Fraser, T., Myat, D., Smart, S., Zhang, J., Diniz da Costa, J. C., Liubinas, A., & Duke, M. (2014). A Pervaporation Study of Ammonia Solutions Using Molecular Sieve Silica Membranes. *Membranes*, 4(1), 40-54. doi:10.3390/membranes4010040

Yang, X., Sheridan, S., Ding, L., Wang, D. K., Smart, S., Diniz da Costa, J. C., Liubinas, A., & Duke, M. (2018). Inter-layer free cobalt-doped silica membranes for pervaporation of ammonia solutions. *Journal of Membrane Science*, 553, 111-116. doi:<https://doi.org/10.1016/j.memsci.2018.02.049>







## Chapter 6.

# Solid oxide fuel cell to generate electricity using ammonia-water mixtures recovered by vacuum membrane stripping

Based on: Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping

Niels van Linden, Henri Spanjers and Jules B. van Lier

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### Abstract

Gaseous ammonia ( $\text{NH}_3$ ) recovered from nitrogen-loaded (N-loaded) residual waters may be used as a fuel in solid oxide fuel cells (SOFCs) to generate energy without the emission of undesirable oxidised nitrogen species.  $\text{NH}_3$  can be directly recovered as a gas by vacuum membrane stripping (VMS), which also results in the evaporation of water ( $\text{H}_2\text{O}$ ), resulting in the recovery of  $\text{NH}_3\text{-H}_2\text{O}$  mixtures. However, in currently available literature, information is lacking on the attainable  $\text{NH}_3$  concentrations in these  $\text{NH}_3\text{-H}_2\text{O}$  mixtures that will be used as a fuel for an oxygen-conducting SOFC (SOFC-O). This chapter presents the assessment of the effect of feed water temperature and the  $\text{NH}_3$  feed water concentration on the attainable  $\text{NH}_3$  concentrations in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate. Besides, this chapter presents the assessment of the feasibility to use dilute  $\text{NH}_3\text{-H}_2\text{O}$  mixtures in the concentration range between 5 and 25 wt%, for the generation of electricity in an SOFC-O. The results showed that increasing the  $\text{NH}_3$  feed water concentration from 1 to 10  $\text{g}\cdot\text{L}^{-1}$  increased the  $\text{NH}_3$  concentration in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate from 1 wt% to up to 11 wt%. Increasing the feed water temperature from 25 to 35 °C also results in an increase in the  $\text{NH}_3$  concentration in the gaseous permeate, whereas increasing the feed water temperature from 35 °C to 55 °C leads to dilution of the  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in VMS permeate. Furthermore, energy was generated in an SOFC-O when the  $\text{NH}_3$  concentration in the  $\text{NH}_3\text{-H}_2\text{O}$  fuel was only 5 wt%. Hence, the obtained  $\text{NH}_3$  concentrations in the  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in gaseous VMS permeate show that VMS and SOFC-O can be combined for the generation of electricity from  $\text{NH}_3$  recovered from water (aqueous solution). Moreover, the electrical energy generation of the SOFC-O, which reached values of 9  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , was higher than the electrical energy consumption for VMS, for which values of 7  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  were calculated.

### Keywords

ammonia recovery; ammonia stripping; ammonia-water mixture; energy generation; vacuum membrane stripping; solid oxide fuel cell;



## 6.1. Introduction

Based on Chapter 1 of this thesis, vacuum membrane stripping (VMS) using porous gas-permeable membranes allow for higher ammonia ( $\text{NH}_3$ ) transfer rates and higher selectivity of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer, compared to dense pervaporation membranes. In addition, the literature review presented in Chapter 2 of this thesis shows that a solid oxide fuel cell (SOFC) is a suitable energy-conversion technology to generate energy from  $\text{NH}_3$ . However, information on the feasibility of combining VMS and SOFC for  $\text{NH}_3$  recovery and subsequent electricity generation is missing.

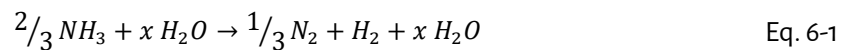
### 6.1.1. Use of gaseous $\text{NH}_3$ for electricity generation by SOFCs

The chemically stored energy in  $\text{NH}_3$ , which equals  $21 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , referring to the lower heating value at  $750^\circ\text{C}$ , can be converted to electricity and heat by various energy-conversion technologies (Valera-Medina et al., 2018).  $\text{NH}_3$  as an energy source opens new opportunities for the application of recovered  $\text{NH}_3$  from nitrogen-loaded (N-loaded) residual waters. Whereas conventional combustion-based technologies initially convert the chemical energy to heat and subsequently generate electricity at efficiencies ranging between 30 - 40%, fuel cells allow for direct generation of electricity at up to 60% efficiency (Stambouli & Traversa, 2002).

Amongst the various fuel cell types, three types are so-called direct  $\text{NH}_3$  fuel cells: 1) alkaline fuel cells (AFCs), 2) alkaline membrane fuel cells (AMFCs) and 3) solid oxide fuel cells (SOFCs). According to review studies of Cheddie (2012) and Lan and Tao (2014b), the reported maximum (peak) power density of AFCs ( $16 \text{ mW}\cdot\text{cm}^{-2}$ ) and AMFCs ( $40 \text{ mW}\cdot\text{cm}^{-2}$ ) are an order of magnitude lower than the reported peak power density of SOFCs (ranging between 580 and  $1,190 \text{ mW}\cdot\text{cm}^{-2}$ ), using gaseous  $\text{NH}_3$  directly as a fuel. Moreover, the use of AMFCs is challenged by catalyst poisoning by adsorbed N species at the anode, diffusion of  $\text{NH}_3$  through the membrane electrolyte, and slow kinetics due to the low operating temperature (between  $25$  and  $80^\circ\text{C}$ ) (Suzuki et al., 2012). Furthermore, the use of AFCs is challenged by carbonate formation in the liquid hydroxide electrolyte (Lan & Tao, 2010, 2014b).

The high peak power densities of SOFCs are explained by the fast kinetics and the low resistances, as SOFCs operate at temperatures ranging between  $600$  and  $1,000^\circ\text{C}$ , allowing for electrical efficiencies up to 60% and total energy efficiencies up to 90% when the high-grade generated heat is used (Stambouli & Traversa, 2002). The operational temperature combined with the presence of nickel catalysts allows for spontaneous cracking of  $\text{NH}_3$  to hydrogen ( $\text{H}_2$ ) and  $\text{N}_2$  (Eq. 6-1) (Staniforth & Ormerod, 2003), without the need to change the materials or design of  $\text{H}_2$ -fuelled SOFCs to use  $\text{NH}_3$  as a fuel (Wojcik et al., 2003). SOFC types are distinguished based on their electrolyte properties (Stambouli & Traversa, 2002; Ni et al., 2009). SOFC-Os have an oxygen-conducting electrolyte, while SOFC-Hs have a proton-conducting solid electrolyte. In both types of SOFCs, cracking of  $\text{NH}_3$  takes place at the anode. However, in SOFC-Os, oxygen ( $\text{O}_2$ ) reduction to oxygen ions ( $\text{O}^{2-}$ ) takes place at the cathode (Eq. 6-2). Subsequently,  $\text{O}^{2-}$  transfer from the cathode to the anode allows for the reaction of  $\text{O}^{2-}$  with  $\text{H}_2$  (Eq. 6-3), resulting in the release of electrons. The electrons go through an electrical circuit to the cathode, allowing again for  $\text{O}_2$  reduction. In contrast, in SOFC-Hs, protons ( $\text{H}^+$ ) are formed at the anode and subsequent  $\text{H}^+$  transfer takes place from the anode to the cathode. At the

cathode,  $H^+$  reacts with  $O_2$ , resulting in the release of electrons, which are again used at the anode to form  $H^+$  from  $H_2$ . Currently, the reported peak power densities of SOFC-Os exceed the reported peak power densities of SOFC-Hs, due to optimal material selection and design of SOFC-Os as a result of extensive research (Ni et al., 2009; Afif et al., 2016). Moreover, the conversion of  $NH_3$  in SOFC-Os leads to very low emission of N-species. Dekker and Rietveld (2006) reported near-complete (> 99.9%) cracking of  $NH_3$  at the anode and only traces of  $NO_x$  (ranging between 0.5 and 4 ppm) in the anode off-gas of their SOFC-O. Research conducted by Staniforth and Ormerod (2003), Ma et al. (2006) and Okanishi et al. (2017) confirmed these findings and detected no  $NH_3$ ,  $NO$ ,  $NO_2$  nor  $N_2O$  in the anode off-gas of their SOFC-O. Hence, SOFC-Os are potentially suitable to efficiently convert the chemically stored energy from recovered  $NH_3$  to energy, without the emission of undesirable oxidised N-species.



#### 6.1.2. Direct gaseous $NH_3$ recovery from water by VMS

To allow for using the recovered  $NH_3$  as a fuel for SOFC-Os,  $NH_3$  must be extracted from the water phase as a gas. Hereto, vacuum stripping of  $NH_3$  can be used, which avoids the presence of  $O_2$  in the recovered gas. In contrast, applying air stripping will lead to the deactivation of the nickel anode catalyst of SOFC-Os by oxidation of nickel to nickel oxide (NiO). The use of membranes in vacuum membrane stripping (VMS) configurations, results in large gas-liquid exchange areas in a small volume, allowing for compact systems. However, stripping of  $NH_3$  from water (aqueous solution) is accompanied by the evaporation of  $H_2O$ , resulting in gaseous  $NH_3$ - $H_2O$  mixtures in the VMS permeate. El-Bourawi et al. (2006) and Ding et al. (2006) studied the effects of the solution pH, feed water temperature, vacuum pressure, feed flow velocity, and feed water concentration  $NH_3$  concentration on the  $NH_3$  mass transfer coefficient, which relates the mass flux and the corresponding driving force. However, both studies did not report the effects on the individual transfer of  $NH_3$  and  $H_2O$ , nor on the obtained  $NH_3$  concentration in the recovered  $NH_3$  stream. On the other hand, the studies of He et al. (2017) and He et al. (2018) reported concentrations of  $NH_3$  in a range between 4 and 18  $g \cdot N \cdot L^{-1}$  in the gaseous  $NH_3$ - $H_2O$  mixtures recovered from biogas slurry by VMS, corresponding to a range between 0.5 and 2.2 wt% (weight %) of  $NH_3$ .

#### 6.1.3. Direct use of recovered $NH_3$ from water as a fuel for SOFCs

Only recent studies of Stoeckl et al. (2019a) and Stoeckl et al. (2020) mentioned the use of recovered  $NH_3$  as fuel for an SOFC-O. However, the authors used fuel with an  $NH_3$  concentration of 70 wt%, as an  $NH_3$ - $H_2O$  mixture, and did not mention for what kind of feed water and operating conditions this  $NH_3$  concentration can be obtained. Hence, currently reported  $NH_3$  concentrations, which are obtained by VMS (up to 2 wt%) and those that are used in  $NH_3$ - $H_2O$  mixtures as fuel for SOFC-Os (70 wt%), do not match. This discrepancy

makes it unclear whether VMS and SOFC-Os can be combined for the recovery of  $\text{NH}_3$  from water (aqueous solution) and the subsequent direct use of the recovered  $\text{NH}_3$  as a fuel. Therefore, more information is needed to bridge the gap in applicable  $\text{NH}_3$  concentrations in  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures that can be obtained by VMS and directly be used by SOFC-O.

To obtain more concentrated  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures during the recovery of  $\text{NH}_3$  by VMS, the amount of  $\text{H}_2\text{O}$  evaporated relative to the amount of  $\text{NH}_3$  stripped must be minimised. In currently available literature on  $\text{NH}_3$  recovery by VMS, feed water temperatures ranging between 40 and 75 °C are used ([Ding et al., 2006](#); [El-Bourawi et al., 2007](#); [He et al., 2017](#); [He et al., 2018](#); [Scheepers et al., 2020](#)). All mentioned studies showed that when the feed water temperature increased, the  $\text{NH}_3$  in the gaseous permeate was diluted. Therefore, VMS seems to be a suitable technology only for feed water temperatures below 40 °C. In addition, when increased  $\text{NH}_3$  concentrations are present in the feed water, also the  $\text{NH}_3$  flux increases ([Ding et al., 2006](#); [El-Bourawi et al., 2007](#); [He et al., 2017](#); [Scheepers et al., 2020](#)). Based on the study of [van Linden et al. \(2019a\)](#),  $\text{NH}_3$  concentrations of 10  $\text{g}\cdot\text{L}^{-1}$  can be obtained, using electrodialysis to concentrate  $\text{NH}_4^+$ , followed by chemical addition for pH increase. As an alternative for adding chemicals to obtain dissolved  $\text{NH}_3$ , bipolar membrane electrodialysis can be applied, which allows for the direct production of concentrated dissolved  $\text{NH}_3$  without the addition of chemicals ([van Linden et al., 2020](#)).

#### 6.1.4. Research objectives

This chapter aimed to link VMS and SOFC-O for  $\text{NH}_3$  recovery from water (aqueous solution) and to directly use the recovered  $\text{NH}_3$  for energy generation. The first goal of this chapter was to determine what  $\text{NH}_3$  concentrations in the recovered  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate can be obtained for various feed water temperatures ranging between 25 and 55 °C and  $\text{NH}_3$  feed water concentrations ranging between 1 and 10  $\text{g}\cdot\text{L}^{-1}$ , which is considered a relevant range for  $\text{NH}_3$  recovery from N-loaded residual waters. The second goal of this chapter was to determine the required  $\text{NH}_3$  concentrations for electricity generation in an SOFC-O, using  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations ranging between 5 and 25 wt%. As the third goal of this chapter, the electrical energy consumption to recover  $\text{NH}_3$  by VMS, as well as the electricity generation of the SOFC-O using  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures as a fuel were calculated.



## 6.2. Materials and methods

### 6.2.1. Materials

#### 6.2.1.1. Experimental VMS set-up

For the VMS experiments, an acrylic Sterlitech flow-cell was used, containing a flat-sheet polytetrafluoroethylene (PTFE) hydrophobic membrane with polypropylene (PP) backing, with a pore size of  $0.1 \mu\text{m}$  and a membrane area of  $34 \text{ cm}^2$ . A wire mesh spacer with a filament thickness of  $0.8 \text{ mm}$  and a void fraction of  $91\%$  was placed at the feed side to create the desired turbulence, while another wire mesh spacer was placed at the permeate side to avoid the membrane from sticking to the flow-cell.

The feed waters were stored in a  $1 \text{ L}$  borosilicate bottle and were recirculated through the flow-cell by a calibrated peristaltic Watson Marlow 520S pump equipped with Watson-Marlow 313 pump heads ( $0.3 - 46 \text{ L}\cdot\text{h}^{-1}$ ). A calibrated digital Festo IP40 pressure sensor ( $100 - 200,000 \text{ Pa}$ ) was used to measure the hydraulic pressure drop over the VMS flow cell. The pH and electrical conductivity (EC) of the feed waters were continuously measured in the bottle, using a calibrated IDS SenTix 940 pH sensor and a calibrated TetraCon 925 EC-sensor, respectively. The data was automatically logged on a WTW Multi 3630 IDS multimeter and stored on a laptop. The feed water bottle was sealed during operation to avoid the loss of water and  $\text{NH}_3$  from the feed water to the atmosphere. The feed water bottle was placed on an IKA RH Digital KT/C heating plate and magnetic stirrer combination, while an IKA Ikatron ETC 1 temperature sensor measured the temperature of the feed water and controlled the heating plate to maintain a stable feed water temperature. The heating-mixing combination and feed water bottle were placed on a Kern PCB 6000-1 mass balance ( $0.1 - 6,000 \text{ g}$ ) to continuously measure the total mass of the feed water. The data was automatically logged and stored on a laptop.

A calibrated KNF N816.3KT.45.18 vacuum pump was used to create a partial vacuum of  $1,500 \text{ Pa}$  at the permeate side of the membrane. The gaseous VMS permeate was scrubbed in a cooled acid trap containing  $200 \text{ mL}$   $1 \text{ M}$  hydrochloric acid (HCl) solution (Merck), to protect the vacuum pump. Ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) (Sigma Aldrich Reagent Plus) and  $1 \text{ M}$  sodium hydroxide (NaOH) (Merck) was used to prepare the feed waters. Finally, the  $\text{NH}_3$  concentrations in the feed waters were measured with Machery-Nagel NANOCOLOR 2,000 test kits (concentration range  $0.4 - 2.0 \text{ g}\cdot\text{L}^{-1}$ ). Figure 6-1 shows a schematic representation of the experimental VMS setup.

#### 6.2.1.2. Experimental SOFC set-up

For the SOFC-O experiments, a Fiaxell Open Flanges Set-up was used, which contained a  $10 \text{ cm}^2$  planar anode-supported membrane electrode assembly (MEA). The MEA consisted of a NiO-8YSZ (nickel oxide coated zirconia stabilised by  $8\%$  yttria) anode, an  $\text{O}^{2-}$ -conducting 8YSZ electrolyte and a 20GDC-LSCF (lanthanum strontium cobalt ferrite stabilised by  $20\%$  gallium doped ceria) cathode. The MEA was sealed by a  $0.5 \text{ mm}$  thick mica sheet to limit the leakage of fuel from the anode to the cathode. At the anode, nickel foam with a thickness of  $0.6 \text{ mm}$  and a diameter of  $40 \text{ mm}$  was placed to provide extra surface area to crack

$\text{NH}_3$ . A golden mesh grid current collector was placed on top of the cathode to measure the electric potential and to draw electric current. Alumina sheets were placed at the cathode side of the MEA to avoid contact between the anode and cathode. The MEA and associating accessories were placed between a fuel and an air diffuser, both made of Inconel 601 (nickel-chromium alloy), which were put together by wired rods and wing nuts. The anode and cathode temperature during the operation were measured by two K-type thermocouples, which were connected to a TM-947SD thermometer (max. 1,700 °C, accuracy of 0.1 °C) to read and log the temperature. An electrical circuit including the SOFC-O anode and cathode and a Rigol DL3021 electronic load (0.001 – 40 A) was made to draw and measure the electric current. By connecting cables with alligator clips to the fuel diffuser and the current collector at the top of the Open Flanges Set-up, the electric potential was measured on a UNI-T UT58E multimeter (0.001 – 1,000 V). Finally, a Manson HCS-3202 power supply (1 – 36 V) was used as a booster to compensate for the electric potential loss caused by the electrical resistance of the electrical circuit when drawing an electric current.

The Open Flanges Set-up was placed in a Kitted Squadro SQ11 oven (max. 1,320 °C, accuracy of 1 °C) to control the operating temperature. Calibrated rotameters were used to control the supply of industrial grade pressurised air to the cathode (40 – 800 mL·min<sup>-1</sup>) and forming gas, consisting of 5 v% (volume %)  $\text{H}_2$  and 95 v%  $\text{N}_2$ , to the anode (20 – 400 mL·min<sup>-1</sup>). The connections of the gas cylinders and connections to the Open Flange Set-up were Swagelok fittings to limit any gas leakages. For the fuel, Acros Organics 25%  $\text{NH}_4\text{OH}$  solution and demineralised water were used to obtain various  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures. A calibrated Lead Fluid BT101L peristaltic pump (0.001 – 575 mL·min<sup>-1</sup>) was used to supply liquid  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures to the anode. Finally, 1 M HCl solution was used to capture any remaining  $\text{NH}_3$  in the anode off-gas. The complete SOFC-O set-up is schematically presented in Figure 6-2.

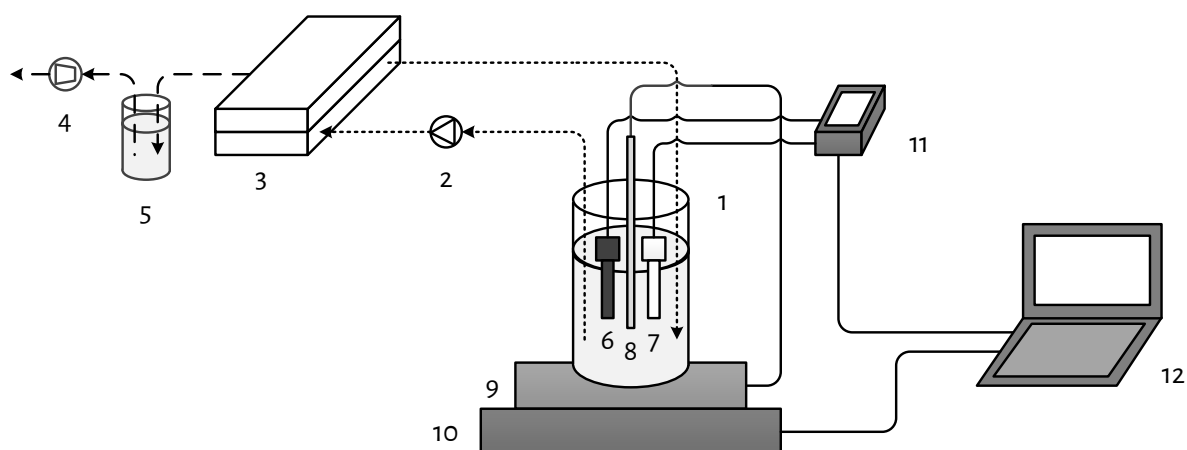


Figure 6-1 - A schematic representation of the used experimental VMS setup including a feed water bottle (1), peristaltic pump (2), flow-cell including membrane (3), vacuum pump (4), permeate scrubber (5), EC-sensor (6), pH-sensor (7), temperature sensor (8), pressure sensor (9), integrated heating and mixing plate (10), balance (11), multimeter (12) and laptop (13).

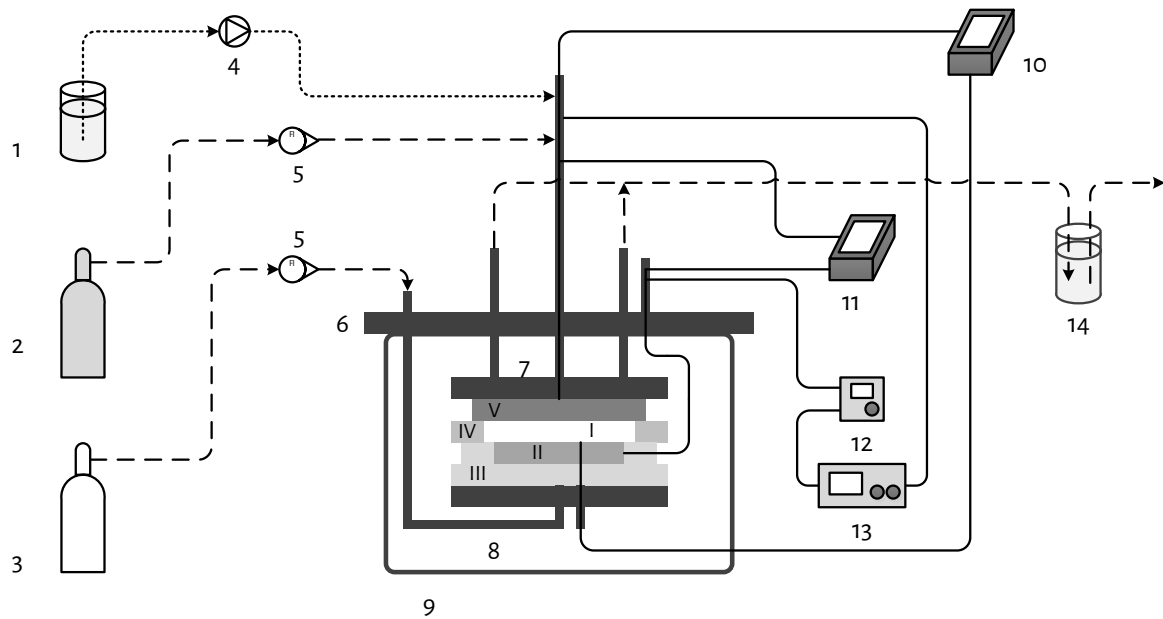


Figure 6-2 - A schematic representation of the used experimental SOFC setup including a fuel storage bottle (1), forming gas cylinder (2), air cylinder (3), peristaltic pump (4), fuel diffuser (5), Open Flange set-up (6), fuel diffuser (7), air diffuser (8), oven (9), thermometer (10), multimeter for electric potential (11), electric potential booster (12), electronic load (13) and off-gas scrubbing bottle (14). The MEA (I), electric current collector (II), alumina isolation sheets (III), mica sealing sheet (IV) and nickel foam (V) are all placed between the fuel and air diffuser.

## 6.2.2. Methods

### 6.2.2.1. VMS experiments

For the VMS experiments, feed waters with various initial  $\text{NH}_3$  concentrations were prepared by adding  $\text{NH}_4\text{HCO}_3$  to demi water.  $\text{NH}_4\text{HCO}_3$  was used as representative salt for N-loaded residual waters with high TAN concentrations, because bicarbonate ( $\text{HCO}_3^-$ ) is typically the main counter ion of  $\text{NH}_4^+$  in N-loaded residual waters as industrial condensates, sludge reject waters and hydrolysed urine. To obtain  $\text{NH}_3$  in the feed water, the solution pH was increased to 10 by adding NaOH to the  $\text{NH}_4\text{HCO}_3$  solutions.

During the stripping of  $\text{NH}_3$  from the feed waters, the  $\text{NH}_3$  feed water concentration decreased. By taking samples of the feed water to measure the  $\text{NH}_3$  concentration, the  $\text{NH}_3$  flux at various  $\text{NH}_3$  feed water concentrations was determined. Besides, the  $\text{H}_2\text{O}$  fluxes were determined to assess how much water evaporated along with the stripped  $\text{NH}_3$ . Based on both the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  fluxes, the concentrations of  $\text{NH}_3$  in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate as a function of the  $\text{NH}_3$  feed water concentration were determined. Next, the effect of the feed water temperature on both the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  flux was assessed for feed water temperatures of 25, 35, 45 and 55 °C. For the two mentioned variables, a full factorial design of experiments was set up, and each combination of feed water temperature and  $\text{NH}_3$  feed water concentration was assessed in duplicate.

The feed waters were recirculated over the hydrophobic membrane under so-called unsteady hydraulic conditions, corresponding to a Reynolds number of 500 in spacer-filled channels ([Mojab et al., 2014](#)). The pump speed was adjusted accordingly to maintain unsteady conditions for the various feed waters and the cross-flow velocity for the various feed waters ranged between 10 and 20  $\text{cm}\cdot\text{s}^{-1}$ . A detailed description of the determination of the cross-flow velocity to obtain unsteady hydraulic conditions based on the feed water characteristics and the dimensions of the flow channel can be found in the Supporting Information of the paper of [van Linden et al. \(2022a\)](#). At the permeate side of the membrane, an absolute pressure of 1.5 kPa was maintained by the vacuum pump. Throughout each run, the total mass, temperature, EC and pH of the feed water were continuously logged and samples were taken every 15 minutes to measure the  $\text{NH}_3$  concentration in the feed water.

### 6.2.2.2. SOFC experiments

When the MEA was installed and the Open Flange Set-up was placed in the oven, the oven temperature was increased at a ramping speed of 120 °C per hour to 400 °C, followed by 200 °C per hour to 750 °C. During the heating of the oven, air was supplied to the cathode at a flow rate of 400  $\text{mL}\cdot\text{min}^{-1}$ , while forming gas was supplied to the anode at a flow rate of 200  $\text{mL}\cdot\text{min}^{-1}$  to supply  $\text{H}_2$  to gradually reduce NiO to nickel, which catalyses the cracking of  $\text{NH}_3$  and the oxidation of  $\text{H}_2$ . When the oven temperature reached 750 °C, various  $\text{NH}_3\text{-H}_2\text{O}$  mixtures were supplied to the anode.  $\text{NH}_3\text{-H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations of 5, 7.5, 10, 12.5 and 25% were prepared by mixing 25 wt%  $\text{NH}_4\text{OH}$  stock solution with demi water. Throughout all

experiments, the airflow rate remained  $400 \text{ mL}\cdot\text{min}^{-1}$ , corresponding to  $0.1 \text{ mol}\cdot\text{O}_2\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$ , based on an  $\text{O}_2$  concentration of 21% in air and an air pressure of 101,325 Pa.

After a stabilisation period of 15 minutes, the open circuit potential (OCP) was measured for each fuel. Subsequently, the electrical circuit was closed and an electric current was drawn in steps of  $10 \text{ mA}\cdot\text{cm}^{-2}$ . By logging the electric potential measured between the anode and cathode for each electric current step, the peak power density achieved by the SOFC-O for the various fuels was determined. A fuel flow rate of  $200 \mu\text{L}\cdot\text{min}^{-1}$  was used, based on the recommendations of the MEA supplier, which corresponded to an  $\text{NH}_3$  flux of  $12 \text{ kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , considering a fuel density ranging from 950 to  $986 \text{ g}\cdot\text{L}^{-1}$ . Each  $\text{NH}_3$  concentration in the fuel was tested in duplicate experiments.

### 6.2.3. Performance indicators

#### 6.2.3.1. VMS

The  $\text{NH}_3$  and  $\text{H}_2\text{O}$  fluxes were determined using the respective mass differences per unit of membrane area and time (Eq. 6-4 and Eq. 6-5, respectively), which were based on the measured feed water masses,  $\text{NH}_3$  concentrations, salt concentrations and solution densities at each time instant. A more detailed description of the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  mass determination is presented in the Supporting Information of the paper of [van Linden et al. \(2022a\)](#).

$$J_{\text{NH}_3} = \frac{-(m_{\text{NH}_3,i+1} - m_{\text{NH}_3,i})}{A_m \cdot (t_{i+1} - t_i)} \quad \text{Eq. 6-4}$$

$$J_{\text{H}_2\text{O}} = \frac{-(m_{\text{H}_2\text{O},i+1} - m_{\text{H}_2\text{O},i})}{A_m \cdot (t_{i+1} - t_i)} \quad \text{Eq. 6-5}$$

Where  $J_{\text{NH}_3}$  and  $J_{\text{H}_2\text{O}}$  = ammonia and water mass flux (in  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ),  $m_{\text{NH}_3,i}$  and  $m_{\text{H}_2\text{O},i}$  = ammonia and water mass at time  $t_i$  (in kg),  $A_m$  = membrane area (in  $\text{m}^2$ ,  $A_m = 0.034 \text{ m}^2$ ) and  $t_i$  = time instant 'i' (in h).

Subsequently, the concentration of  $\text{NH}_3$  obtained by VMS in the permeate followed from the ratio of the  $\text{NH}_3$  flux and the total flux (Eq. 6-6).

$$c_{\text{NH}_3} = \frac{J_{\text{NH}_3}}{J_{\text{NH}_3} + J_{\text{H}_2\text{O}}} \quad \text{Eq. 6-6}$$

Where  $c_{\text{NH}_3}$  =  $\text{NH}_3$  concentration in  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate (unitless).

The total molar flow rate through the VMS membrane was determined based on the mass flow rates of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  (Eq. 6-7). Subsequently, the volumetric flow rate was determined by using the ideal gas law (Eq. 6-8).

$$n_t = \frac{J_{\text{NH}_3} \cdot A_m}{MW_{\text{NH}_3}} + \frac{J_{\text{H}_2\text{O}} \cdot A_m}{MW_{\text{H}_2\text{O}}} \quad \text{Eq. 6-7}$$

$$Q_{t,in} = \frac{n_t \cdot R \cdot T_f}{p_v} \quad \text{Eq. 6-8}$$

Where,  $n_t$  = total molar flow rate ( $\text{mol}\cdot\text{s}^{-1}$ ),  $MW_{\text{NH}_3}$  and  $MW_{\text{H}_2\text{O}}$  = molecular weight of  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , respectively (in  $\text{g}\cdot\text{mol}^{-1}$ ,  $MW_{\text{NH}_3} = 17 \text{ g}\cdot\text{mol}^{-1}$  and  $MW_{\text{H}_2\text{O}} = 18 \text{ g}\cdot\text{mol}^{-1}$ ),  $Q_{t,\text{in}}$  = volumetric gas flow rate ( $\text{m}^3\cdot\text{s}^{-1}$ ),  $R$  = universal gas constant (in  $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ,  $R = 8.31 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ ),  $T_f$  = feed water temperature (in K) and  $p_v$  = vacuum pressure (in Pa,  $p_v = 1,500 \text{ Pa}$ ).

The required electrical power for the vacuum pump was determined based on the study of [Huttunen et al. \(2017\)](#) (Eq. 6-9):

$$P_{v.p.} = \frac{Q_{t,\text{in}} \cdot p_v \cdot \ln\left(\frac{p_{\text{atm}}}{p_v}\right)}{\eta_{v.p.}} \quad \text{Eq. 6-9}$$

Where  $P_{v.p.}$  = electrical power vacuum pump (in  $\text{W} = \text{J}\cdot\text{s}^{-1}$ ),  $p_{\text{atm}}$  = atmospheric pressure (in Pa,  $p_{\text{atm}} = 101,325 \text{ Pa} = 101,325 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2}$ ),  $\eta_{v.p.}$  = vacuum pump efficiency (unitless,  $\eta_{v.p.} = 60\%$ ).

In addition, the required power of the feed pump to recirculate the feed waters was determined based on the feed flow rate and the measured hydraulic pressure loss over the VMS flow-cell (Eq. 6-10).

$$P_{f.p.} = \frac{Q_f \cdot \Delta p_h}{\eta_{f.p.}} \quad \text{Eq. 6-10}$$

Where  $P_{f.p.}$  = electrical power feed pump (in  $\text{J}\cdot\text{s}^{-1}$ ),  $Q_f$  = flow rate feed pump (in  $\text{m}^3\cdot\text{s}^{-1}$ ),  $\Delta h$  = hydraulic pressure loss (in Pa,  $\Delta p_h = 15,490 \text{ Pa}$ ),  $\eta_{f.p.}$  = feed pump efficiency (unitless,  $\eta_{f.p.} = 60\%$ ).

At last, the electrical energy consumption for  $\text{NH}_3$  stripping from the various feed water at various feed water temperatures and various  $\text{NH}_3$  feed water concentrations was determined using Eq. 6-11.

$$E_{VMS} = \frac{P_{v.p.} + P_{f.p.}}{J_N \cdot A_m} \quad \text{Eq. 6-11}$$

Where  $E_{VMS}$  = electrical energy consumption of VMS to strip  $\text{NH}_3$  (in  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ),  $J_N$  = nitrogen mass flux (in  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ).

### 6.2.3.2. SOFC

For each of the tested fuels, the theoretical Nernst potential was calculated using Eq. 6-12. The Nernst potential represents the theoretical potential of the oxidation of  $\text{H}_2$  (Eq. 6-3) after  $\text{NH}_3$  cracking in the presence of excess  $\text{H}_2\text{O}$  in the fuel (Eq. 6-1). The effect of the excess of  $\text{H}_2\text{O}$  is incorporated in the molar fraction of  $\text{H}_2$  and  $\text{H}_2\text{O}$  in Eq. 6-12.

$$U_{Nernst} = \frac{-\Delta_r G(T)}{N_{e^-, \text{H}_2} \cdot F} + \frac{R \cdot T}{N_{e^-, \text{H}_2} \cdot F} \cdot \ln\left(\frac{[\gamma_{\text{H}_2}] \cdot [\gamma_{\text{O}_2}]^{0.5}}{[\gamma_{\text{H}_2\text{O}}]}\right) \quad \text{Eq. 6-12}$$

Where  $U_{Nernst}$  = Nernst potential (in V),  $\Delta_r G(T)$  = Gibbs Free Energy of reaction at a certain temperature (in  $\text{kJ}\cdot\text{mol}^{-1}$ ,  $\Delta_r G(750^\circ\text{C}) = -196 \text{ kJ}\cdot\text{mol}^{-1}$ , lower heating value),  $T$  = operating temperature (in K,  $T = 750^\circ\text{C} = 1023 \text{ K}$ ),  $N_{e^-, \text{H}_2}$  = number of electrons per mole of hydrogen during oxidation (unitless,  $n = 2$ ),  $F$  = Faraday constant

( $C \cdot mol^{-1}$ ,  $F = 96,485 C \cdot mol^{-1}$ ),  $R =$  universal gas constant ( $J \cdot mol^{-1} \cdot K^{-1}$ ,  $R = 8.31 J \cdot mol^{-1} \cdot K^{-1}$ ),  $\gamma_{H_2}$ ,  $\gamma_{O_2}$  and  $\gamma_{H_2O} =$  molar fraction of hydrogen, oxygen and water, respectively (unitless).

Subsequently, the power density, representing the generated electrical power per unit of MEA area, followed from the measured electric potential at a certain electric current (Eq. 6-13).

$$p_{SOFC} = \frac{U \cdot I}{A_{MEA}} \quad \text{Eq. 6-13}$$

Where  $p_{SOFC}$  (in  $mW \cdot cm^{-2}$ ),  $U =$  electric potential (in mV),  $I =$  electric current (in mA) and  $A_{MEA} =$  membrane electrode assemble area (in  $cm^2$ ,  $A_{MEA} = 10 cm^2$ )

Furthermore, the fuel (Eq. 6-14) and oxygen utilisation (Eq. 6-15) were determined to assess how efficient  $NH_3$  in the fuel and  $O_2$  in the air were used to generate electricity, based on the measured amount of charge (electric current) and the supplied amounts of reactants ( $H_2$  and  $O_2$ ) for the oxidation of  $H_2$ . In addition, the electrical efficiency of the SOFC-O was determined based on the generated power and supplied amount of chemical energy per unit of time (Eq. 6-16).

$$\mu_f = \frac{I}{n_{H_2} \cdot N_{e^-,H_2} \cdot F} \quad \text{Eq. 6-14}$$

$$\mu_{O_2} = \frac{I}{n_{O_2} \cdot N_{e^-,O_2} \cdot F} \quad \text{Eq. 6-15}$$

Where  $\mu_f$  and  $\mu_{O_2} =$  fuel and oxygen utilisation (unitless), respectively,  $n_{H_2}$  and  $n_{O_2} =$  molar flow rate of  $H_2$  and  $O_2$ , respectively ( $mol \cdot s^{-1}$ ) and  $N_{e^-,O_2} =$  the number of electrons per mole of oxygen in the hydrogen oxidation reaction (unitless,  $n = 4$ ).

$$\eta_{elec} = \frac{p_{SOFC} \cdot A_{MEA}}{n_{H_2} \cdot -\Delta_r H(T)} \quad \text{Eq. 6-16}$$

Where,  $\eta_{elec} =$  electrical efficiency (unitless),  $p_{SOFC} =$  electric power generated by the SOFC (in  $W = J \cdot s^{-1}$ ) and  $\Delta_r H(T) =$  enthalpy of reaction at a certain temperature (in  $kJ \cdot mol^{-1}$ ,  $\Delta_r H(750 \text{ } ^\circ C) = -237 kJ \cdot mol^{-1}$ , lower heating value).

Finally, the electrical energy generation of the SOFC-O was calculated using Eq. 6-17.

$$E_{SOFC-O} = \frac{p_{SOFC} \cdot A_{MEA}}{m_N} \quad \text{Eq. 6-17}$$

Where,  $E_{SOFC-O} =$  electrical energy generation of the SOFC-O ( $MJ \cdot kg^{-1} \cdot N^{-1}$ ).

6.3. Results and discussion6.3.1. Recovery of NH<sub>3</sub>-H<sub>2</sub>O mixtures by VMS6.3.1.1. NH<sub>3</sub> flux for various feed water temperatures and NH<sub>3</sub> feed water concentrations

For the VMS experiments, various feed waters consisting of NH<sub>4</sub>HCO<sub>3</sub> at a pH of 10.0 ± 0.1 (average ± standard deviations, n = 17) were prepared. Subsequently, NH<sub>3</sub> was stripped at feed water temperatures of 25, 35, 45 and 55 °C. The deviation in feed water temperature during the experiments was less than 1% of the respective feed water temperature. Due to the addition of NaOH to form dissolved NH<sub>3</sub> in the feed waters, sodium (Na<sup>+</sup>), HCO<sub>3</sub><sup>-</sup> and carbonate (CO<sub>3</sub><sup>2-</sup>) ions were also present in the feed waters. The transfer of CO<sub>2</sub> was neglected, because the CO<sub>2</sub> vapour pressure of the feed water was ten times lower than the NH<sub>3</sub> and H<sub>2</sub>O vapour pressure of the feed water; at a pH of 10, inorganic carbon is only present as HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>.

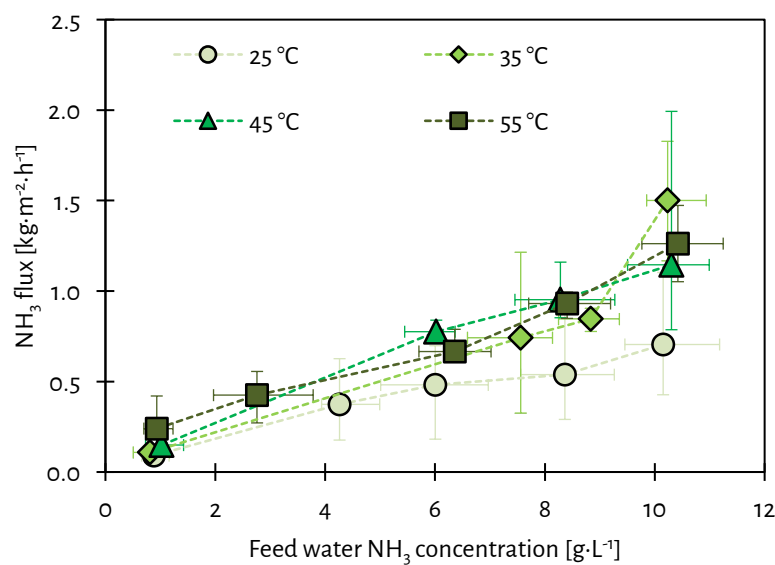


Figure 6-3 - The NH<sub>3</sub> flux as a function of NH<sub>3</sub> feed water concentration for various feed water temperatures. The vertical error bars represent the minimum and maximum deviations of the measured NH<sub>3</sub> flux of at least triplicate measurements, whereas the horizontal error bars represent the minimum and maximum deviations in the measured feed water NH<sub>3</sub> concentration.



The reported values of the  $\text{NH}_3$  flux in Figure 6-3 and the  $\text{NH}_3$  feed water concentration for the various feed water temperatures were calculated based on the measured TAN concentration, temperature, pH and ionic strength, and feed water temperature. At a feed water temperature of 25 °C, the  $\text{NH}_3$  flux increased from 0.1 to 0.7  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for an increase in  $\text{NH}_3$  feed water concentration from 1 to 10  $\text{g}\cdot\text{L}^{-1}$ . For the same  $\text{NH}_3$  feed water concentration range, the  $\text{NH}_3$  flux increased from 0.1 to 1.5  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  at a feed water temperature of 35 °C, from 0.1 to 1.1  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  at 45 °C and from 0.2 to 1.2  $\text{kg}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for 55 °C.

For all measured temperatures, the  $\text{NH}_3$  flux increased linearly ( $R^2 = 0.86 - 0.99$ ) as a function of the increasing  $\text{NH}_3$  feed water concentration, in line with the studies of [El-Bourawi et al. \(2007\)](#) and [Scheepers et al. \(2020\)](#). The linear increase in  $\text{NH}_3$  flux as a function of the  $\text{NH}_3$  feed water concentration was in contrast to findings of [He et al. \(2017\)](#), who found a logarithmic relationship for an  $\text{NH}_3$  concentration ranging between 1 and 4  $\text{g}\cdot\text{L}^{-1}$ , which was probably a result of a high mass transfer resistance, as biogas slurry was used as feed. Henry's Law states that the vapour pressure of dissolved gases in water at a certain temperature is a linear function of the concentration of the respective dissolved gas. Figure 6-4 presents the vapour pressures of  $\text{NH}_3$  in water as a function of both the feed water temperature and the  $\text{NH}_3$  feed water concentration. The vapour pressures of the feed water are obtained by PHREEQC simulation software, taking the  $\text{NH}_3$  concentrations, pH, ionic strength and temperature into account to determine chemical equilibria and vapour pressures of solutes ( $\text{NH}_3$ ) and solvent ( $\text{H}_2\text{O}$ ). Furthermore, the Dusty Gas Model and Fick's Law, which are applicable for vapour transfer through porous hydrophobic membranes ([Lawson & Lloyd, 1997](#)), describe that the diffusion flux is linearly proportional to the driving force of gas transfer. Hence, the observed linear increase in  $\text{NH}_3$  flux as a function of the  $\text{NH}_3$  feed water concentration at each tested feed water temperature was caused by the increase in  $\text{NH}_3$  vapour pressure of the feed water. The observed linear increase in  $\text{NH}_3$  flux as a function of the  $\text{NH}_3$  feed water concentration indicated that the  $\text{NH}_3$  mass transfer coefficient remained unaffected, suggesting that no concentration polarisation phenomena affected the  $\text{NH}_3$  transfer at increased  $\text{NH}_3$  feed water concentrations.

According to Figure 6-4, the  $\text{NH}_3$  vapour pressure of the feed water increased exponentially with increasing feed water temperatures for a certain  $\text{NH}_3$  feed water concentration, which is explained by the temperature dependency of Henry's constant, determined using the van 't Hoff equation, and the decreased solubility of gases for higher feed water temperatures. However, according to Figure 6-3, the  $\text{NH}_3$  fluxes did not increase consistently as a function of the feed water temperature. The  $\text{NH}_3$  fluxes increased when the feed water temperature increased from 25 to 35 °C. However, a further increase in temperature from 35 to 45 and 55 °C, did not result in an increased  $\text{NH}_3$  flux. Apparently, when the feed water temperature increased to 45 and 55 °C, the  $\text{NH}_3$  mass transfer coefficient decreased, counteracting the increase in  $\text{NH}_3$  vapour pressure of the feed water. The decrease in  $\text{NH}_3$  mass transfer coefficient over the increasing feed water temperature can be assigned to  $\text{NH}_3$  depletion, concentration polarisation, and temperature polarisation, of which the effects become more severe at increased feed water temperatures ([He et al., 2017](#); [He et al., 2018](#)). However, to draw firm conclusions on which polarisation phenomenon affected the  $\text{NH}_3$  mass transfer most, more research is required.

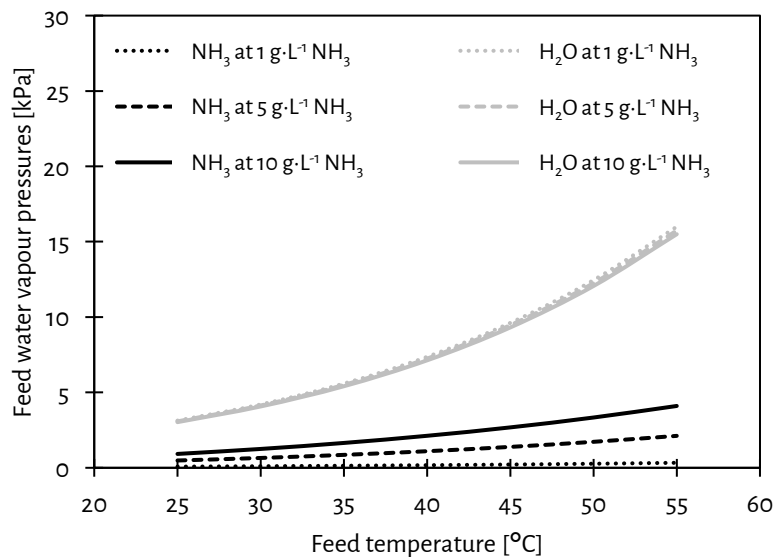


Figure 6-4 - The NH<sub>3</sub> and H<sub>2</sub>O vapour pressure of the feed water as a function of the feed water temperature for various NH<sub>3</sub> feed water concentrations. The vapour pressures were obtained by simulations with PHREEQC software, using the phreeqc.dat database.

#### 6.3.1.2. H<sub>2</sub>O flux for various feed water temperatures and NH<sub>3</sub> feed water concentrations

Besides the stripping of NH<sub>3</sub>, also evaporation of H<sub>2</sub>O through the hydrophobic membrane took place during the VMS experiments. Figure 6-5 presents the H<sub>2</sub>O flux as a function of the concentration of NH<sub>3</sub> in the feed and the feed water temperature. At a feed water temperature of 25 °C, the H<sub>2</sub>O flux decreased from 10 to 7 kg·m<sup>-2</sup>·h<sup>-1</sup> for an increase in NH<sub>3</sub> feed water concentration from 1 to 10 g·L<sup>-1</sup>. When the NH<sub>3</sub> feed water concentration increased from 1 to 10 g·L<sup>-1</sup> at a feed water temperature of 35 and 45 °C, the H<sub>2</sub>O flux decreased from 16 to 12 kg·m<sup>-2</sup>·h<sup>-1</sup> and from 24 to 22 kg·m<sup>-2</sup>·h<sup>-1</sup>, respectively. The H<sub>2</sub>O flux at a feed water temperature of 55 °C remained stable at 30 kg·m<sup>-2</sup>·h<sup>-1</sup> as the NH<sub>3</sub> feed water concentration increased from 1 to 10 g·L<sup>-1</sup>.

According to Figure 6-4, the H<sub>2</sub>O vapour pressure of the feed water increased exponentially with the feed water temperature, following the Clausius–Clapeyron relation. However, according to the data, the H<sub>2</sub>O flux increased linearly ( $R^2 = 0.96–1.00$ ) as a function of the increase in feed water temperature. The observation that the H<sub>2</sub>O flux increased linearly while the driving force increases exponentially indicates that the H<sub>2</sub>O mass transfer coefficient decreased over the increasing feed water temperature, which might be attributed to temperature polarisation (Martínez-Díez & Vázquez-González, 1999; Ding et al., 2006; El-Bourawi et al., 2007).

According to Figure 6-5, the H<sub>2</sub>O flux decreased as a function of the increasing NH<sub>3</sub> feed water concentration. For increasing NH<sub>3</sub> in the feed water, increased amounts of NH<sub>4</sub>HCO<sub>3</sub> and NaOH were added, resulting in higher ion concentrations during NH<sub>3</sub> stripping. Raoult's Law describes that the vapour pressure of a solvent decreases when the molar fraction of the solutes increases. Based on the data presented in Figure 6-4, the H<sub>2</sub>O vapour decreased by 3% when the NH<sub>3</sub> concentration increased from 1 to 10 g·L<sup>-1</sup>. The decrease in H<sub>2</sub>O flux as a function of the increasing NH<sub>3</sub> concentration might also be explained by temperature polarisation,

which decreases the H<sub>2</sub>O mass transfer coefficient, as described by [Martínez-Díez and Vázquez-González \(1999\)](#).

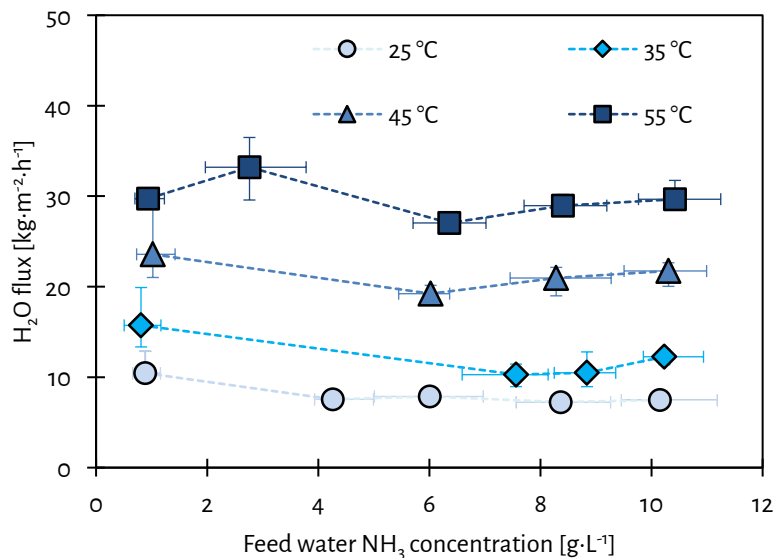


Figure 6-5 - The H<sub>2</sub>O flux as a function of the increasing NH<sub>3</sub> feed water concentration for various feed water temperatures. The vertical error bars represent the minimum and maximum deviations of the measured H<sub>2</sub>O flux of at least triplicate measurements, whereas the horizontal error bars represent the minimum and maximum deviations in the measured feed water NH<sub>3</sub> concentration.

### 6.3.1.3. NH<sub>3</sub> concentration in gaseous VMS permeate for various feed water temperatures and NH<sub>3</sub> feed water concentrations

One of the objectives of this chapter was to determine the attainable NH<sub>3</sub> concentration in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate for NH<sub>3</sub> reuse purposes. Figure 6-6 presents the concentration of NH<sub>3</sub> in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate for the various tested feed water temperatures as a function of the NH<sub>3</sub> feed water concentration. For an increase in the NH<sub>3</sub> feed water concentration from 1 to 10 g·L<sup>-1</sup>, the NH<sub>3</sub> concentration in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the VMS permeate increased from 1 to 8 wt% at a feed water temperature of 25 °C. For the same increase in NH<sub>3</sub> feed water concentration, the NH<sub>3</sub> concentration in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate increased from 1 to 11 wt% for a feed water temperature of 35 °C, from 1 to 5 wt% for 45 °C and from 1 to 4 wt% for 55 °C. Hence, increasing the NH<sub>3</sub> feed water concentration resulted in a more NH<sub>3</sub> concentrated gaseous NH<sub>3</sub>-H<sub>2</sub>O mixture obtained in VMS permeate, for all tested feed water temperatures, which can also be derived from the experimental results obtained by [Ding et al. \(2006\)](#) and [El-Bourawi et al. \(2007\)](#) and the modelling study conducted by [Scheepers et al. \(2020\)](#). The increasing NH<sub>3</sub> concentrations in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate as a function of the increasing NH<sub>3</sub> feed water concentration can be attributed to the increased NH<sub>3</sub> fluxes, while the H<sub>2</sub>O flux did not increase.

By increasing the feed water temperature from 25 to 45 and 55 °C, the H<sub>2</sub>O flux increased more than the NH<sub>3</sub> flux, leading to more diluted NH<sub>3</sub> in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate, in line with

Scheepers et al. (2020). According to Figure 6-4, the H<sub>2</sub>O vapour pressure of the feed water increases faster than the NH<sub>3</sub> vapour pressure of the feed water as a function of the feed water temperature, which explains the observed higher increase in H<sub>2</sub>O flux compared to NH<sub>3</sub> flux as a function of the feed water temperature. Interestingly, by increasing the feed water temperature from 25 to 35 °C, more concentrated NH<sub>3</sub> in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate was obtained, while further increasing the feed water temperature diluted the NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate. The feed water temperature increase from 25 to 35 °C resulted in a higher increase in NH<sub>3</sub> flux than the increase in H<sub>2</sub>O flux. The initial increase in gaseous NH<sub>3</sub> concentration for the feed water temperature increase from 25 to 35 °C can be explained by the combined effect of the various polarisation phenomena: temperature polarisation, accumulated ion concentration polarisation and NH<sub>3</sub> depletion concentration polarisation.

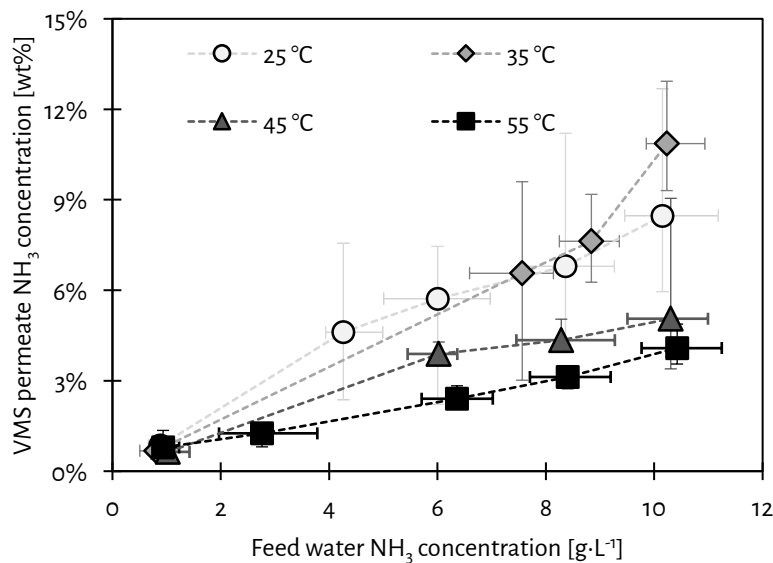


Figure 6-6 - The concentration of NH<sub>3</sub> in NH<sub>3</sub>-H<sub>2</sub>O mixtures obtained in the gaseous VMS permeate as a function of the increasing NH<sub>3</sub> feed water concentration for various feed water temperatures. The vertical error bars represent the minimum and maximum deviations of the measured NH<sub>3</sub> concentrations of at least triplicate measurements, whereas the horizontal error bars represent the minimum and maximum deviations in the measured feed water NH<sub>3</sub> concentration.

6.3.2. Use of NH<sub>3</sub>-H<sub>2</sub>O mixtures as fuel for an SOFC6.3.2.1. Open circuit potential for various NH<sub>3</sub>-H<sub>2</sub>O mixtures used as a fuel

For the SOFC-O experiments, NH<sub>3</sub>-H<sub>2</sub>O mixtures with various NH<sub>3</sub> concentrations were prepared. During all experiments, the anode and cathode temperatures were stable at 755 and 761 °C, respectively.

Figure 6-7A shows the calculated Nernst potential as a function of the NH<sub>3</sub> concentration in the fuel, based on the respective Nernst potential calculation for H<sub>2</sub> oxidation (Eq. 6-12), the relevant reactions of NH<sub>3</sub> cracking, and subsequent H<sub>2</sub> oxidation in the presence of H<sub>2</sub>O in the fuel (Eq. 6-1, 6-2 and 6-3). When more NH<sub>3</sub> is present in the fuel, the molar fraction of H<sub>2</sub> at the anode increases, while the molar fraction of H<sub>2</sub>O decreases, leading to a higher Nernst potential at a certain temperature.

Figure 6-7B shows that by increasing the NH<sub>3</sub> concentration in the fuel from 5 to 25 wt%, the open circuit electric potential increased from 0.82 to 0.93 V. The differences between the measured open circuit electric potential and the calculated Nernst potentials (Figure 6-7B) were always below 2% for fuels with 7.5, 10, 12.5 and 25 wt% NH<sub>3</sub>, suggesting that even in the presence of excess H<sub>2</sub>O, almost complete cracking of NH<sub>3</sub> took place. However, the open circuit electric potential of fuel with 5 wt% NH<sub>3</sub> was unstable throughout the measurements, suggesting that the cracking of NH<sub>3</sub> was affected by the high content of H<sub>2</sub>O in this fuel.

According to mass balance calculations based on the amount of supplied NH<sub>3</sub> in the fuel and absorbed in the off-gas scrubber, 95% of the supplied NH<sub>3</sub> in the various fuels was cracked during open-circuit conditions, which is lower than the at least 99.9 % reported by [Dekker and Rietveld \(2006\)](#) and [Ma et al. \(2006\)](#) in absence of H<sub>2</sub>O in the fuel. According to [Ni et al. \(2009\)](#), the NH<sub>3</sub> cracking efficiency decreases when the partial pressure of NH<sub>3</sub> decreases, explaining the obtained results in this chapter.

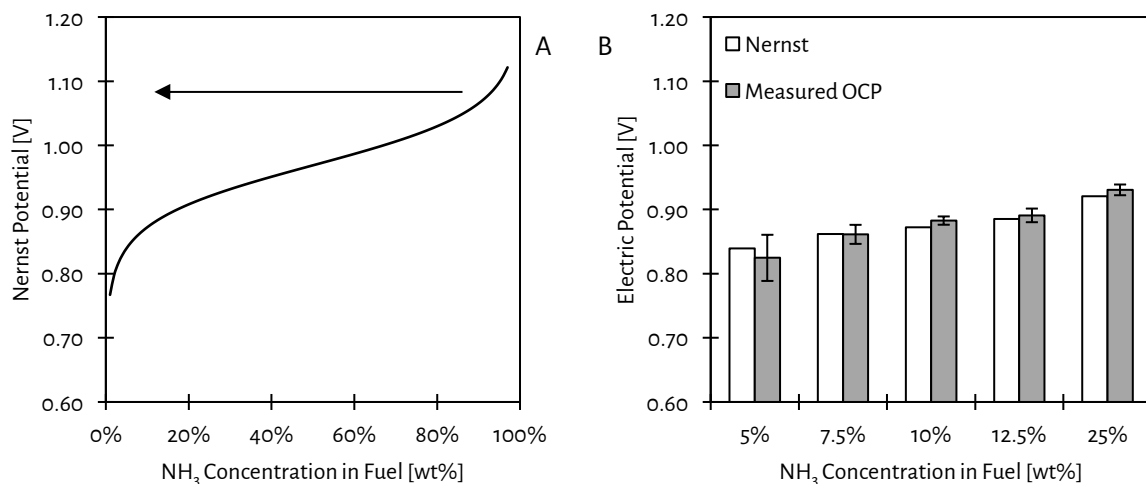


Figure 6-7 - The Nernst potential as a function of NH<sub>3</sub> concentration in the fuel (A). The arrow indicates the direction of interpreting the Nernst potential when the fuel becomes diluted with increasing amounts of water. The measured open circuit electric potentials and calculated Nernst potentials for the various NH<sub>3</sub> concentrations in the fuel (B). The vertical error bars represent the minimum and maximum deviations of at least triplicate measurements.

6.3.2.2. Generation of energy using various NH<sub>3</sub>-H<sub>2</sub>O mixtures as a fuel for an SOFC

Figure 6-8 presents the measured closed circuit electric potentials and power densities as a function of the current densities for the various fuels in a representative duplicate experiment. In addition, Table 6-1 presents the average and the minimum and maximum deviations of the peak power density, fuel utilisation, O<sub>2</sub> utilisation and electrical efficiency for the NH<sub>3</sub>-H<sub>2</sub>O fuels with various NH<sub>3</sub> concentrations in the fuel. The peak power densities, ranging between 114 and 347 mW·cm<sup>-1</sup> were in line with studies in which pure NH<sub>3</sub> was used as a fuel (Ni et al., 2009; Lan & Tao, 2014b; Afif et al., 2016). According to the results, the peak power density increased as a function of the increasing NH<sub>3</sub> concentrations in the fuel. However, the fuel utilisation decreased when the NH<sub>3</sub> concentration in the fuel increased. Interestingly, the fuel utilisation was 68% when the fuel only contained 5 wt% NH<sub>3</sub>, indicating that besides the cracking of NH<sub>3</sub> also subsequent oxidation of H<sub>2</sub> still effectively took place in the presence of high concentrations of H<sub>2</sub>O. Hence, although the peak power density of the SOFC-O increased with increasing NH<sub>3</sub> concentrations in the fuel, not all additionally supplied NH<sub>3</sub> resulted in the generation of electricity. To maximise fuel utilisation, all produced H<sub>2</sub> after NH<sub>3</sub> cracking must come in contact with transferred O<sup>2-</sup> at the triple-phase boundary, which is the interface of the electrolyte, the anode and the electric current collector. However, the O<sub>2</sub> utilisation was at most 31%, suggesting that there was no lack of O<sub>2</sub> supply to the cathode. Therefore, the decrease in fuel utilisation at higher NH<sub>3</sub> concentrations in the fuel was probably caused by less efficient NH<sub>3</sub> cracking, which agrees with the results of Stoeckl et al. (2020), who found a similar decrease when more NH<sub>3</sub> was fed to the anode. The electrical efficiency using NH<sub>3</sub>-H<sub>2</sub>O mixtures with concentrations between 5 and 25 wt% NH<sub>3</sub> as fuel for the SOFC-O ranged between 22 and 36%. According to these results, a SOFC-O can be used to generate energy, applying NH<sub>3</sub>-H<sub>2</sub>O mixtures with NH<sub>3</sub> concentrations as low as 5 wt%.

Table 6-1 - The obtained peak power density, fuel and oxygen utilisation, and the electrical efficiency of the SOFC-O for various concentrations of NH<sub>3</sub> in the fuel. The presented values represent the averages and the minimum and maximum deviations of duplicate measurements.

NH <sub>3</sub> in the fuel	Peak Power Density	Fuel Utilisation	Oxygen Utilisation	Electric Efficiency
-	mW·cm <sup>-2</sup>	-	-	-
25%	347 ± 11	42 ± 1%	31 ± 1%	22 ± 1%
12.5%	212 ± 14	51 ± 3%	19 ± 1%	26 ± 2%
10%	157 ± 1	52 ± 7%	16 ± 2%	25%
7.5%	138 ± 6	54 ± 1%	12%	29 ± 2%
5%	114	68%	10%	36%

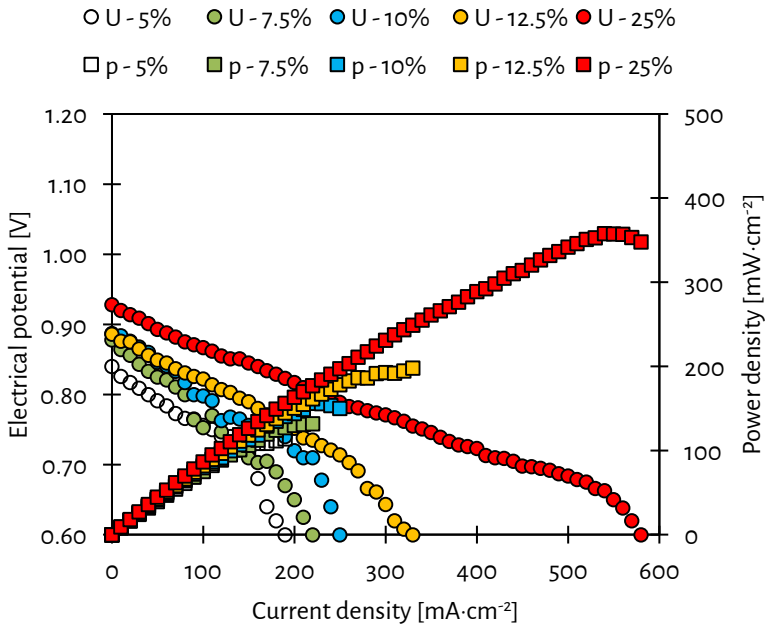


Figure 6-8 - The measured electric potentials (in circles) and the power densities (in squares) as a function of the generated current density for the tested NH<sub>3</sub>-H<sub>2</sub>O mixtures with various NH<sub>3</sub> concentrations.

6.3.3. Energetic evaluation of VMS and SOFC for the recovery and the use of NH<sub>3</sub>

No previous studies quantified the electrical energy consumption to drive the pumps during the stripping of NH<sub>3</sub> in a VMS configuration, although [Scheepers et al. \(2020\)](#) assessed the thermal energy consumption to strip NH<sub>3</sub> by VMS. Notably, N-loaded residual waters with high TAN concentrations, such as sludge reject water, often already have temperatures in the range of 30 - 40 °C, because they originate from anaerobic digesters. Therefore, heat addition for VMS may not be needed. Figure 6-9 shows the electrical energy consumption for stripping NH<sub>3</sub> from water (aqueous solution) by VMS as a function of the feed water temperature and the NH<sub>3</sub> feed water concentration. The electrical energy consumption ranged between 84 and 113 MJ·kg-N<sup>-1</sup> at an NH<sub>3</sub> feed water concentration of 1 g·L<sup>-1</sup> and decreased to between 7 and 17 MJ·kg-N<sup>-1</sup> when the NH<sub>3</sub> feed water concentration increased to 10 g·L<sup>-1</sup>. The electrical energy consumption was mainly used for the transfer of H<sub>2</sub>O water by the vacuum pump. The electrical energy consumption to strip NH<sub>3</sub> decreased with increasing NH<sub>3</sub> feed water concentration. The recirculation of the feed water accounted at most for 2% of the electrical energy consumption and can therefore be neglected.

The SOFC-O reached electrical efficiencies ranging between 22% and 36% using NH<sub>3</sub>-H<sub>2</sub>O mixtures with NH<sub>3</sub> concentrations ranging between 5 and 25 wt%. Based on the determined electrical efficiencies and additional calculations using Eq. 6-17, the electrical energy generation of the SOFC-O ranged between 6 and 9 MJ·kg-N<sup>-1</sup>.

Hence, the NH<sub>3</sub> concentrations obtained in the gaseous permeate of VMS reaching up to 11 wt% agreed with the NH<sub>3</sub> concentrations in NH<sub>3</sub>-H<sub>2</sub>O mixtures that were used for the generation of electricity in an SOFC-O, which were as low as 5 wt%. Moreover, also the electrical energy consumption of VMS of 7 MJ·kg-N<sup>-1</sup> and the electrical energy electricity of the SOFC-O of 9 MJ·kg-N<sup>-1</sup> aligned, suggesting that the consumed energy of recovering NH<sub>3</sub> from water (aqueous solution) can be provided by converting the NH<sub>3</sub> to energy in an SOFC-O.

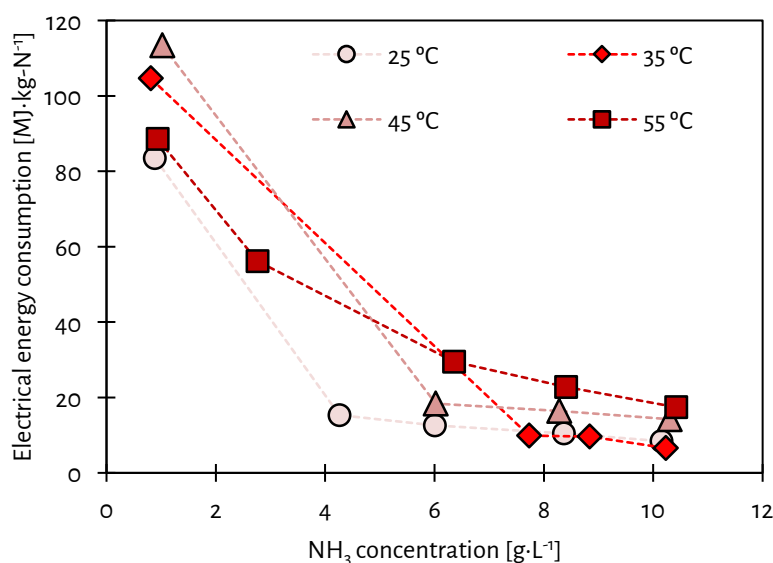


Figure 6-9 - The calculated average electrical energy consumption to strip NH<sub>3</sub> from water (aqueous solution) by VMS as a function of the NH<sub>3</sub> concentration for the various feed temperatures.



#### 6.4. Conclusions

The experimental study to assess the feasibility of combining VMS and SOFC to recover  $\text{NH}_3$  from water (aqueous solution) and subsequently generate energy from the recovered  $\text{NH}_3$  resulted in the following conclusions:

- VMS allowed for the recovery of  $\text{NH}_3$  as gaseous  $\text{NH}_3\text{-H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations ranging between 1 and 11 wt% at  $\text{NH}_3$  feed water concentrations ranging between 1 and 10  $\text{g}\cdot\text{L}^{-1}$ ;
- The  $\text{NH}_3$  concentration in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate increased when the feed water temperature increased from 25 to 35 °C. However, the  $\text{NH}_3$  concentration in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate decreased when the feed water temperature increased to 45 and 55 °C;
- The  $\text{NH}_3$  concentration in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures obtained in the gaseous VMS permeate increased as a function of the increasing  $\text{NH}_3$  feed water concentration;
- The electrical energy consumption for  $\text{NH}_3$  stripping by VMS decreased from 113 to 7  $\text{MJ}\cdot\text{kg}\text{-N}^{-1}$  when the  $\text{NH}_3$  feed water concentrations increased from 1 to 10  $\text{g}\cdot\text{L}^{-1}$ , respectively;
- The SOFC-O generated energy from  $\text{NH}_3\text{-H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations ranging between 5 and 25 wt%, indicating that  $\text{NH}_3$  cracking and subsequent  $\text{H}_2$  oxidation still took place in the presence of excess  $\text{H}_2\text{O}$  at the anode;
- The efficiency of cracking  $\text{NH}_3$  at the anode was lower than reported in studies that used dry  $\text{NH}_3$  as a fuel, suggesting that  $\text{NH}_3$  cracking is affected by excess  $\text{H}_2\text{O}$  at the anode;
- The electrical efficiency of the SOFC-O ranged between 22 and 36% and decreased as a function of the increasing  $\text{NH}_3$  concentration in the fuel;
- The electrical energy consumption of VMS of 7  $\text{MJ}\cdot\text{kg}\text{-N}^{-1}$  for stripping  $\text{NH}_3$  from water (aqueous solution) was lower than the electrical energy generation of the SOFC-O of 9  $\text{MJ}\cdot\text{kg}\text{-N}^{-1}$ .

## 6.5. References

- Afif, A., Radenahmad, N., Cheok, Q., Shams, S., Kim, J. H., & Azad, A. K. (2016). Ammonia-fed fuel cells: a comprehensive review. *Renewable and Sustainable Energy Reviews*, *60*, 822-835.  
doi:<http://dx.doi.org/10.1016/j.rser.2016.01.120>
- Cheddie, D. (2012). Ammonia as a Hydrogen Source for Fuel Cells: A Review. In D. Minic (Ed.), *Hydrogen Energy - Challenges and Perspectives* (pp. Ch. 13). Rijeka: InTech.
- Dekker, N. J. J., & Rietveld, G. (2006). Highly efficient conversion of ammonia in electricity by solid oxide fuel cells. *Journal of Fuel Cell Science and Technology*, *3*(4), 499-502. doi:10.1115/1.2349536
- Ding, Z., Liu, L., Li, Z., Ma, R., & Yang, Z. (2006). Experimental study of ammonia removal from water by membrane distillation (MD): The comparison of three configurations. *Journal of Membrane Science*, *286*(1-2), 93-103. doi:10.1016/j.memsci.2006.09.015
- El-Bourawi, M. S., Ding, Z., Ma, R., & Khayet, M. (2006). A framework for better understanding membrane distillation separation process. *Journal of Membrane Science*, *285*(1), 4-29.  
doi:<https://doi.org/10.1016/j.memsci.2006.08.002>
- El-Bourawi, M. S., Khayet, M., Ma, R., Ding, Z., Li, Z., & Zhang, X. (2007). Application of vacuum membrane distillation for ammonia removal. *Journal of Membrane Science*, *301*(1-2), 200-209.  
doi:10.1016/j.memsci.2007.06.021
- He, Q., Tu, T., Yan, S., Yang, X., Duke, M., Zhang, Y., & Zhao, S. (2018). Relating water vapor transfer to ammonia recovery from biogas slurry by vacuum membrane distillation. *Separation and Purification Technology*, *191*(Supplement C), 182-191.  
doi:<https://doi.org/10.1016/j.seppur.2017.09.030>
- He, Q., Yu, G., Tu, T., Yan, S., Zhang, Y., & Zhao, S. (2017). Closing CO<sub>2</sub> Loop in Biogas Production: Recycling Ammonia As Fertilizer. *Environmental Science & Technology*, *51*(15), 8841-8850.  
doi:10.1021/acs.est.7b00751
- Huttunen, M., Nygren, L., Kinnarinen, T., Häkkinen, A., Lindh, T., Ahola, J., & Karvonen, V. (2017). Specific energy consumption of cake dewatering with vacuum filters. *Minerals Engineering*, *100*, 144-154.  
doi:<https://doi.org/10.1016/j.mineng.2016.10.025>
- Lan, R., & Tao, S. (2010). Direct Ammonia Alkaline Anion-Exchange Membrane Fuel Cells. *Electrochemical and Solid-State Letters*, *13*(8), B83-B86. doi:<https://doi.org/10.1149/1.3428469>
- Lan, R., & Tao, S. (2014b). Ammonia as a Suitable Fuel for Fuel Cells. *Frontiers in Energy Research*, *2*(35).  
doi:10.3389/fenrg.2014.00035
- Lawson, K. W., & Lloyd, D. R. (1997). Membrane distillation. *Journal of Membrane Science*, *124*(1), 1-25.  
doi:[https://doi.org/10.1016/S0376-7388\(96\)00236-0](https://doi.org/10.1016/S0376-7388(96)00236-0)
- Ma, Q., Peng, R., Tian, L., & Meng, G. (2006). Direct utilization of ammonia in intermediate-temperature solid oxide fuel cells. *Electrochemistry Communications*, *8*(11), 1791-1795.  
doi:<http://dx.doi.org/10.1016/j.elecom.2006.08.012>

- Martínez-Díez, L., & Vázquez-González, M. I. (1999). Temperature and concentration polarization in membrane distillation of aqueous salt solutions. *Journal of Membrane Science*, *156*(2), 265-273. doi:[https://doi.org/10.1016/S0376-7388\(98\)00349-4](https://doi.org/10.1016/S0376-7388(98)00349-4)
- Mojab, S. M., Pollard, A., Pharoah, J. G., Beale, S. B., & Hanff, E. S. (2014). Unsteady Laminar to Turbulent Flow in a Spacer-Filled Channel. *Flow, Turbulence and Combustion*, *92*(1), 563-577. doi:10.1007/s10494-013-9514-4
- Ni, M., Leung, M. K. H., & Leung, D. Y. C. (2009). Ammonia-fed solid oxide fuel cells for power generation—A review. *International Journal of Energy Research*, *33*(11), 943-959. doi:10.1002/er.1588
- Okanishi, T., Okura, K., Srifa, A., Muroyama, H., Matsui, T., Kishimoto, M., Saito, M., Iwai, H., Yoshida, H., Saito, M., Koide, T., Iwai, H., Suzuki, S., Takahashi, Y., Horiuchi, T., Yamasaki, H., Matsumoto, S., Yumoto, S., Kubo, H., Kawahara, J., Okabe, A., Kikkawa, Y., Isomura, T., & Eguchi, K. (2017). Comparative Study of Ammonia-fueled Solid Oxide Fuel Cell Systems. *Fuel Cells*, *17*(3), 383-390. doi:10.1002/fuce.201600165
- Scheepers, D. M., Tahir, A. J., Brunner, C., & Guillen-Burrieza, E. (2020). Vacuum membrane distillation multi-component numerical model for ammonia recovery from liquid streams. *Journal of Membrane Science*, *614*, 118399. doi:<https://doi.org/10.1016/j.memsci.2020.118399>
- Stambouli, A. B., & Traversa, E. (2002). Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. *Renewable and Sustainable Energy Reviews*, *6*(5), 433-455. doi:[https://doi.org/10.1016/S1364-0321\(02\)00014-X](https://doi.org/10.1016/S1364-0321(02)00014-X)
- Staniforth, J., & Ormerod, R. M. (2003). Clean destruction of waste ammonia with consummate production of electrical power within a solid oxide fuel cell system. *Green Chemistry*, *5*(5), 606-609. doi:10.1039/B307396N
- Stoeckl, B., Preininger, M., Subotić, V., Gaber, C., Seidl, M., Sommersacher, P., Schroettner, H., & Hochenauer, C. (2019a). High Utilization of Humidified Ammonia and Methane in Solid Oxide Fuel Cells: An Experimental Study of Performance and Stability. *Journal of The Electrochemical Society*, *166*(12), F774-F783. doi:10.1149/2.0781912jes
- Stoeckl, B., Preininger, M., Subotić, V., Megel, S., Folgner, C., & Hochenauer, C. (2020). Towards a wastewater energy recovery system: The utilization of humidified ammonia by a solid oxide fuel cell stack. *Journal of Power Sources*, *450*, 227608. doi:<https://doi.org/10.1016/j.jpowsour.2019.227608>
- Suzuki, S., Muroyama, H., Matsui, T., & Eguchi, K. (2012). Fundamental studies on direct ammonia fuel cell employing anion exchange membrane. *Journal of Power Sources*, *208*(Supplement C), 257-262. doi:<https://doi.org/10.1016/j.jpowsour.2012.02.043>
- Valera-Medina, A., Xiao, H., Owen-Jones, M., David, W. I. F., & Bowen, P. J. (2018). Ammonia for power. *Progress in Energy and Combustion Science*, *69*, 63-102. doi:<https://doi.org/10.1016/j.pecs.2018.07.001>

- van Linden, N., Bandinu, G. L., Vermaas, D. A., Spanjers, H., & van Lier, J. B. (2020). Bipolar membrane electro dialysis for energetically competitive ammonium removal and dissolved ammonia production. *Journal of Cleaner Production*, 120788. doi:<https://doi.org/10.1016/j.jclepro.2020.120788>
- van Linden, N., Spanjers, H., & van Lier, J. B. (2019a). Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electro dialysis. *Water Research*, 114856. doi:<https://doi.org/10.1016/j.watres.2019.114856>
- van Linden, N., Spanjers, H., & van Lier, J. B. (2022a). Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping. *Chemical Engineering Journal*, 428, 131081. doi:<https://doi.org/10.1016/j.cej.2021.131081>
- Wojcik, A., Middleton, H., Damopoulos, I., & Van herle, J. (2003). Ammonia as a fuel in solid oxide fuel cells. *Journal of Power Sources*, 118(1–2), 342–348. doi:[http://dx.doi.org/10.1016/S0378-7753\(03\)00083-1](http://dx.doi.org/10.1016/S0378-7753(03)00083-1)



## Chapter 7.

# Removal and recovery of ammoniacal nitrogen from real residual streams



### Abstract

This chapter assesses the feasibility of total ammoniacal nitrogen (TAN) removal and recovery from various real nitrogen-loaded (N-loaded) residual waters. The N-loaded residual waters were algae digestion reject water (ADRW), sludge digestion reject water (SDRW) and fertiliser industry condensate (FIC).

At least 85% TAN removal proved to be feasible by electrodialysis (ED) for all three N-loaded residual waters, with an electrical energy consumption ranging between 5 and 15 MJ·kg-N<sup>-1</sup>. The electrical energy consumption was consistently higher for the real residual waters compared to the synthetic ADRW and SDRW, due to lower current efficiencies to transport TAN as ammonium (NH<sub>4</sub><sup>+</sup>), as a result of the transport of other cations than NH<sub>4</sub><sup>+</sup>. The use of ED allowed for the simultaneous removal of TAN (as NH<sub>4</sub><sup>+</sup>) and volatile fatty acids from ADRW. Furthermore, during the production of a concentrated NH<sub>4</sub><sup>+</sup> solution by ED from SDRW, accumulation of multivalent ions took place in the concentrate, resulting in scaling and subsequent clogging of the spacers. For FIC, no interfering processes were encountered for the removal of TAN by ED.

For the treatment of FIC, a sequencing batch experiment (SBE) was performed, in which multiple batches of FIC were treated by ED. The TAN that was removed by ED was converted to dissolved NH<sub>3</sub> by bipolar membrane electrodialysis (BPMED) and vacuum membrane stripping (VMS) allowed for the recovery of an ammonia-water (NH<sub>3</sub>-H<sub>2</sub>O) mixture from the produced dissolved NH<sub>3</sub> solution. The combination of ED, BPMED and VMS allowed for 93% TAN removal from real FIC, at the expense of 37–39 MJ·kg-N<sup>-1</sup> of electrical energy. Finally, the recovered NH<sub>3</sub>-H<sub>2</sub>O with an ammonia (NH<sub>3</sub>) concentration of 4 wt% was used as the fuel for a solid oxide fuel cell (SOFC). The SOFC generated 11 MJ·kg-N<sup>-1</sup> of electrical energy. Hence, the combination of ED, BPMED, VMS and SOFC allowed for the removal of TAN (as NH<sub>4</sub><sup>+</sup>) from real FIC and the subsequent generation of electricity from the recovered NH<sub>3</sub>, but still had a net electrical energy consumption of 26–28 MJ·kg-N<sup>-1</sup>.

### Keywords

nitrogen-loaded residual water; total ammoniacal nitrogen; energy generation; electrodialysis; bipolar membrane electrodialysis; vacuum membrane stripping; solid oxide fuel cell;





## 7.1. Introduction

In the previous chapters, only synthetic feed waters were used to demonstrate the removal of total ammoniacal nitrogen (TAN) and subsequent recovery of ammonia ( $\text{NH}_3$ ), using electro dialysis (ED), bipolar membrane electro dialysis (BPMED) and vacuum membrane stripping (VMS). Furthermore, only synthetic fuels were used to generate energy from  $\text{NH}_3$  using a solid oxide fuel cell (SOFC). This chapter assesses the feasibility of TAN removal from three different nitrogen-loaded (N-loaded) residual waters by ED. In addition, this chapter assesses the feasibility to remove TAN and subsequently recover  $\text{NH}_3$  from one of the N-loaded residual waters by ED, BPMED and VMS for the generation of electricity in an SOFC. The three N-loaded residual waters were: algae digestion reject water (ADRW), sludge digestion reject water (SDRW) and fertiliser industry condensate (FIC).

### 7.1.1. Nitrogen-loaded residual waters

The research of [Magdalena Cadelo \(2020\)](#) focused on the production of VFAs during anaerobic digestion (AD) of algae biomass by steering the AD process towards the maximisation of VFA production. However, algae typically have a high nitrogen content. According to the review of [Deng et al. \(2021\)](#), during AD, practically all organic nitrogen will eventually become present in the form of TAN following hydrolysis of the biopolymers. Hence, AD of algae results in the presence of high TAN concentrations, in addition to the high VFA concentrations, in the obtained liquid fraction after solid-liquid separation of the digestate: the ADRW. According to the review of [Atasoy et al. \(2018\)](#), ED can be used for the removal and recovery of VFA from the digestate of algae digestion. However, limited experimental information is available on the simultaneous recovery of VFAs and TAN after algae digestion, especially on the achievable TAN removal efficiency and the energy consumption. Therefore, ADRW was selected as the first N-loaded residual stream to assess the feasible TAN removal and the associating electrical energy consumption.

More common than the digestion of algae is the AD of waste activated sludge from sewage treatment plants, as described in Chapter 2. [Ward et al. \(2018\)](#) and [Kedwell et al. \(2021\)](#) assessed the feasibility to remove TAN from the liquid fraction obtained after solid-liquid separation of the digestate from sludge digestion: SDRW. However, the respective studies showed TAN removal efficiencies that were yet not competitive to current state-of-the-art TAN removal processes. Whereas [Ward et al. \(2018\)](#) and [Kedwell et al. \(2021\)](#) reached TAN removal efficiencies ranging between 23% and 70%, competitive state-of-the-art TAN removal processes, such as the biochemical partial nitrification + anammox process reach TAN removal efficiencies up to 90% ([Lackner et al., 2014](#)). Hence, it remains unclear whether ED can be used to achieve competitive TAN removal after sludge digestion. Moreover, previous research showed that SDRW also contains various other cations, which may affect the TAN removal and the associating energy consumption from SDRW. To this end, SDRW was selected as the second N-loaded residual stream to assess the feasible TAN removal and the associating electrical energy consumption.

The third selected N-loaded residual water is condensate generated in the fertiliser industry (see also Chapter 2), more specifically, during the production of urea. In such condensates, TAN is present along with

bicarbonate ( $\text{HCO}_3^-$ ) as the main anion, while also several alcohols and other organics are present in the FIC. However, in literature, no studies report on the removal of TAN from FIC by ED. Therefore, the feasibility of using ED for TAN removal remains unclear, as well as the possible interference of organics present in FIC during ED.

#### 7.1.2. Objectives

The first objective of this chapter was to determine the feasibility of TAN removal by ED from three N-loaded real residual streams. To assess the feasibility of treating N-loaded residual waters, ED is characterised in terms of the TAN removal efficiency and the associating electrical energy consumption. The second objective of this chapter was to assess the feasibility of TAN removal and subsequent  $\text{NH}_3$  recovery by BPMED and VMS for one of the real N-loaded residual streams. Finally, the recovered  $\text{NH}_3$  from one of the real N-loaded residual streams was used as a fuel of an SOFC, to determine the feasibility of electrical energy generation from the recovered  $\text{NH}_3$ . To this end, experiments with a combination of ED, BPMED, VMS and SOFC focused on the achievable TAN concentrations and the energy balance.

## 7.2. Materials and methods

### 7.2.1. Algae digestion reject water

For the ADRW experiments, the same experimental setup as described in Chapter 3.2 was used, including the corresponding analytical methods and associated materials. Additionally, the concentrations of eight (8) major VFAs were measured by high-performance liquid chromatography (HPLC). The real ADRW (see Figure 7-1) was produced within the research of [Magdalena Cadelo \(2020\)](#) and was provided for the assessment of TAN removal by ED. Before using the real ADRW for the ED experiments, the ADRW was filtered through a 20-micron filter to minimise the presence of particulate and suspended solids that could clog the spacers in the membrane stack.

The treatment of real ADRW was compared to the treatment of synthetic ADRW, which consisted of an ammonium bicarbonate ( $\text{NH}_4\text{HCO}_3$ ) solution with an EC equal to that of the real ADRW sample:  $26 \text{ mS}\cdot\text{cm}^{-1}$ . During treatment of both synthetic and real ADRW, the EC was decreased to  $3 \text{ mS}\cdot\text{cm}^{-1}$ , corresponding to a decrease of 90%. A dynamic current density (DCD) with a safety factor of 0.62 was used, based on the results presented in Chapter 3.3. The treatment of ADRW comprised the treatment of only one single batch, due to the limited availability of ADRW. The initial concentrate consisted of a sodium chloride (NaCl) solution with an EC equal to the synthetic and real ADRW.

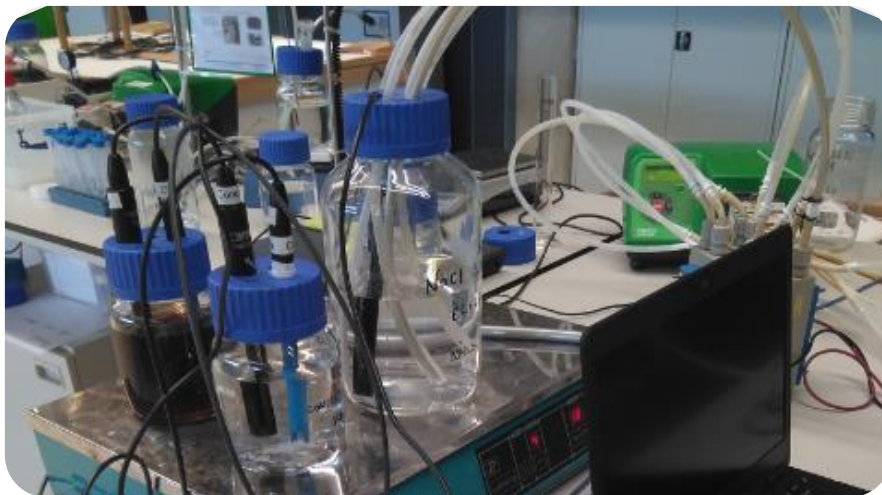


Figure 7-1 - The experimental setup for the removal of TAN from ADRW, with on the left the dark-brown ADRW.

### 7.2.2. Sludge digestion reject water

The real SDRW (see Figure 7-2) originated from the sludge processing line in a biological phosphorous removing sewage treatment plant. The real SDRW sample was obtained after the centrifuges that are used for solid-liquid separation of the digestate produced by AD of waste (activated) sludge. In addition to TAN, the real SDRW also contained metal cations sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ) and calcium ( $\text{Ca}^{2+}$ ), in concentrations of 312, 234, 219 and  $130 \text{ mg}\cdot\text{L}^{-1}$ , respectively. The analyses of the metal cations present in the real SDRW were conducted by ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS). The relatively high concentrations of  $\text{Mg}^{2+}$  may be explained by the

over-dosing of magnesium chloride ( $MgCl_2$ ) to the digestate, to allow for controlled struvite precipitation. To avoid clogging of the spacers in the membrane stack, the SDRW was filtered using 20-micron filters. In line with the ADRW experiments, unless stated differently, the used experimental and analytical materials, conditions and methods for the SDRW experiments can be found in Chapter 3.2. Based on the outcomes of Chapter 3, DCD was used during the SDRW experiments, using a safety factor of 0.62.

In addition to the treatment of the real SDRW, a synthetic SDRW consisting of  $NH_4HCO_3$  at a similar EC as the real SDRW was treated. The synthetic and real SDRW had a pH of 7.6 and an EC of approximately  $7 \text{ mS}\cdot\text{cm}^{-1}$ , whereas the initial TAN concentrations were  $1,410$  and  $777 \text{ mg}\cdot\text{L}^{-1}$ , respectively. The initial concentrate consisted of the same synthetic and real SDRW as the initial diluate. The treatment of the synthetic and real SDRW was stopped when the diluate EC decreased to  $1 \text{ mS}\cdot\text{cm}^{-1}$ , aiming for a TAN removal efficiency of approximately 90%.

After the initial experiment with synthetic and real SDRW, multiple batches of real SDRW were processed, in a so-called sequencing batch experiment (SBE). During the SBE, the treated real SDRW (diluate) was replaced with a new batch of 1 L real SDRW, while the produced concentrate solution was used as the concentrate for the subsequent batch treatment. For the SBE, the initial concentrate solution consisted of an  $NH_4HCO_3$  solution with an initial EC of  $7 \text{ mS}\cdot\text{cm}^{-1}$  and an initial volume of 0.5 L. Throughout the SBE, the cation concentrations in the diluate and concentrate were measured to determine the ion removal efficiency, the cation current efficiency and the electrical energy consumption for TAN removal. To calculate the current efficiency for each cation, Eq. 7-1 was used. The calculation of the electrical energy consumption for TAN removal can be found in Chapter 3.2.2 of this thesis.

$$\eta_i = \frac{z \cdot F \cdot n_{i,d}}{N \cdot \sum_{t=0}^t I_t \cdot \Delta t} \cdot 100\% \quad \text{Eq. 7-1}$$

where  $\eta_i$  = current efficiency of cation 'i' (unitless),  $z_i$  = valence of cation 'i' (unitless,  $z = 1$  for  $NH_4^+$ ,  $Na^+$  and  $K^+$  and  $z = 2$  for  $Mg^{2+}$  and  $Ca^{2+}$ ),  $F$  = Faraday constant (in  $C\cdot\text{mol}^{-1}$ ,  $F = 96,485 \text{ C}\cdot\text{mol}^{-1}$ ),  $n_{i,d}$  = amount of transported cation 'i' from diluate (mol),  $N$  = number of cell pairs (unitless),  $I_t$  = electrical current (in A) and  $\Delta t$  = time interval (in s).

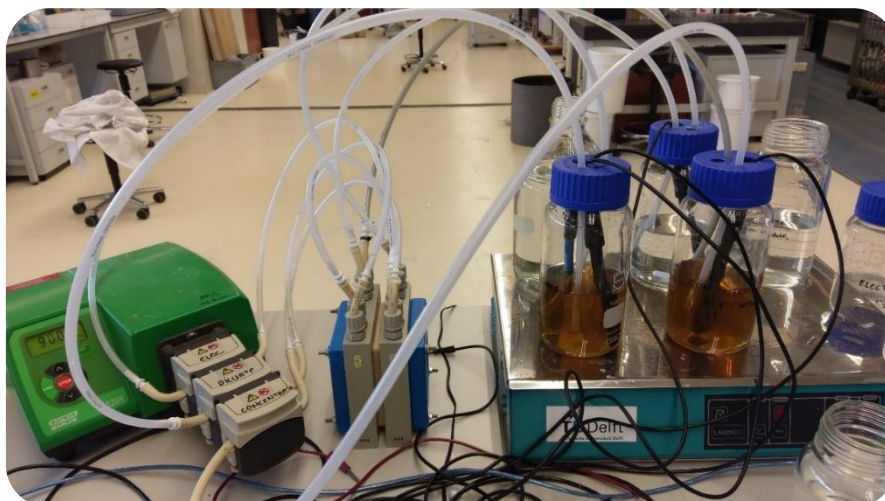


Figure 7-2 - The used experimental setup for the experiments on TAN removal by ED from real SDRW.

### 7.2.3. Fertiliser industry condensate

#### 7.2.3.1. Removal of TAN by ED

The FIC originated from an industrial process involving the condensation of water during the production of urea. Because carbon dioxide and ammonia are also present in the vapours to be condensed, an aqueous solution containing mainly  $\text{NH}_4\text{HCO}_3$  is formed. The FIC also contained organic solutes, such as methanol, ethanol and methyl diethanolamine (MDEA). Additional gas chromatography (GC) measurements were conducted to determine the concentrations of methanol, ethanol, whereas MDEA concentrations were determined by IC. The concentration of TAN in the real FIC was  $781 \text{ mg}\cdot\text{L}^{-1}$ . In line with the experiments with ADRW and SDRW, a synthetic feed solution comprising a similar concentration of TAN in the form of  $\text{NH}_4\text{HCO}_3$  was prepared as a reference. During the initial experiments with synthetic and real FIC, the EC was decreased from approximately  $5$  to  $0.5 \text{ mS}\cdot\text{cm}^{-1}$ , corresponding to a 90% decrease. The initial concentrate consisted of a  $0.5 \text{ L}$  synthetic  $\text{NH}_4\text{HCO}_3$  solution with an EC of  $5 \text{ mS}\cdot\text{cm}^{-1}$ . In contrast to the previous experiments, the safety factor for DCD was set to  $0.8$ , to limit the back-diffusion of  $\text{NH}_4^+$  to the diluate. A higher back diffusion was expected during the FIC experiments due to high  $\text{NH}_4^+$  concentrations in the concentrate and low  $\text{NH}_4^+$  concentrations in the final diluate, agreeing with  $0.5 \text{ mS}\cdot\text{cm}^{-1}$ .

#### 7.2.3.2. TAN removal and $\text{NH}_3$ recovery for energy generation

After the initial experiment focusing on TAN removal from real FIC, the actual recovery of  $\text{NH}_3$  for the generation of electricity was tested. To this end, ED was combined with BPMED and VMS during three different phases. During Phase 1, three consecutive batches (B1 – B3) of  $1.6 \text{ L}$  real FIC were treated by ED to produce a concentrated  $\text{NH}_4^+$  solution. The initial concentrate consisted again of  $0.5 \text{ L}$  synthetic  $\text{NH}_4\text{HCO}_3$  solution.

Subsequently, in Phase 2, the produced concentrate was kept used as the concentrate solution for subsequent batches in ED, but it was also used as the feed solution for BPMED. In the combination of ED and BPMED, ions were simultaneously transported from the FIC to the concentrate in ED and from the feed to

the acid and base in BPMED. To balance the amount of TAN transported from the FIC to the concentrate by ED and from the concentrate to the base, a BPMED membrane stack with four cell triplets was used at a fixed current density of  $100 \text{ A} \cdot \text{m}^{-2}$ . The details of the used materials for BPMED can be found in Chapter 4.2.1. Four additional batches of 1.6 L FIC were processed during the combination of ED and BPMED (B4–B7), to produce a concentrated  $\text{NH}_3$  solution.

In Phase 3, the combination of ED and BPMED was extended by including VMS, to recover gaseous  $\text{NH}_3$  from the produced concentrated  $\text{NH}_3$  solution. To this end, based on the findings of Chapter 1, a porous gas-permeable polytetrafluoroethylene (PTFE) membrane was used. Unless stated otherwise, the same materials and methods for VMS were used as described in Chapters 5.2.1 and 6.2.1. In contrast to Chapter 1 and Chapter 6, the recovered  $\text{NH}_3$  gas was not scrubbed in an acid solution, but condensed, resulting in the recovery of a liquid  $\text{NH}_3\text{-H}_2\text{O}$  mixture. During Phase 3, four additional batches (B8 – B11) of 1.6 L FIC were treated in the combination of ED, BPMED and VMS. Figure 7-3 shows a schematic representation of the experimental setup combining ED, BPMED and VMS and Figure 7-4 shows the actual experimental setup. As a final step, the recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixture was used as a fuel for an SOFC. The same materials and methods for the SOFC were used as described in Chapter 6.

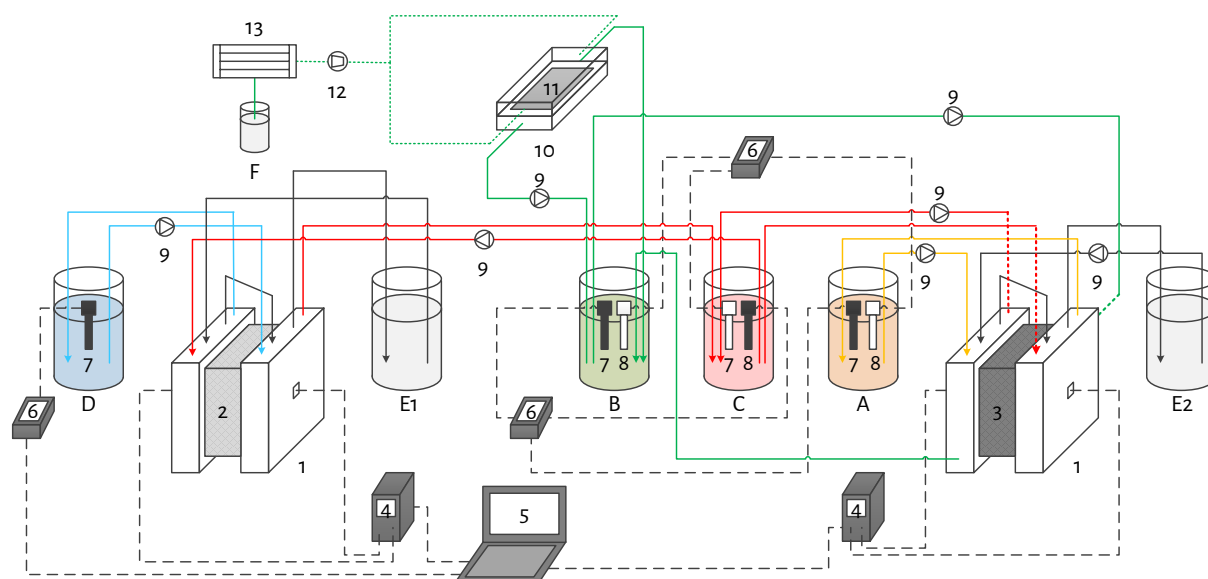


Figure 7-3 - A schematic representation of the used experimental setup of the combination of ED, BPMED and VMS: ED cell (1), ED membrane stack (2), BPMED membrane stack (3), direct current supply (4), laptop (5), multimeter (6), electrical conductivity (7), pH sensor (8), peristaltic pump (9), vacuum membrane stripping cell (10), porous gas-permeable membrane (11), vacuum pump (12) and condenser (13). With the following solutions: diluate, consisting of FIC (D), concentrate, also serving as BPMED feed (C), acid (A), base (B), electrode rinse for ED and BPMED (E1 and E2, respectively) and the condensed  $\text{NH}_3\text{-H}_2\text{O}$  mixture (F). The condensed  $\text{NH}_3\text{-H}_2\text{O}$  mixture served as the fuel for the SOFC, which is schematically presented in Chapter 6.2.1.



Figure 7-4 - The used experimental setup of the combination of ED, BPMED and VMS (left) and the SOFC (right).



### 7.3. Results

#### 7.3.1. Removal of TAN from residual waters

##### 7.3.1.1. Algae digestion reject water

Table 7-1 shows that the decrease in EC by 90% resulted in similar TAN removal efficiencies for the synthetic and real ADRW: 94% and 96%, respectively. Hence, for the removal of TAN from real ADRW, the EC was a suitable indicator of the TAN removal efficiency. In line with the findings in Chapter 3 and Chapter 4, accumulation of TAN (10 – 28% of the TAN that was transported from the diluate) in the electrode rinse solution (ERS) took place, as a result of the used combination of end membranes (cation exchange end membranes) and the composition of the ERS. The  $\text{NH}_4^+$  current efficiency for the synthetic ADRW was 86%, which is lower than the values presented in Chapter 3, in which  $\text{NH}_4\text{HCO}_3$  solutions with a TAN concentration of  $1.5 \text{ g}\cdot\text{L}^{-1}$  were used as the feed water (96% for the first treated batch at DCD). The difference in  $\text{NH}_4^+$  current efficiency can be explained by the higher  $\text{NH}_4^+$  concentration gradient that was present during the synthetic ADRW experiment, compared to the experiments described in Chapter 3. In both experiments, the removal efficiencies and operational run times were similar, whereas the initial TAN concentration was approximately  $6 \text{ g}\cdot\text{L}^{-1}$  for the synthetic ADRW compared to  $1.5 \text{ g}\cdot\text{L}^{-1}$  as reported in Chapter 3. Therefore, during the synthetic ADRW experiment, a higher  $\text{NH}_4^+$  concentration gradient was present between the diluate and concentrate. Results in Chapter 3 showed that an increase in  $\text{NH}_4^+$  concentration gradient for similar operational run times resulted in more back-diffusion, leading to a lower  $\text{NH}_4^+$  current efficiency. The electrical energy consumption for the synthetic ADRW ( $9 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ) was higher than that reported in Chapter 3 ( $5 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ ), which was in the first place caused by the lower  $\text{NH}_4^+$  current efficiency. Because the EC throughout the experiment was higher during the synthetic ADRW experiment than during the SBE experiments with the application of DCD presented in Chapter 3, a higher current density was applied:  $148$  versus  $42 \text{ A}\cdot\text{m}^{-2}$ . Hence, the second contributor to the higher electrical energy consumption for the synthetic ADRW compared to Chapter 3 was the higher applied current density, because as explained in Chapter 3, higher applied current densities result in higher electrical energy consumption.

According to Table 7-1, the  $\text{NH}_4^+$  current efficiency of the real ADRW was lower than that of the synthetic ADRW: 63% and 86%, respectively. The difference in  $\text{NH}_4^+$  current efficiency may be caused by the transport of other cations than  $\text{NH}_4^+$ . However, there is no information on the presence and fate of other cations during the real ADRW experiment, as these were not measured. Furthermore, the average electrical resistance during the experiment with real ADRW was  $17 \Omega$ , which was higher compared to the experiment with synthetic ADRW, when it was  $12 \Omega$ . This difference might be explained by increased mass transfer resistance due to the presence of organics, instead of solely bicarbonate ( $\text{HCO}_3^-$ ), which was the case for synthetic ADRW. Hence, the lower  $\text{NH}_4^+$  current efficiency and higher average electrical resistance contributed to the higher electrical energy consumption during the real ADRW treatment of  $15 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , compared to the electrical energy consumption for the synthetic ADRW treatment of  $9 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .

In addition to the removal of TAN from the ADRW, also VFAs were removed and recovered in the concentrate. Table 7-2 provides an overview of the VFA concentrations in the real initial and final ADRW, as well as the concentrations obtained in the ED concentrate. Because the pH of all solutions was consistently above 6, the VFAs were predominantly present as anions. The mass balance for VFAs fitted within a 5% error, while a negligible amount (< 1%) of VFAs accumulated in the electrode rinse solution. The latter can be explained by the used end-membranes, which do not allow for the transport of anions to the ERS. 87% of the volume of the real ADRW was recovered as treated water and the removal efficiency of VFAs ranged between 72 and 96%. Table 7-2 shows that the removal efficiency differed amongst the various VFAs, which were present in different initial concentrations. The current efficiency of the VFAs was 72% and the highest current efficiency was represented by acetic acid (29%), followed by butyric acid (19%). The loss in current efficiency may be attributed to the transport of other anions, such as bicarbonate and chloride, and back-diffusion of anions from the concentrate to the diluate.

Table 7-1 - Process performance indicators for the removal of TAN from ADRW by ED.

	unit	Synthetic	Real
Initial diluate $\text{NH}_4^+$ concentration	$\text{mg}\cdot\text{L}^{-1}$	6,036	5,253
TAN removal efficiency	-	94%	96%
Water recovery		90%	87%
$\text{NH}_4^+$ current efficiency	-	86%	63%
Average electrical resistance	$\Omega$	12	17
Energy consumption	$\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$	9	15

Table 7-2 - The initial diluate and final concentrate concentrations, and the removal and current efficiency of VFAs during the treatment of real ADRW.

Name of acids and corresponding anions	Diluate Initial	Removal Efficiency	Current Efficiency	Concentrate Final
	$\text{mg}\cdot\text{L}^{-1}$	-	-	$\text{mg}\cdot\text{L}^{-1}$
Acetic acid / acetate	7,996	96%	29%	11,867
Propionic acid / propionate	3,106	93%	9%	4,187
Isobutyric acid / isobutyrate	1,417	82%	3%	1,687
Butyric acid / butyrate	7,057	87%	19%	8,777
Isovaleric acid / isovalerate	1,853	72%	3%	1,932
Valeric acid / valerate	2,343	84%	4%	2,801
Isocaproic acid / isocaproate	1,306	77%	2%	1,406
Caproic acid / caproate	1,652	83%	3%	1,911

7.3.1.2. Sludge digestion reject water

Table 7-3 shows that experiments with synthetic and real SDRW resulted in a similar TAN removal efficiency while decreasing the EC from 7 to 1 mS·cm<sup>-1</sup> (88% decrease): 89 and 86%, respectively. Hence, in line with the treatment of ADRW, the decrease in EC agreed well with the TAN removal efficiencies. The TAN removal efficiencies were associated with water recoveries of 96–97%. The NH<sub>4</sub><sup>+</sup> current efficiency for the real SDRW (58%) was lower than that for the synthetic solutions (97%), for the treatment of a single batch. Also, the electrical energy consumption to remove NH<sub>4</sub><sup>+</sup> from the real SDRW (8 MJ·kg-N<sup>-1</sup>) was higher than that for the synthetic SDRW (4 MJ·kg-N<sup>-1</sup>). In addition to NH<sub>4</sub><sup>+</sup>, also other cations (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>) were transported from the diluate to the concentrate, with a removal efficiency ranging between 39 and 95% (Figure 7-5A), affecting the transport of NH<sub>4</sub><sup>+</sup>. Figure 7-6A presents the current efficiency per transferred ion and shows that the sum of the current efficiencies of the other cations is almost similar to the NH<sub>4</sub><sup>+</sup> current efficiency: 50 and 58%, respectively. In addition to the additional electric charge supply, also the electrical resistance of the membrane stack was higher for the real (36 Ω) than for the synthetic SDRW (31 Ω), which can be attributed to the presence of organic solutes and the transport of ions with lower diffusion coefficients. The lower NH<sub>4</sub><sup>+</sup> current efficiency and the higher electrical resistance throughout the experiments contributed to a higher electrical energy consumption for the real SDRW, compared to the synthetic SDRW. Hence, the differences in NH<sub>4</sub><sup>+</sup> current efficiency and electrical energy consumption can be attributed to the presence and transport of other solutes than NH<sub>4</sub><sup>+</sup> in the real SDRW.

Table 7-3 - Process performance indicators for the removal of TAN from SDRW by ED.

	unit	Synthetic	Real
Initial diluate NH <sub>4</sub> <sup>+</sup> concentration	mg·L <sup>-1</sup>	1,410	777
TAN removal efficiency	-	89%	85%
Water recovery	-	96%	97%
NH <sub>4</sub> <sup>+</sup> current efficiency	-	97%	58%
Average electrical resistance	Ω	31	36
Energy consumption	MJ·kg-N <sup>-1</sup>	4	8

For real SDRW, four additional sequencing batches were treated. During this SBE, the diluate was replaced with a new batch of real SDRW, while the concentrate was again used to allow for the production of a concentrated TAN (as NH<sub>4</sub><sup>+</sup> solution). The removal efficiency of the various cations and water recovery remained stable throughout the SBE. On the contrary, the NH<sub>4</sub><sup>+</sup> current efficiency decreased from 58 to 50%, which can be attributed to back-diffusion (see Chapter 3.4) as the NH<sub>4</sub><sup>+</sup> concentration difference between the diluate and concentrate increased due to the accumulation of NH<sub>4</sub><sup>+</sup> in the concentrate, as shown in Figure 7-5B. Furthermore, the sum of the current efficiencies of the various ions also decreased from 104 to 85% throughout the SBE, suggesting that back-diffusion also affected the current efficiency of the transport

of the other cations. The decrease in current efficiency resulted in an increase in electrical energy consumption from 8 to 9 MJ·kg-N<sup>-1</sup> throughout the SBE, as presented in Figure 7-6B.

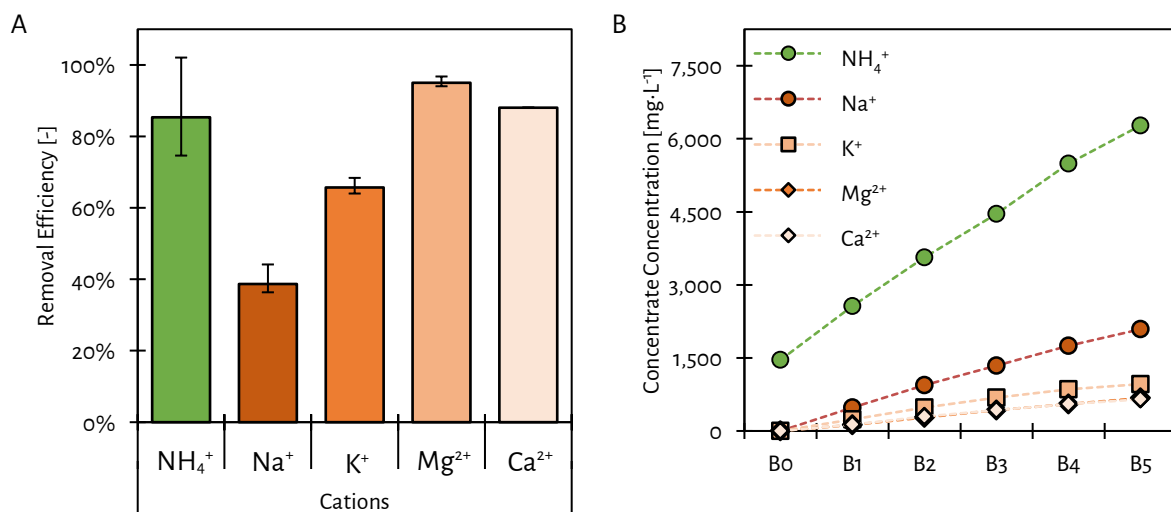


Figure 7-5 - The average ion removal efficiency (A) and the ion concentration in the concentrate during the SBE (B) during the removal of TAN from real SDRW by ED. The markers for Ca<sup>2+</sup> and Mg<sup>2+</sup> overlapped.

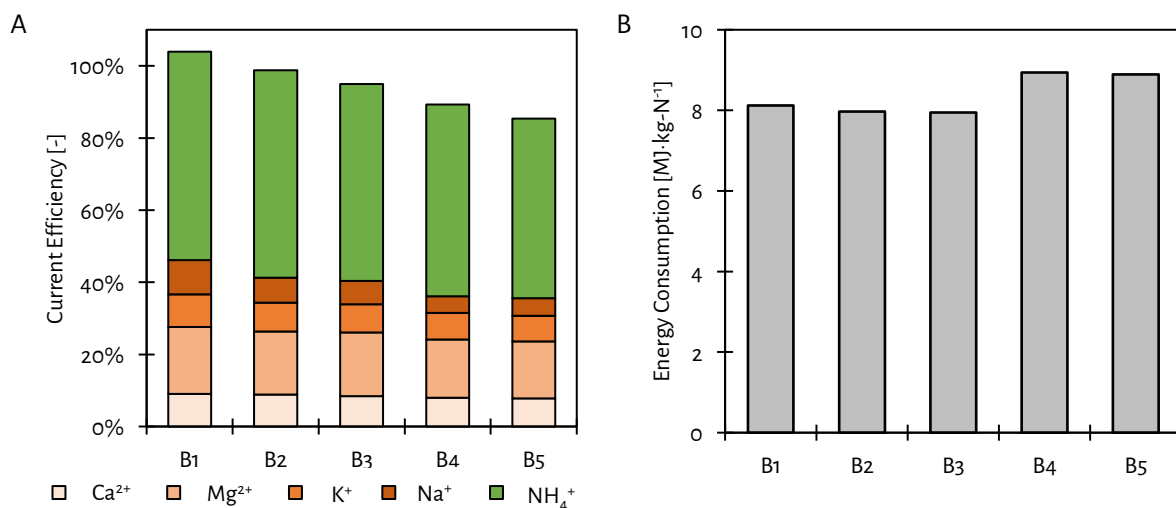


Figure 7-6 - The ion current efficiency (A) and the electrical energy consumption (B) throughout the SBE during the removal of TAN from real SDRW by ED.

At the end of the fifth batch during the SBE, the recirculation of concentrate through the ED membrane stack stagnated and eventually even stopped. Opening the membrane stack and a visual inspection resulted in the observation of white crystalline solids in the concentrate spacers (see Figure 7-7A). Especially at the locations where the concentrate entered the spacers that form the flow channels for the various solutions, these white precipitates accumulated, as shown in Figure 7-7B. The pH of the concentrate solution throughout the SBE ranged between 7.9 and 8.1. After taking a sample of the precipitate and dissolution in water, ion analysis was performed, showing that the dominant ions in the scale were Ca<sup>2+</sup>, Mg<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup>. In addition, simulations with PHREEQC chemical equilibrium software, using the water composition of the concentrate at a pH of 8, showed theoretical supersaturation (saturation index > 0) of mineral species such

as dolomite ( $\text{CaMg}(\text{CO}_3)_2$ ). Hence, the accumulating precipitates probably consisted of carbonate species. This result aligns with the mass imbalance of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , which were off by more than 50%.



Figure 7-7 - The accumulation of, mostly Mg-based, precipitated minerals in the concentrate spacers in the ED membrane stack (A) after the treatment of multiple batches of real SDRW. The white precipitates especially accumulated at the entrance (at the right) of the spacer (B).

#### 7.3.1.3. Fertiliser industry condensate

The third tested N-loaded residual water was FIC. Table 7-4 shows the decrease of 90% in EC for the synthetic and real FIC corresponding to a TAN removal efficiency of 93%, indicating that in line with the ADRW and SDRW experiments, the decrease in EC was a suitable indicator for TAN removal from FIC. The water recovery for both synthetic and real FIC was 98 – 99%. The  $\text{NH}_4^+$  current efficiency was similar for the synthetic (90%) and real FIC (88%), indicating that there were limited losses in current efficiency due to the transport of other ions. Based on GC measurements of initial and final FIC solutions, no methanol and ethanol transfer from the diluate to the concentrate took place. These solutes were not transported because they are not charged when dissolved in water. However, the methanol and ethanol concentrations in both the diluate and concentrate decreased during the experiment. Because the ERS also did not have increased methanol and ethanol concentrations, the loss (21% in mass) of these alcohols may be attributed to volatilisation during the experiment. Furthermore, when dissolved in water, MDEA is positively charged and, therefore, can be transported as a cation. Because the MDEA mass balance fitted within 5%, the decrease in MDEA from the real FIC can be explained by electro-migration of cationic MDEA. However, due to the relatively high molecular weight ( $119 \text{ g}\cdot\text{mol}^{-1}$ ) and relatively low concentration ( $9\text{--}11 \text{ mg}\cdot\text{L}^{-1}$ ) compared to  $\text{NH}_4^+$  ( $18 \text{ g}\cdot\text{mol}^{-1}$  and  $993 \text{ mg}\cdot\text{L}^{-1}$ , respectively), only 64% of MDEA was transported from the FIC to the concentrate. The transport of MDEA contributed with less than 1% to the loss in  $\text{NH}_4^+$  current efficiency. Hence, the loss in  $\text{NH}_4^+$  current efficiency was predominantly caused by the back-diffusion of  $\text{NH}_4^+$ . Furthermore, the average electrical resistance during the experiments with synthetic and real FIC was similar: 48 and 47  $\Omega$ , respectively. Due to the similar  $\text{NH}_4^+$  current efficiency and the similar average electrical

resistance, the same electrical energy consumption of  $5 \text{ MJ}\cdot\text{kg-N}^{-1}$  to remove 93% of TAN from synthetic and real FIC was observed.

Table 7-4 - Process performance indicators for the removal of TAN from synthetic and real FIC by ED.

	unit	Synthetic	Real
Initial diluate $\text{NH}_4^+$ concentration	$\text{mg}\cdot\text{L}^{-1}$	1,050	781
TAN removal efficiency	-	93%	93%
Water recovery		99%	98%
$\text{NH}_4^+$ current efficiency	-	90%	88%
Average electrical resistance	$\Omega$	48	47
Energy consumption	$\text{MJ}\cdot\text{kg-N}^{-1}$	5	5

### 7.3.2. Ammonia recovery for electricity generation from FIC

Based on the results described in 7.3.1., FIC proved to be a readily suitable N-loaded residual for the removal of TAN and the subsequent recovery of  $\text{NH}_3$  for the generation of electricity. To assess the combination between ED, BPMED and VMS, the same FIC was used, but from a different batch. Hence, the composition of the FIC differed from the experiments conducted in 7.2.3. The results are presented per phase, considering:

- Phase 1: ED (B1 – B3);
- Phase 2: ED + BPMED (B4 – B7);
- Phase 3: ED + BPMED + VMS (B8 – B11).

#### 7.3.2.1. Phase 1: ED

For the first three batches (B1 – B3), ED produced a concentrated  $\text{NH}_4^+$  solution, while achieving 93% TAN removal, on average. After the treatment of three batches of 1.6 L FIC, in which the TAN was transported as  $\text{NH}_4^+$  to the 0.5 L of concentrate solution, the  $\text{NH}_4^+$  concentration in the concentrate increased to  $6.1 \text{ g}\cdot\text{L}^{-1}$ . The  $\text{NH}_4^+$  current efficiency ranged between 77 and 81% and was lower than in the experiments described in Section 7.2.3 (88%). The difference in  $\text{NH}_4^+$  current efficiency was caused by the longer run time and larger volumes treated per batch, resulting in an  $\text{NH}_4^+$  concentration gradient ranging between 2.5 and  $6.0 \text{ g}\cdot\text{L}^{-1}$ , compared to  $1.5 \text{ g}\cdot\text{L}^{-1}$  for the previous experiments. The additional loss in  $\text{NH}_4^+$  current efficiency can be attributed to the transport of MDEA. The FIC used for the SBE contained seventy times more MDEA ( $798 \text{ mg}\cdot\text{L}^{-1}$ ) than the real FIC described in 7.2.3., while 63% of the MDEA was removed, representing 8% of the current efficiency. After the first three batches, the MDEA concentration in the concentrate reached  $5.4 \text{ g}\cdot\text{L}^{-1}$ . Furthermore, the methanol concentration ( $161 \text{ mg}\cdot\text{L}^{-1}$ ) was more than one order of magnitude lower than in the real FIC described in 7.2.3. Both methanol and ethanol remained in the diluate, suggesting that volatilisation was negligible, which can be due to the lower concentration present in the FIC (lower driving force for volatilisation) and improved solution preservation (closed bottles), compared to the experiment

described in 7.2.3. Eventually, the higher applied current density (dynamic current density with a safety factor of 0.8, instead of 0.62 as used in 7.2.3.) and the lower  $\text{NH}_4^+$  current efficiency resulted in an increase in electrical energy consumption to 8 – 10  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , compared to 5  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  for the previous FIC experiments.

#### 7.3.2.2. Phase 2: ED + BPMED

Subsequently, the concentrated  $\text{NH}_4^+$  solution produced by ED served as feed solution for BPMED to produce dissolved  $\text{NH}_3$ . Throughout this phase, four batches of FIC (B4 – B7) were treated by ED, while the concentrate served as the feed for BPMED. The  $\text{NH}_4^+$  current efficiency and electrical energy consumption for ED were similar (75 – 82% and 8 - 9  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , respectively) to Phase 1, with a TAN removal of 94%. After B7, the TAN concentration stabilised at 4  $\text{g}\cdot\text{L}^{-1}$  in the concentrate, while the TAN concentration in the base reached 8.5  $\text{g}\cdot\text{L}^{-1}$ , as shown in Figure 7-8. Because the base pH was 10.2 after B7, the  $\text{NH}_3$  concentration in the base was 7  $\text{g}\cdot\text{L}^{-1}$ . The concentrate pH increased steadily throughout the SBE, from 7.9 to 8.7, due to the leakage of  $\text{OH}^-$  and the diffusion of  $\text{NH}_3$  from the base (see Chapter 4.3). Furthermore, also the TAN concentration in the acid increased from 0.8 to 1.9  $\text{g}\cdot\text{L}^{-1}$  between B4 and B7, in line with the results presented in Chapter 4.3. The accumulation of TAN can be attributed to the diffusion of  $\text{NH}_3$  from the base to the acid, as described in Chapter 4.3. Because the acid pH ranged between 6.4 and 6.7, the predominant form of TAN was  $\text{NH}_4^+$ .

The  $\text{NH}_4^+$  current efficiency for BPMED decreased from 88% for B4 to 63% for B7. The loss in  $\text{NH}_4^+$  current efficiency for B4 partly (10%) can be attributed to the transport of MDEA from the base to the concentrate. Furthermore, the loss in  $\text{NH}_4^+$  current efficiency can be attributed to  $\text{OH}^-$  leakage and  $\text{NH}_3$  diffusion, as described in Chapter 4.3. Because the concentration gradients of  $\text{OH}^-$  and  $\text{NH}_3$  between the BPMED feed and base increased and therefore more  $\text{OH}^-$  leakage and  $\text{NH}_3$  diffusion took place, the  $\text{NH}_4^+$  current efficiency for BPMED decreased between B4 and B7. However, despite the decrease in  $\text{NH}_4^+$  current efficiency for BPMED, the electrical energy consumption to produce dissolved  $\text{NH}_3$  in the base by BPMED decreased from 31 to 27  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  between B4 and B7 (see Figure 7-9). In line with the results presented in Chapter 4.3, the average electrical resistance for each consecutive batch decreased, due to the accumulation of ionic species (such as  $\text{NH}_4^+$  and  $\text{HCO}_3^-$ ) in the acid and base. Hence, the decrease in electrical resistance resulted in a lower applied electric potential per consecutive batch, leading to a lower electrical energy consumption.

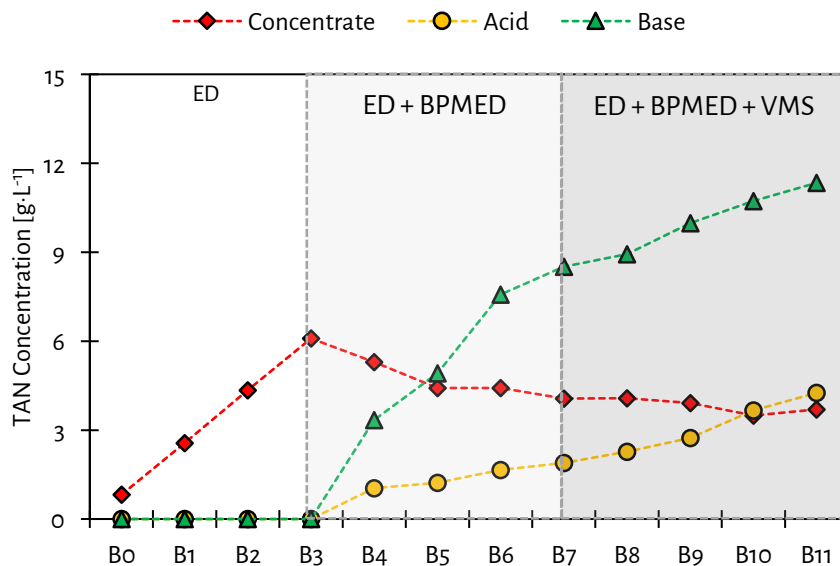


Figure 7-8 - TAN concentrations during the SBE for the treatment of FIC in the various phases using a combination of ED, BPMED and VMS.

### 7.3.2.3. Phase 3: ED + BPMED + VMS + SOFC

During B8 through B11, VMS was included in the system to strip dissolved  $\text{NH}_3$  from the base, while the ED continued to remove TAN from the FIC and BPMED continued to produce dissolved  $\text{NH}_3$ . The addition of VMS did not affect the operation of ED in terms of TAN removal efficiency (93%) and  $\text{NH}_4^+$  current efficiency (78%) between B8 and B11. Also, the  $\text{NH}_4^+$  current efficiency for BPMED again averaged 78%. Figure 7-8 shows that the TAN concentration in the acid increased further throughout Phase 3, due to  $\text{NH}_3$  diffusion from the base. To avoid excessive accumulation of TAN in the acid in the long term, periodic purging of the acid may be considered. Interestingly, as shown in Figure 7-9, the electrical energy consumption for ED and BPMED decreased to 7 – 8  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  and 24 – 26  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ , respectively, after the inclusion of VMS. The decrease in electrical energy consumption for the BPMED can be attributed to the further decrease in electrical resistance as a result of ion accumulation in the acid and base.

The stripped  $\text{NH}_3$  was condensed along with  $\text{H}_2\text{O}$  that evaporated and was transported through the hydrophobic membrane, in line with the results presented in Chapter 5 and Chapter 6. The concentration of  $\text{NH}_3$  in the recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixture was 4 wt%. Figure 7-8 shows that the TAN concentration in the base continued to increase, reaching 11  $\text{g}\cdot\text{L}^{-1}$ , at a pH of 10.1 and an  $\text{NH}_3$  concentration of 9  $\text{g}\cdot\text{L}^{-1}$ . To achieve steady-state operation, the mass transport and transfer should be improved, for example by higher  $\text{NH}_3$  recovery by VMS, using a larger membrane area. The electrical energy consumption of VMS to recover  $\text{NH}_3$  ranged between 6 and 7  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .



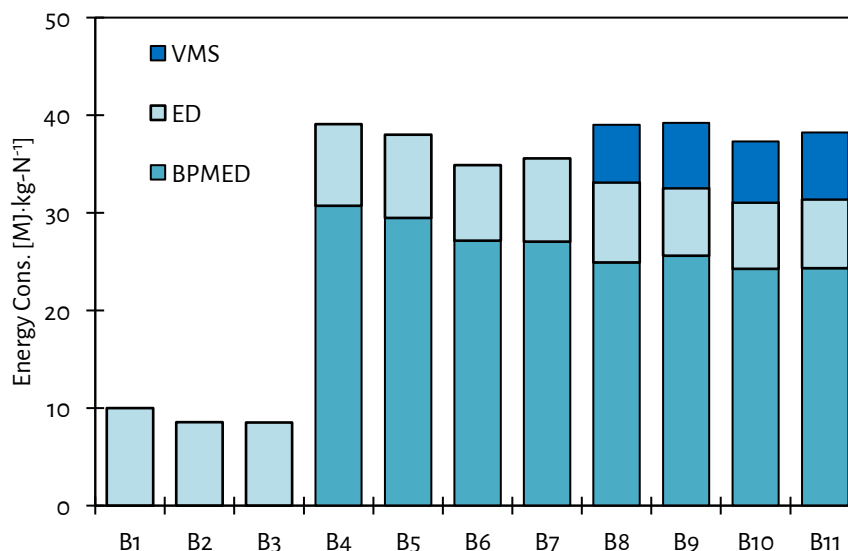


Figure 7-9 - Electrical energy consumption of ED, BPMED and VMS during 93% removal of TAN by ED from FIC, and recovery of NH<sub>3</sub> as 4 wt% NH<sub>3</sub>-H<sub>2</sub>O mixture for the generation of electricity.

### 7.3.3. Energy balance for the treatment of real FIC by ED, BPMED, VMS and SOFC

Figure 7-10 presents a flow scheme of the combination of technologies, along with the TAN concentrations, pH of the various streams and the electrical energy consumption for each technology. The total electrical energy consumption to remove TAN and recover NH<sub>3</sub> from FIC by ED, BPMED and VMS ranged between 37 and 39 MJ·kg-N<sup>-1</sup>. Feeding the 4 wt% NH<sub>3</sub> fuel to a SOFC resulted in a peak power density of 114 mW·cm<sup>2</sup>, corresponding to an electrical efficiency of 42% and an electrical energy generation of 11 MJ·kg-N<sup>-1</sup>. Hence, the net energy consumption of the combined ED + BPMED + VMS + SOFC system was 27 – 28 MJ·kg-N<sup>-1</sup>.

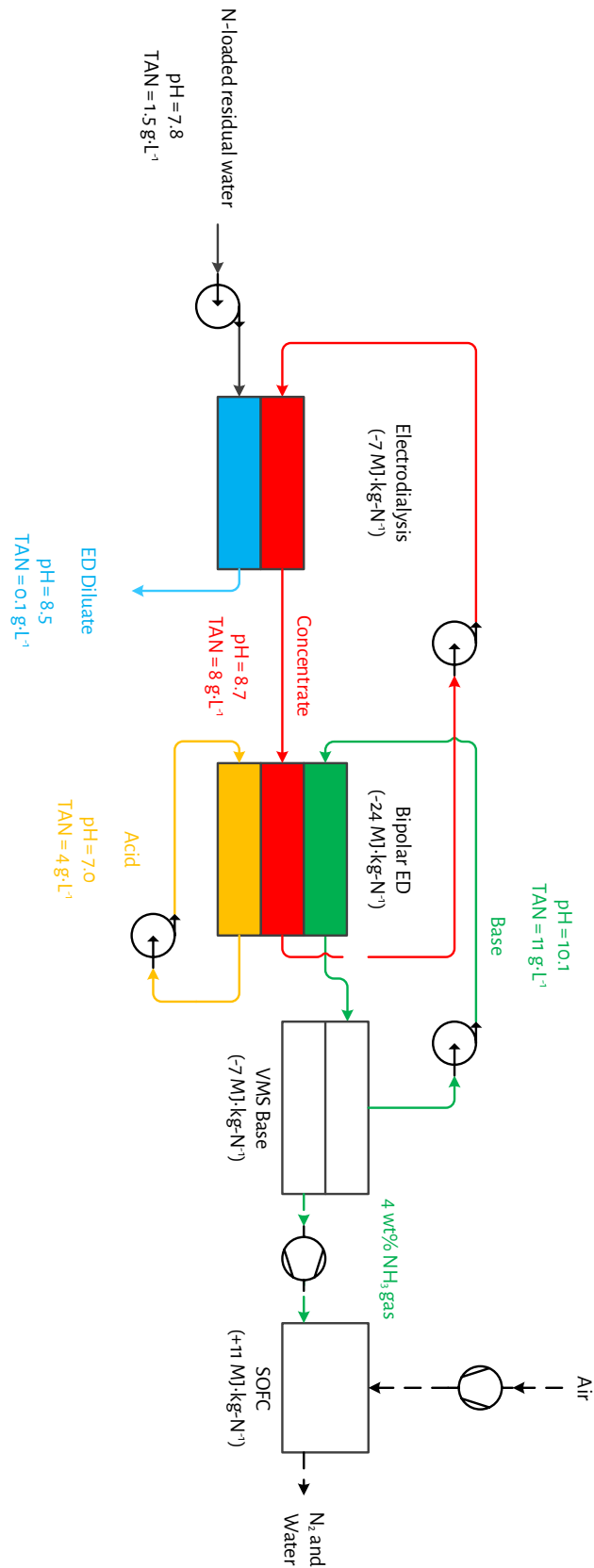


Figure 7-10 - A scheme of the combination of ED, BPMED and VMS for 93% removal of TAN by ED from FIC, and recovery of NH<sub>3</sub> as 4 wt% NH<sub>3</sub>-H<sub>2</sub>O mixture for the generation of electricity in an SOFC.

#### 7.4. Conclusions

The objective of this chapter was to assess the feasibility of removing TAN from real N-loaded residual streams. Based on the experimental results, the following conclusions can be derived:

- ED allows for competitive (approximately 90%) TAN removal at a water recovery of at least 87% from the N-loaded residual waters ADRW, SDRW and FIC;
- The electrical energy consumption for  $\text{NH}_4^+$  removal was consistently higher for real residual streams, compared to the synthetic residual waters;
- The  $\text{NH}_4^+$  current efficiency for ED to remove TAN from SDRW was affected by the competitive transport of other cations including  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ ;
- Accumulation of multivalent cations  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  in the concentrate during the treatment of SDRW by ED resulted in scaling that caused blockage of the flow channels;
- The presence of the organics methanol, ethanol and MDEA in FIC did not affect the electrical energy consumption to remove TAN by ED;

Furthermore, FIC served as the N-loaded residual water to assess the feasibility of removing TAN and recovering  $\text{NH}_3$  for electricity generation in a combination of ED, BPMED, VMS and SOFC. Based on the experimental results, the following conclusions can be derived:

- The removal efficiency of TAN from FIC by ED was not affected by the inclusion of BPMED and VMS and remained 93%;
- BPMED allowed for the production of a concentrated  $\text{NH}_3$  solution of  $9 \text{ g}\cdot\text{L}^{-1}$  in the base, using the concentrate of the ED as the feed;
- VMS allowed for the recovery of an  $\text{NH}_3\text{-H}_2\text{O}$  mixture with an  $\text{NH}_3$  concentration of 4 wt% by stripping the base produced by BPMED;
- The recovered  $\text{NH}_3\text{-H}_2\text{O}$  mixtures successfully served as a fuel for an SOFC, resulting in the generation of  $11 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$  of electrical energy;
- The combination of ED, BPMED, VMS and SOFC successfully allowed for TAN removal from FIC and subsequent electricity generation from the recovered  $\text{NH}_3$ ;
- The combination of ED, BPMED and VMS used more electrical energy ( $37 - 39 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$ ) than the SOFC generated, resulting in a net electrical energy consumption of  $26 - 28 \text{ MJ}\cdot\text{kg}\text{-N}^{-1}$ .

7.5. References

- Atasoy, M., Owusu-Agyeman, I., Plaza, E., & Cetecioglu, Z. (2018). Bio-based volatile fatty acid production and recovery from waste streams: Current status and future challenges. *Bioresource Technology*, *268*, 773-786. doi:<https://doi.org/10.1016/j.biortech.2018.07.042>
- Deng, Z., van Linden, N., Guillen, E., Spanjers, H., & van Lier, J. B. (2021). Recovery and applications of ammoniacal nitrogen from nitrogen-loaded residual streams: A review. *Journal of Environmental Management*, *295*, 113096. doi:<https://doi.org/10.1016/j.jenvman.2021.113096>
- Kedwell, K. C., Jørgensen, M. K., Quist-Jensen, C. A., Pham, T. D., Van der Bruggen, B., & Christensen, M. L. (2021). Selective electrodialysis for simultaneous but separate phosphate and ammonium recovery. *Environmental Technology*, *42*(14), 2177-2186. doi:10.1080/09593330.2019.1696410
- Lackner, S., Gilbert, E. M., Vlaeminck, S. E., Joss, A., Horn, H., & van Loosdrecht, M. C. M. (2014). Full-scale partial nitrification/anammox experiences - An application survey. *Water Research*, *55*, 292-303. doi:10.1016/j.watres.2014.02.032
- Magdalena Cadelo, J. A. (2020). *Anaerobic digestion of microalgae biomass for volatile fatty acids production*. (PhD). Universidad Complutense de Madrid, Madrid. Retrieved from <https://eprints.ucm.es/id/eprint/63697/>
- Ward, A. J., Arola, K., Thompson Brewster, E., Mehta, C. M., & Batstone, D. J. (2018). Nutrient recovery from wastewater through pilot scale electrodialysis. *Water Research*, *135*, 57-65. doi:<https://doi.org/10.1016/j.watres.2018.02.021>



# Chapter 8.

## Conclusions and recommendations



8.1. Residual N-loaded streams and technologies (Chapter 2)

8.1.1. Conclusions

Chapter 2 assesses the feasibility of various technologies for the removal of total ammoniacal nitrogen (TAN) from so-called nitrogen-loaded (N-loaded) residual streams with subsequent electricity generation from the recovered ammonia ( $\text{NH}_3$ ).

The results presented in Chapter 2.2 lead to the first conclusion that there is a large potential for TAN recovery from N-loaded residual streams, based on the thirteen (13) identified N-loaded residual streams with total Kjeldahl nitrogen concentrations  $> 0.5 \text{ g}\cdot\text{L}^{-1}$ . After the removal of suspended solids from the N-loaded residual streams, TAN can be recovered by various technologies from the obtained N-loaded residual waters. The various technologies available for the removal of TAN and the recovery of TAN from N-loaded residual waters are based on different driving forces, for example, electricity, heat or chemicals. The evaluated technologies cover a wide range of achievable TAN concentrations in the various recovered products, such as concentrated ammonium ( $\text{NH}_4^+$ ) solutions, solid  $\text{NH}_4^+$ -salt and  $\text{NH}_3$  gas. The second conclusion derived from the results presented in Chapter 2.3 is that there is a lack of information on the (normalised) energy consumption that is associated with each technology. In addition, Chapter 2.4 reports on various technologies to generate energy from recovered  $\text{NH}_3$ . Thirdly, it was concluded that the reviewed literature in Chapter 2.4 lacks information on the feasible fuel composition and tolerance of contaminants in the fuel, when using  $\text{NH}_3$  recovered from N-loaded residual waters as a fuel.

8.1.2. Recommendations

To address the lack of information on energy consumption regarding technologies to remove and recover TAN from water, Chapter 3, Chapter 4, Chapter 5 and Chapter 6 of this thesis consistently reported the normalised energy consumption as  $\text{MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ . For electro dialysis (ED), bipolar membrane electro dialysis (BPMED) and vacuum membrane stripping (VMS), the  $\text{kg}\cdot\text{N}^{-1}$  refers to kg of nitrogen transferred, whereas for the solid oxide fuel cells (SOFC),  $\text{kg}\cdot\text{N}^{-1}$  refers to one kg of nitrogen fed as fuel. Furthermore, Chapter 6 provides information on the minimum  $\text{NH}_3$  concentration that still allows for electricity generation when using  $\text{NH}_3$  recovered from water (aqueous solution) as a fuel in an SOFC.

The application potentials of recovered TAN from N-loaded residual streams depend on specific local conditions. For example, if there is a need for TAN as fertiliser near the location where TAN is present in residual streams, recovery of TAN as fertiliser may be proposed. However, in absence of such a need, perhaps the generation of electricity from  $\text{NH}_3$  is a better option. Based on the categorisation of the N-loaded residual streams, strategies for TAN recovery can be defined and technologies can be selected: Category 1 requires conversion of organic-N to TAN, Category 2 requires solids removal and Category 3 is suitable for TAN recovery.



## 8.2. Electrodialysis (Chapter 3)

### 8.2.1. Conclusions

Chapter 3 optimises the ED operation in terms of maximising the concentration factor and minimising energy consumption for achieving  $\text{NH}_4^+$  removal that is competitive to currently applied alternative methods, as described in Chapter 2.2, such as partial nitrification in combination with anammox (approximately 90% removal, hereafter representing competitive  $\text{NH}_4^+$  removal), while producing concentrated  $\text{NH}_4^+$  solutions. The experimental work focused on the application of dynamic current density during the ED operation, aiming to maximise the concentration factor and to minimise the energy consumption.

The results presented in Chapter 3 lead to the conclusion that ED allows for competitive (approximately 90%)  $\text{NH}_4^+$  removal from synthetic feed water with a TAN (as  $\text{NH}_4^+$ ) concentration of  $1.5 \text{ g}\cdot\text{L}^{-1}$ , while producing 6.7 times concentrated  $\text{NH}_4^+$  solutions ( $10 \text{ g}\cdot\text{L}^{-1}$ ) at an electrical energy consumption of  $5 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .

### 8.2.2. Recommendations

The operation of ED to remove  $\text{NH}_4^+$  and concentrate  $\text{NH}_4^+$  inevitably results in ion concentration gradients and thus osmotic pressure gradients between the diluate and the concentrate; therefore, driving forces for back-diffusion and osmosis cannot be avoided. The results in Chapter 3 show that the application of dynamic current density resulted in less back-diffusion and osmotic water transfer, compared to the application of a fixed current density, resulting in a higher concentration factor and lower energy consumption.

The following recommendations may allow for further improved operation of ED for the removal of TAN from N-loaded residual waters, while producing concentrated  $\text{NH}_4^+$  solutions:

1. The use of membranes with lower water ( $\text{H}_2\text{O}$ ) permeabilities, for example with higher crosslinking densities, to achieve higher concentration factors, while having minimal impact on the resistances for  $\text{NH}_4^+$  transport;
2. The use of improved spacer material and design to make more efficient use of the membrane area and to lower the electrical resistance and ultimately the energy consumption, for example with spacers that have higher void fractions than those used in this thesis (59% void fraction) and are made of conductive materials.

Furthermore, because Chapter 3 only reports on tests using synthetic feed waters, additional research should focus on the use of real N-loaded residual streams, as identified in Chapter 2, leading to the following recommendation:

3. More extensive assessment of the effect of the transfer of other cations on the  $\text{NH}_4^+$  current efficiency and electrical energy consumption of ED;

### 8.3. Bipolar membrane electro dialysis (Chapter 4)

#### 8.3.1. Conclusions

Chapter 1 assessed whether bipolar membrane electro dialysis (BPMED) can be used to achieve  $\text{NH}_4^+$  removal that is competitive to partial nitrification in combination with anammox while producing concentrated  $\text{NH}_3$  solutions. The experimental work focused on the fate of TAN and corresponding TAN concentrations and the energy consumption during the BPMED operation.

The results presented in Chapter 4 lead to the conclusion that BPMED allows for competitive (85 - 91%)  $\text{NH}_4^+$  removal from synthetic feed water with a TAN concentration of  $1.5 \text{ g}\cdot\text{L}^{-1}$  (as  $\text{NH}_4^+$ ), while producing concentrated  $\text{NH}_3$  solutions ( $4.5 \text{ g}\cdot\text{L}^{-1}$ ) that can be used for TAN recovery. In addition, using BPMED to produce concentrated  $\text{NH}_3$  solutions proved to be energetically competitive to the use of ED in combination with the addition of chemicals. For the latter, the energetic equivalence of the addition of chemicals was calculated and added to the electrical energy consumption of ED. To produce solutions with  $4.5 \text{ g}\cdot\text{L}^{-1}$  of  $\text{NH}_3$ , BPMED required  $19 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  of electrical energy, while ED in combination with chemical addition required  $22 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$ .

#### 8.3.2. Recommendations

Similar to ED, concentration gradients cannot be avoided in BPMED during the production of concentrated  $\text{NH}_3$  in the base. Chapter 4 shows that hydroxide ( $\text{OH}^-$ ) leakage, dissolved  $\text{NH}_3$  diffusion and ionic species diffusion (such as  $\text{NH}_4^+$ ), resulted in a loss in  $\text{NH}_4^+$  current efficiency and ultimately in an increase in energy consumption. In addition, due to  $\text{NH}_3$  diffusion from the base and the accumulation of TAN in the electrode rinse, only approximately half of the transported TAN (as  $\text{NH}_4^+$ ) from the feed water ended up as  $\text{NH}_3$  in the base. To improve the operation of BPMED, the following recommendations are suggested:

1. The use of membranes with lower  $\text{OH}^-$  and  $\text{NH}_3$  permeabilities to achieve higher  $\text{NH}_4^+$  current efficiencies and ultimately a lower energy consumption, while having minimal impact on the resistances for  $\text{NH}_4^+$  transport;
2. The use of improved spacer material and design to make more efficient use of the membrane area and to lower the electrical resistance and ultimately the energy consumption, as described in Chapter 8.2.2.

Since Chapter 4 again only reports on tests using synthetic feed waters, additional research should focus on the use of real N-loaded residual streams, as identified in Chapter 2. For the treatment of real N-loaded residual waters, the following recommendations are suggested:

3. An assessment of the effect of the transfer of other cations on the  $\text{NH}_4^+$  current efficiency and energy consumption of BPMED;
4. The use of (pre-)concentrated  $\text{NH}_4^+$  solutions as feed water, for example by using ED, to allow for operating at higher current densities and to minimise the  $\text{NH}_4^+$  current efficiency and potentially the energy consumption.

#### 8.4. Vacuum membrane stripping (Chapter 5 and 6)

##### 8.4.1. Conclusions

Chapter 5 and Chapter 6 assessed the selectivity of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer, as well as to assess the achievable  $\text{NH}_3$  concentrations and energy consumption when recovering gaseous  $\text{NH}_3$  by vacuum membrane stripping (VMS). The experimental work in Chapter 5 focused on the transfer rates and selectivity of  $\text{NH}_3$  over  $\text{H}_2\text{O}$  transfer for various types of membranes and various feed water compositions ( $\text{NH}_3$  feed water concentration and ionic strength), feed water temperature and hydraulic conditions. The experimental work in Chapter 6 focused on the achievable concentrations and energy consumption of VMS for various feed water temperatures and  $\text{NH}_3$  feed water concentrations.

The results from Chapter 5 and 6 lead to multiple conclusions on the recovery of  $\text{NH}_3$  by VMS. Firstly,  $\text{H}_2\text{O}$  transfer during the recovery of  $\text{NH}_3$  by VMS proved to be inevitable, resulting in the recovery of  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures. Secondly, the use of dense pervaporation membranes does not allow for more selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$ , compared to porous gas-permeable membranes and results in consistently lower  $\text{NH}_3$  transfer rates. In fact, the transfer of  $\text{H}_2\text{O}$  was consistently preferred over  $\text{NH}_3$  transfer, throughout all conducted experiments. Thirdly, adjusting the feed water composition ( $\text{NH}_3$  concentration and ionic strength) and the operating conditions (temperature and hydraulic conditions) allowed for optimisation of the VMS process to achieve recovery of more concentrated  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures. Eventually, VMS allowed for the recovery of  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations up to 11 wt%, when recovering  $\text{NH}_3$  at a temperature of 35 °C, at unsteady hydraulic conditions, at an  $\text{NH}_3$  feed water concentration of 10 g·L<sup>-1</sup>. To achieve such high  $\text{NH}_3$  concentrations in the recovered  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures, most N-loaded residual waters must be firstly concentrated by (BPM)ED, because most N-loaded residual waters are characterised by much lower N concentrations, as described in Chapter 2.

##### 8.4.2. Recommendations

Based on the conclusions on the recovery of  $\text{NH}_3$  by VMS, various attempts failed to selectively transfer  $\text{NH}_3$  over  $\text{H}_2\text{O}$ . The use of various feed water compositions, operation conditions and membranes all resulted in the selective transfer of  $\text{H}_2\text{O}$  compared to  $\text{NH}_3$ . However, by optimising the operation of VMS in terms of  $\text{NH}_3$  feed water concentration, feed water temperature and hydraulic conditions, the concentration of  $\text{NH}_3$  in the recovered  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures increased from 1 to 11 wt%. To recover more concentrated  $\text{NH}_3$ - $\text{H}_2\text{O}$  mixtures, the following recommendations are suggested:

1. To strip  $\text{NH}_3$  from feed waters with  $\text{NH}_3$  feed water concentrations higher than 10 g·L<sup>-1</sup>, by producing concentrated  $\text{NH}_3$  solutions from N-loaded residual streams using ED and BPMED.
2. The use of membranes that allow for selective transfer of  $\text{NH}_3$  over  $\text{H}_2\text{O}$ , for example, making use of a selective layer of dense membranes. The materials of the selective layer of the membrane should then avoid the dissolution of  $\text{H}_2\text{O}$  and allow for solution and diffusion of  $\text{NH}_3$ . Alternatively, the selective layer should strongly bind  $\text{H}_2\text{O}$ , while allowing for solution and diffusion of  $\text{NH}_3$ , for

example by taking advantage of the difference in acidity coefficients ( $pK_a$ ) between  $NH_3$  and  $H_2O$ . By allowing for less strong bonding of  $NH_3$  than  $H_2O$  to the membrane material after sorption due to the differences in  $pK_a$ , potentially higher transfer rates of  $NH_3$  compared to  $H_2O$  can be established.

3. To condense the recovered  $NH_3$ - $H_2O$  mixtures, allowing for  $H_2O$  condensation while avoiding the dissolution of  $NH_3$  in the condensed  $H_2O$  (flash condensation), to obtain more concentrated  $NH_3$ - $H_2O$  mixtures.

Because also Chapter 5 and Chapter 6 only report on the use of synthetic feed waters and fuels, additional research should focus on the use of  $NH_3$  recovered from real N-loaded residual streams or waters, as identified in Chapter 2. It must be realised that (BPM)ED is firstly required to produce concentrated TAN solutions, meaning that  $NH_3$  recovery by VMS will not directly be applied to the N-loaded residual streams. Nonetheless, when VMS will be used to recover  $NH_3$  from real N-loaded residual waters, the following recommendation is suggested:

4. An assessment of the presence of possible contaminants in the recovered  $NH_3$ - $H_2O$  mixtures. Even though inorganic metal-based salts are not volatile and solutes such as volatile fatty acids, sulphide and (bi)carbonate are ionised at high pH, contaminants may be present in the recovered  $NH_3$ - $H_2O$  mixtures when recovering  $NH_3$  from real N-loaded residual streams or waters (aqueous solutions) that contain  $NH_3$  originating from real N-loaded residual waters.

8.5. Solid oxide fuel cell (Chapter 6)

8.5.1. Conclusions

Chapter 6 determined the minimum  $\text{NH}_3$  concentration in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures when such mixture will be used as fuel for electricity generation in an SOFC. The results from Chapter 6 lead to the conclusion that an SOFC allowed for electrical energy generation of  $9 \text{ MJ}\cdot\text{kg}\cdot\text{N}^{-1}$  when using  $\text{NH}_3\text{-H}_2\text{O}$  mixtures with  $\text{NH}_3$  concentrations of 5 wt%.

8.5.2. Recommendations

The results in Chapter 6 show that the concentrations of  $\text{NH}_3$  in  $\text{NH}_3\text{-H}_2\text{O}$  mixtures recovery by VMS from water (aqueous solution) are high enough to allow for electricity generation in an SOFC. However, the following aspects were not studied yet and are recommended to serve as research topics for future work:

1. To validate whether and how much oxidised N-species are emitted by SOFC using  $\text{NH}_3\text{-H}_2\text{O}$  mixtures as a fuel, as current literature only reports on using pure  $\text{NH}_3$  as a fuel;
2. An assessment of mass, electricity and heat balance of an SOFC using  $\text{NH}_3\text{-H}_2\text{O}$  mixtures as a fuel;
3. An assessment of the long-term effect of  $\text{H}_2\text{O}$  presence in the fuel on the SOFC;
4. An assessment and optimisation of the operating conditions, such as fuel flow rate, air flow rate and operating temperature, to allow for high power densities, electrical efficiencies, while emitting no oxidised-N species;

Again, because Chapter 6 only report on the use of synthetic solutions that served as fuel, additional research may focus on the use of real N-loaded residual streams, as identified in Chapter 2. To this end, the following recommendation can be taken into account:

5. An assessment of the presence and effect of contaminants present in the recovered  $\text{NH}_3$  fuel.

## 8.6. Removal and recovery of TAN from real N-loaded residual waters (Chapter 7)

### 8.6.1. Conclusions

The objective of Chapter 7 was to assess the feasibility of TAN removal and subsequent  $\text{NH}_3$  recovery from real N-loaded residual streams. Based on the experimental results, ED allowed for the removal of approximately 90% of TAN from algae digestion reject water (ADRW), sludge digestion reject water (SDRW) and fertiliser industry condensate (FIC), while reaching a recovery of the treated water of at least 87%. During the production of concentrated  $\text{NH}_4^+$  solution by ED from SDRW, scaling took place in the concentrate flow channels, hampering the further treatment of SDRW. The treatment of FIC allowed for the production of a concentrated  $\text{NH}_4^+$  solution (ranging between 4 and 6  $\text{g}\cdot\text{L}^{-1}$ ) by ED, while consistently achieving 93% TAN removal. The concentrated  $\text{NH}_4^+$  solution was subsequently used for the production of a concentrated solution with 9  $\text{g}\cdot\text{L}^{-1}$  of  $\text{NH}_3$  by BPMED, which in its turn was used at the feed water for VMS for the recovery of  $\text{NH}_3$ . The obtained  $\text{NH}_3\text{-H}_2\text{O}$  mixture had an  $\text{NH}_3$  concentration of 4 wt%. Finally, the  $\text{NH}_3\text{-H}_2\text{O}$  mixture was used as the fuel of an SOFC, which generated 11  $\text{MJ}\cdot\text{kg-N}^{-1}$  of electrical energy. Hence, the combination of ED, BPMED, VMS and SOFC successfully allowed for competitive TAN removal from N-loaded residual water and subsequent electricity generation from the recovered  $\text{NH}_3$ . However, the combination of ED, BPMED and VMS used more electrical energy (37 – 39  $\text{MJ}\cdot\text{kg-N}^{-1}$ ) than the SOFC generated, resulting in a net electrical energy consumption of 26 – 28  $\text{MJ}\cdot\text{kg-N}^{-1}$ .

### 8.6.2. Recommendations

The results in Chapter 7 show that the production of concentrated  $\text{NH}_4^+$  solutions by ED from SDRW was hampered by scaling. To this end, the following recommendation is suggested:

1. The use of monovalent selective membranes to minimise the transport of multivalent ions to the concentrate, as the transfer of multivalent ions causes scaling when accumulated in the concentrate;

Furthermore, the results in Chapter 7 show that it is possible to achieve competitive TAN removal from FIC while  $\text{NH}_3$  is recovered for the generation of electricity in an SOFC. However, the combination of ED, BPMED and VMS consumed more energy than the SOFC generated. In the previous paragraphs, various recommendations were given to decrease the energy consumption of ED, BPMED and VMS and increase the electricity generation by an SOFC, which potentially may lead to an energy-positive system for TAN removal from N-loaded residual waters.



# Acknowledgements

After six years, I finally wrapped up my PhD research. Ten years I spent in Delft to obtain my bachelor's, master's and now also my PhD degree. What started with calculating structures and flood protection, ended with a book combining water treatment and energy generation. The big transition from the hardcore civil engineering disciplines started at the end of my bachelor's, when I chose to do a project mainly because it was abroad: the design of a water treatment plant in Portugal. After this experience, I was more intrigued about water treatment and continued with the MSc Watermanagement with a specialisation in Sanitary Engineering. After two three month trips to Indonesia and Spain, I was certain that I wanted to continue working in the field of water treatment.

I start by thanking Henri Spanjers, who first allowed me to conduct my MSc thesis on zero liquid discharge. I want to thank you for offering me the opportunity to do my PhD research, and for your trust in allowing me to conduct the research how I had in mind. I always enjoyed our late-night communications about the research, the Zero Brine project and the Industry Water course. Especially the latter two where for me a great nice introduction to the world of industrial water treatment. I also want to thank Jules van Lier for giving me the freedom and trust during my research. Furthermore, I want to thank Henri and Jules for the smooth collaboration and constructive feedback during the whole period of research.

To the students I supervised during my research, being Willy, Rob, Christiaan, Lasse, Sam, Matthijs, Evelien, Jan-Max, Lotte, Giacomo and Yundan: thanks a lot for all your efforts, critical thinking and discussions! Without all your input, I would not have been able to finish my research. I want to thank Mohammed, Armand, Patricia and all other Waterlab staff members for all their help and input. I claimed quite some space, but I hope I kept it all organised and tidy. To Mariska, Tamara and all other secretaries: thank you for all the support with scheduling and arranging meetings for having the door always open to help out. To Zhe and Elena: thank you for the great collaboration on the research paper. It took a long time, but we put together a nice piece of work! I also want to thank Ali Saadabadi for his patience and time to explain me the ins and outs of solid oxide fuel cells. I want to thank David Vermaas and Ernst Sudhölter for their input and the discussion we had on mass transport phenomena: I truly learned a lot from you! Subsequently, I would like to thank all the involved parties (KU Leuven, Fiaxell, Yara International, Waternet, Inopsys, Royal Haskoning DHV, Bioelectric and HoSt) from the N2kWh project for their contributions and feedback during the half-yearly meetings. I want to thank all my fellow PhD colleagues for all the serious notes, such as the First Year PhD Meetings, but especially for all the fun times we had in PSOR. A special thanks to those who had to share an office with me for three years. Magela, Pamela and Victor: it was a pleasure to spend my days with you. It was always interesting to see daily who showed up, at what time, what language we would speak that day, what to have for lunch and at what time, but especially to see who was in charge of the temperature control. Thank you for all the research-related and non-research-related discussions, which could become



## Acknowledgements

quite intense. I still stand with the modest oneliners on the whiteboard, which are probably still there: I was the sunshine of the office and I am like a milky way (brown on the outside, white on the inside). I also want to thank another Latin representation, being Javier, Sara and David for involving me in your version of your Spanish language, your cultures and habits and I always enjoyed the Sinterklaas celebrations. To Victor and Steef: if only we spent the time we spent on Pokemon GO on our research, we would have finished incredibly much earlier. Either way, I really needed this distraction to motivate me to continue the actual work, so thanks for joining me on this journey. Another big thank you to all my colleagues at Lenntech, for your patience to listen to me when I was ventilating my thoughts and experiences while finishing the thesis in combination with working at Lenntech. A special thanks to David, Tobias, Eddy and Adriaan, for your trust and efforts to bring the technology to practice.

To my friends: jaaahaaa, mijn werkstuk is eindelijk af en ik hoop dat jullie mijn spreekbeurt leuk vonden. Mark en Bob, heel erg voor jullie geduld om naar dat eindeloze gepraat over ammoniak en water te luisteren. Ik ben alleen bang dat dat nog niet helemaal over is. Ik ben erg blij dat jullie mij wilden bijstaan als paranimf. Voor pap en mam: zoals jullie weten, zei ik altijd dat ik nooit zou gaan promoveren. Maar goed, dat zei ik ook over het behalen van een bachelor en een master. Misschien moet ik maar niets meer zeggen.. Bedankt voor jullie eindeloze steun gedurende mijn studie en mijn onderzoek, maar ook vooral voor alles daarnaast. Tot slot, Loran: zonder jou had ik dit nooit kunnen doen. Jij bent er altijd voor mij geweest. Bedankt voor alle ruimte en tijd die je mij al die jaren gegeven hebt. Vaak was ik nog tot laat bezig of zat ik vast in mijn gedachten. Dankzij jou bleef ik daar nooit te lang in hangen. Jij hebt me zoveel andere dingen geleerd in het leven die nog veel belangrijker zijn dan onderzoek en werk. Nu is het tijd om te genieten van het belangrijkste in ons leven: Sen.

# Curriculum vitae

## *Summary*

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I am passionate researcher and engineer and I am highly motivated to work on water treatment related challenges. With my creativity, systematic and pragmatic thinking and ability to set priorities, I aim to solve the problem. I like to work in a team and I am not afraid to take risks, take the lead and carry the associating responsibilities. With my wide variety of working experience, I think I am able to communicate well with people from different educational and geographical backgrounds.

## *Competences*

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Communicating, conceptual thinking, delegating, innovative, pragmatic, planning and organising, responsibility, teamwork, vision

## *Personal*

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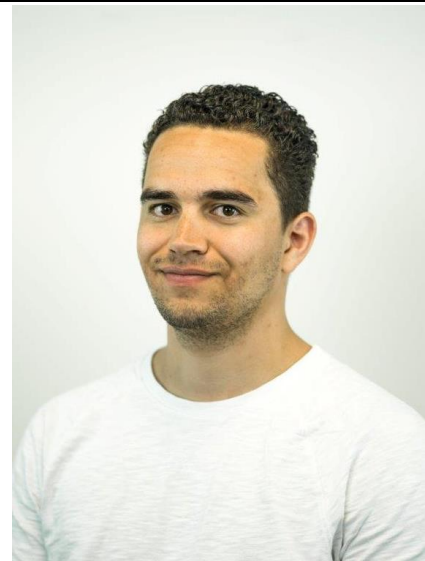
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## *Personal interests*

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Crossfit, mountainbiking, snowboarding, spending time with friends and family

*Education/studies*

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2013 - 2016: Civil Engineering MSc, Watermanagement, Sanitary Engineering, Delft University of Technology

- Diploma: Master of Science (2016)
  - Master Thesis: Sodium chloride recovery from brines for reuse purposes in zero liquid discharge (<http://resolver.tudelft.nl/uuid:ae640132-fbe7-45d3-a62a-479599f308ed>)
  - Multidisciplinary project (3 months): Optimisation study for drinking water treatment in Jakarta, Indonesia
  - Internship (4 months): Experimental assessment of ultrafiltration and reverse osmosis for water recovery from sewage effluent in Barcelona, Spain

2009 - 2013: Civil Engineering BSc, Delft University of Technology

- Diploma: Bachelor of Science (2013)
  - Bachelor Thesis: “Mag het wat zachter”, design of water treatment system in Portugal.

2002 - 2008: Pre University Secondary Education, Lentiz College dep. Groen van Prinsterer, Vlaardingen

- Diploma: VWO (2008)
  - Subjects: Dutch, English, Physics 1, Mathematics B2, Chemistry 1, Informatics, Biology 2

*Languages*

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Dutch: Excellent, mother tongue

English: Good, reading, writing, speaking

French: Reasonable, reading

German: Reasonable, reading, speaking

*Working experience*

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April 2020 – present; Lenntech B.V. (40 hours per week)

*Branch:* Water treatment technology, *Position:* R&D Coordinator

*Proceedings:* Coordination of water treatment related R&D activities, comprising various different technologies at different scales: pilot and demonstration projects with research consortia and commercial proof-of-concept and pilot projects with industrial end-users

April 2016 – April 2020; TU Delft (40 hours per week)

*Branch:* Research, *Position:* PhD researcher

*Proceedings:* Scientific research on the recovery of ammonia from residual waters for the generation of electricity. <https://www.tudelft.nl/citg/onderzoek/stories-of-science/energie-krijgen-van-urine>

February 2015 – May 2015; CETAQUA Barcelona (40 hours per week)

*Branch:* Research, *Position:* Intern

*Proceedings:* Execution of experiments and data analysis on water treatment technologies

August 2013 – March 2016; TU Delft (12 hours per week)

*Branch:* Academic education, *Position:* Student assistant Water Management

*Proceedings:* Supporting BSc- and MSc-courses Water Treatment

January 2013 – September 2013: KneeClinic (12 hours per week)

*Branch:* Medical, *Position:* Project Manager

*Proceedings:* Administration, marketing and IT

June 2010 – November 2014: Argos Zorggroep (16 hours per week)

*Branch:* Healthcare, *Position:* Logistics, restaurant and front-desk employee

*Proceedings:* Logistic and technical proceedings, serving meals and administrative proceedings

October 2009 - March 2010: PWS Rotterdam (8 hours per week)

*Branch:* Engineering, *Position:* Draftsman

*Proceedings:* Digitalizing hardcopy technical drawings

November 2006 – May 2008: Lentiz College Dep. Groen van Prinsterer (5 hours per week)

*Branch:* Secondary education, *Position:* Student tutor

*Proceedings:* Tutoring student, providing study guidance

November 2005 – April 2011: PLUS Woudhoek supermarket (15 hours per week)

*Branch:* Retail, *Position:* Sales employee

*Proceedings:* Leadership of stocking employees, managing daily orders, managing schedules

*Scientific publications*

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- (2022) Niels van Linden, Henri Spanjers and Jules B. van Lier, Fuelling a solid oxide fuel cell with ammonia recovered from water by vacuum membrane stripping, <https://doi.org/10.1016/j.cej.2021.131081>
- (2022) Niels van Linden, Yundan Wang, Ernst Sudhölter, Henri Spanjers, Jules B. van Lier, Selectivity of vacuum ammonia stripping using porous gas-permeable and dense pervaporation membranes under various hydraulic conditions and feed water compositions, <https://doi.org/10.1016/j.memsci.2021.120005>
- (2021) Zhe Deng, Niels van Linden, Elena Guillen, Henri Spanjers, Jules B. van Lier, Recovery and applications of ammoniacal nitrogen from nitrogen-loaded residual streams: A Review, <https://doi.org/10.1016/j.jenvman.2021.113096>
- (2021) S. Ali Saadabadi, Niels van Linden, Abel Heinsbroek, P.V. Aravind: A solid oxide fuel cell fuelled by methane recovered from groundwater, <https://doi.org/10.1016/j.jclepro.2021.125877>
- (2020) Niels van Linden, Ran Shang, Georg Stockinger, Bas Heijman, Henri Spanjers: Separation of natural organic matter and sodium chloride for salt recovery purposes in zero liquid discharge, <https://doi.org/10.1016/j.wri.2019.100117>
- (2020) Niels van Linden, Giacomo L. Bandinu, David A. Vermaas, Henri Spanjers, Jules B. van Lier: Bipolar membrane electrodialysis for energetically competitive ammonium removal and dissolved ammonia production, <https://doi.org/10.1016/j.jclepro.2020.120788>
- (2019) Niels van Linden, Henri Spanjers, Jules B. van Lier: Application of dynamic current density for increased concentration factors and reduced energy consumption for concentrating ammonium by electrodialysis, <https://doi.org/10.1016/j.watres.2019.114856>

*Patent*

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- (2019) Niels van Linden, Henri Spanjers, Jules B. van Lier, Gas recovery from wastewater, Priority No. WO 2019/151855, <https://worldwide.espacenet.com/patent/search/family/065995823/publication/CA3090320A1?q=pn%3DCA3090320A1>

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(54) **GAS RECOVERY FROM WASTEWATER**

**GASRÜCKGEWINNUNG AUS ABWASSER**

**RÉCUPÉRATION DE GAZ PROVENANT D'EAUX USÉES**

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(56) References cited:  
**US-A- 4 969 983 US-A1- 2016 271 562**

- **W. PRONK ET AL: "Treatment of source-separated urine by a combination of bipolar electro dialysis and a gas transfer membrane", WATER SCIENCE AND TECHNOLOGY, vol. 53, no. 3, 1 February 2006 (2006-02-01), pages 139-146, XP055449550, ISSN: 0273-1223, DOI: 10.2166/wst.2006.086 cited in the application**
- **SHUANGCHEN MA ET AL: "Experimental study on desorption of simulated solution after ammonia carbon capture using bipolar membrane electro dialysis", INTERNATIONAL JOURNAL OF GREENHOUSE GAS CONTROL, ELSEVIER, AMSTERDAM, NL, vol. 42, 3 November 2015 (2015-11-03), pages 690-698, XP029325593, ISSN: 1750-5836, DOI: 10.1016/J.IJGGC.2015.09.020 cited in the application**
- **ALIM A B ET AL: "Coupling of bipolar membrane electro dialysis and ammonia stripping for direct treatment of wastewaters containing ammonium nitrate", JOURNAL OF MEMBRANE SCI, ELSEVIER BV, NL, vol. 244, no. 1-2, 15 November 2004 (2004-11-15), pages 89-96, XP004619447, ISSN: 0376-7388, DOI: 10.1016/J.MEMSCI.2004.07.007 cited in the application**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).



## Description

### FIELD OF THE INVENTION

**[0001]** The present invention is in the field of a system for gas recovery from wastewater, a method for treating wastewater, and a method wherein ammonia and carbon dioxide are recovered. Typically a wastewater stream is fed into the system, treated and stripped from ammonia and carbon dioxide, and a cleaner water stream is released.

### BACKGROUND OF THE INVENTION

**[0002]** Typically wastewater originates from households and industry. It may be collected and transferred to a treatment facility.

**[0003]** Wastewater treatment is aimed at converting wastewater into an aqueous effluent that can be returned to the nature water cycle, or aimed at (direct) reuse of water. The latter is also referred to as water reclamation. A minimal impact on the environment is aimed at. The treatment process typically takes place in a wastewater treatment plant or sewage treatment plant. Typically pollutants are removed or broken down. Various processes may be involved, such as phase separation, sedimentation, filtration, oxidation, polishing, tertiary treatment, and biochemical treatment, such as by using microorganisms. By-products from wastewater treatment plants may also be treated in a wastewater treatment plant.

**[0004]** A contaminant typically found in wastewater is nitrogen, such as in the form of urea, nitrate and nitrite. Excessive discharge of nitrogen (N) leads to eutrophication of receiving surface waters and subsequent deterioration of the aquatic environment. To prevent this, nitrogen compounds in wastewaters are preferably removed before discharge of the water. In various types of wastewater, N is present as ammonium ion ( $\text{NH}_4^+$ ) in combination with an ion such as bicarbonate ( $\text{HCO}_3^-$ ). In many industrialized areas in the world,  $\text{NH}_4^+$  is converted to nitrates and eventually to dinitrogen gas, at the expense of considerable capital costs and energy.

**[0005]** The majority of the produced  $\text{NH}_3$  is used as fertilizer. As a consequence of use thereof, ultimately  $\text{NH}_3$  becomes available in waste streams: for example, in manure, urine, and sewage. The total amount of  $\text{NH}_3$  discharged to domestic sewage treatment plants in 2016 in the Netherlands was about 32 million kilogram, while the amount of  $\text{NH}_3$  in manure in 2013 was about 471 million kilograms. Current state-of-the-art technologies require at least 11 MJ/kg- $\text{NH}_3$  to remove  $\text{NH}_3$  from wastewater.

**[0006]** A treatment technology used is Anammox. In wastewater containing  $\text{NH}_4\text{HCO}_3$ ,  $\text{NH}_4^+$  is biochemically oxidized, forming  $\text{N}_2$  and  $\text{H}_2\text{O}$ . This process requires energy. The application of Anammox finally does not lead to the possibility of resource or energy recovery. Also  $\text{CO}_2$  may remain in treated water, leading to amongst

others acidification.

**[0007]** Ammonium nitrate may be removed from wastewater. However, in such as treatment of wastewater containing  $\text{NH}_4\text{NO}_3$  species, the  $\text{NH}_4\text{NO}_3$  can unfortunately not be reused in certain cases because it contains traces of radioactive compounds.

**[0008]** For  $(\text{NH}_4)_2\text{SO}_4$  fertilizer production initially  $\text{CO}_2$  may be stripped and released into the air to increase the pH and lower the buffer capacity. Subsequently,  $\text{NH}_3$  gas is stripped, requiring significant amounts of energy and the addition of chemicals. The  $\text{NH}_3$  is then scrubbed in acid, to produce  $(\text{NH}_4)_2\text{SO}_4$ , which can be used as (resource for) fertilizer. However, the demand and economic yield of  $(\text{NH}_4)_2\text{SO}_4$  are low: the required acid is more valuable per kg than the produced  $(\text{NH}_4)_2\text{SO}_4$ . Additionally, there are extra costs for the required chemicals and energy. Because this fertilizer has a high sulphur content, the applicability is limited to specific situations.

**[0009]** Some prior art documents relate to gas recovery from aqueous systems.

**[0010]** US 2016/271562 A1 recite a process and system for removing ammonia from an aqueous ammonia solution. A first aqueous solution and the ammonia solution are flowed respectively through a first and a second separation chamber of a bipolar membrane electro dialysis stack. The first separation chamber is bounded on an anodic side by a cation exchange membrane and the second separation chamber is bounded on a cathodic side by the cation exchange membrane and on an anodic side by a bipolar membrane. The bipolar membrane has an anion-permeable layer and a cation-permeable layer respectively oriented to face the stack's anode and cathode. While the solutions are flowing through the stack a voltage is applied across the stack that causes the bipolar membrane to dissociate water into protons and hydroxide ions. The protons migrate into the second separation chamber and react there with ammonia to form ammonium ions that migrate to the first separation chamber.

**[0011]** US 4,969,983 A recites an apparatus containing a multiplicity of three chamber units comprising a combination of ion exchange membranes and bipolar membranes with certain of said chambers containing a fluid permeable filler of ion-exchange material. The apparatus can be used in a process to remove weakly ionized gases from fluid mixtures.

**[0012]** An article by Pronk et al. "Treatment of source-separated urine by a combination of bipolar electro dialysis and a gas transfer membrane" in Water Science Technology, 53, 3, p. 139-146, 2006, recites that urine contains nutrients which can be applied usefully as a fertiliser in agriculture, but the relatively high pH can lead to ammonia evaporation. Electro dialysis with bipolar membranes was combined with an additional mass transfer unit in order to render a product containing ammonium and phosphate at a low pH. In one case, the additional mass transfer unit consisted of bubble columns placed in acid and basic concentrate streams, connected with a circulating gas phase. In the other case, the unit

consisted of a gas-filled (hydrophobic) membrane placed in between the circulating acid and basic concentrate streams. The results showed that ammonia was transferred through the gas phase, but also carbonate, which is present in stored urine originating from the hydrolysis of urea. Although the pH in the product stream decreases initially, it rises above pH 7 at longer operation times. This pH increase can be attributed to a combination of proton compensating effects. The use of ammonia-selective membranes for the transfer into the acid concentrate could provide a solution to generate an ammonium phosphate product at low pH and high recoveries.

**[0013]** An article by Shuangchen et al. "Experimental study on desorption of simulated solution after ammonia carbon capture using bipolar membrane electrodialysis", *Int. J. Greenhouse Gas Control*, Elsevier, Vol. 42, November 3, 2015, p. 690-698, recites ammonia capture in solutions.

**[0014]** An article by Ali et al. in *J. Membrane Science*, Elsevier, Vol. 244, Nr. 1-2, November 15, 2004, p. 89-96 recites that splitting of ammonium nitrate to nitric acid and ammonia was achieved by a coupled process including bipolar membrane electrodialysis and in situ ammonia stripping. The effect of homopolar ion-exchange membranes on current efficiency led to the selection of specific membranes. The main parameters influencing the current efficiency were acid and ammonia concentrations. Proton leakage through the anion-exchange membrane is proportional to acid concentration. Ammonia diffuses through the membranes independently of the current. Higher current efficiency was obtained at higher current density. Batch and continuous processing were compared.

**[0015]** A further issue with prior art systems may be potential fouling of the membranes used. Therefore one has to cope with the various contaminants present in wastewater. As mentioned the required energy, the process control strategy, and the economic feasibility, is sub-optimal.

**[0016]** The present invention therefore relates to a system for gas recovery from wastewater, and a method of operating such a system, which solve one or more of the above problems and drawbacks of the prior art, providing reliable results, without jeopardizing functionality and advantages.

#### SUMMARY OF THE INVENTION

**[0017]** The present invention relates to a system for gas recovery from wastewater, a method for treating wastewater, and a method wherein ammonia and carbon dioxide are recovered. The present invention relates to an innovative process in which wastewater with dissolved  $\text{NH}_4\text{HCO}_3$  is treated with a combination of two technologies: electrodialysis with bipolar membranes and stripping of gases, such as with a vacuum membrane. By applying an electrical potential difference in electrodialysis with bipolar membranes it has been found that  $\text{NH}_4^+$

transfers from the wastewater to an alkaline recirculation solution. Simultaneously  $\text{HCO}_3^-$  is found to transfer from the wastewater to an acidic recirculation solution, leading to the depletion of  $\text{NH}_4\text{HCO}_3$  in the wastewater. In addition to ion transfer through ion exchange membranes, bipolar membranes dissociate water into ions under the influence of an electrical potential difference. This results in the generation of  $\text{H}^+$  ions in the acidic recirculation solution, leading to the formation of dissolved carbon dioxide gas ( $\text{CO}_2$ ). In the alkaline solution,  $\text{OH}^-$  is generated, leading to the formation of dissolved ammonia gas ( $\text{NH}_3$ ). The two gases ( $\text{CO}_2$  and  $\text{NH}_3$ ) are subsequently stripped, such as by separate vacuum membrane removal. A hydrophobic membrane (impermeable for liquids, but permeable for gases) may separate the liquid phase from the gaseous phase ( $\text{CO}_2$  and  $\text{NH}_3$ , respectively). On the gaseous side of the membrane an under-pressure (vacuum) may be applied. Because of a vapour pressure difference, the gases are stripped from the liquid, resulting in recovery of  $\text{CO}_2$  and  $\text{NH}_3$  gas. These gases may be used to produce fertilizer, to produce energy (from  $\text{NH}_3$ ), or to be applied directly as a resource in industry. The alkaline and acidic recirculation solutions are recycled in the electrodialysis with bipolar membranes. The present process is found to be very efficient in terms of energy used and in terms of product obtained.

**[0018]** The present combination of technologies enables separate recovery of resources ( $\text{CO}_2$  gas and  $\text{NH}_3$  gas) in treatment of wastewater comprising  $\text{NH}_4^+$  and  $\text{HCO}_3^-$ . Additionally, the invention provides resource recovery in wastewater treatment without addition of chemicals in a continuously operated process. Only electrical energy is required, while additional low-grade energy (waste heat) can be used to improve the efficiency of the invention. Finally, the invention does not continuously generate a residual solution which needs to be treated further;  $\text{CO}_2$  and  $\text{NH}_3$  gas are potential end-products, whereas the treated water can be discharged or reused (optionally after post-treatment). The gases may be obtained in high purity, e.g. >90% pure. For both gaseous species,  $\text{CO}_2$  and  $\text{NH}_3$ , the other species is virtually absent; in both cases water vapour may be present. The present invention is sustainable, as it contributes to a circular economy, where water,  $\text{NH}_3$  and  $\text{CO}_2$  may be reused. It is also very scalable. Both electrodialysis and membrane stripping can be applied in a very wide range of wastewater quantities, e.g. because these technologies can be implemented in a modular way.

**[0019]** The present invention provides economical and material savings for e.g. domestic wastewater treatment and manure. It has been found that 10 MJ/kg- $\text{NH}_3$  can be recovered as electrical energy when using  $\text{NH}_3$  as fuel for a solid oxide fuel cell. This amount of recovered energy can be partly used to remove  $\text{NH}_3$  from wastewater. In this situation, the removal of  $\text{NH}_3$  does not cost energy anymore, resulting in a saving of 0.25 euro/kg- $\text{NH}_3$ , assuming that electricity costs 0.08 euro/kWh. This is a total potential saving of 126 million euro per year in

the Netherlands only.

**[0020]** The production of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  by the Haber-Bosch process requires 25 MJ/kg- $\text{NH}_3$  (theoretical minimum is 20 MJ/kg- $\text{NH}_3$ ). When  $\text{NH}_3$  is recovered as a resource from wastewater and it can be reused 0.31 euro/kg- $\text{NH}_3$  can be saved, as the  $\text{NH}_3$  does not have to be produced anymore. This is a total potential saving of 156 million euro per year in the Netherlands. For this situation, it is assumed that the amount of energy to recover  $\text{NH}_3$  is equal to the current amount of energy for  $\text{NH}_3$  removal from wastewater.

**[0021]** Some drawbacks exist however. At present there are relatively high costs for the membranes, some cleaning is still involved, and it is preferred, in view of transport, to have an application for the generated  $\text{CO}_2$  close to the present system.

**[0022]** The system of the present invention is defined in claim 1 and comprises at least one ion exchange unit 30. Into the at least one exchange unit wastewater is provided through input 70, which is treated by the present system, and released from the system through output 71. In fluid connection with the at least one exchange unit are at least three recirculation units 51,52,74a,b, a first alkaline recirculation unit comprising a gaseous ammonia stripper, a second acidic recirculation unit comprising a gaseous  $\text{CO}_2$  stripper, and a third electrode rinse recirculation unit 74a,b adapted to receive input from a first electrode rinse compartment (21,22), and for providing output to a second electrode rinse compartment, and vice versa. At least one of the gaseous ammonia stripper and of the gaseous  $\text{CO}_2$  stripper comprises a hydrophobic membrane (61a, 62a), a molecular sieve for ammonia or for  $\text{CO}_2$ , respectively, a pervaporation membrane, or a combination thereof, and the system comprises a tube (72) for removing gaseous ammonia, and a tube (73) for removing gaseous  $\text{CO}_2$ . For providing flow of fluids a pump, 81 respectively, is provided. Clearly these alkaline and acidic recirculation units are separate from one and another. In the alkaline recirculation unit  $\text{NH}_3$  (ammonia) is stripped, whereas in the acidic recirculation unit  $\text{CO}_2$  is stripped, both as gaseous species. The stripped gases exit the present system over tubes 72,73, respectively. For stripping and flowing gases pumps 82 may be provided, which typically provide an under-pressure. The stripped gases may be combined to form  $\text{NH}_4\text{HCO}_3$ . Each ion exchange unit comprises at least three compartments separated by membranes. The membranes provide exchange of  $\text{NH}_4^+$  (ammonium) from the second to the first compartment over the cation exchange membrane 12, and of  $\text{HCO}_3^-$  from the second to the third compartment over the anion exchange membrane 13; hence the membranes may be referred to as ion exchange membranes, such as cation and anion exchange membranes. The present also comprises at least two electrode rinse compartment 21,22, and typically two electrode rinse compartments; the at least two electrode rinse compartment have an adjacent membrane, selected from bipolar membranes, cation exchange mem-

branes, and anion exchange membranes, respectively, which may provide exchange of  $\text{NH}_4^+$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , or  $\text{HCO}_3^-$ , to or from the electrode rinse compartment 21,22, respectively. The third recirculation unit replenishes the at least electrode rinse compartment. The first electrode rinse compartment 21 is in electrical contact with an anode 41 and the second electrode rinse compartment 22 may be in electrical contact with a cathode 42. To the anode/cathode an electrical current is provided. Water and electrons form  $\text{H}^+$  and  $\text{OH}^-$ . Typically the following redox reactions occur: Anode:  $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^-$ ; Cathode:  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$ . If the electrode drain recirculates from compartment 21 to compartment 22, and vice versa, water is formed again. The bipolar membrane (11a,b) is typically facing the alkaline compartment 31 or electrode rinse compartment 22 with a positive side and mutatis mutandis is typically facing the acidic compartment 33 or electrode rinse compartment 21 with a negative side. The bipolar membranes can generate  $\text{H}^+$ , at a negative side thereof, and  $\text{OH}^-$ , at a positive side thereof.

**[0023]** In a second aspect the present invention relates to a method of treating wastewater, comprising  $\text{NH}_4^+$ , and  $\text{HCO}_3^-$ , using the present system.

**[0024]** Thereby the present invention provides a solution to one or more of the above mentioned problems and drawbacks.

**[0025]** Advantages of the present description are detailed throughout the description.

#### DETAILED DESCRIPTION OF THE INVENTION

**[0026]** The present invention relates in a first aspect to a system according to claim 1.

**[0027]** In the present system the third recirculation unit 74a,b is adapted to receive input from the first electrode rinse compartment 21, and for providing output to the second electrode rinse compartment 22, and vice versa. Therewith the liquids in the compartments may be replenished. A salt level in the compartments 21,22 may be 0.1-2 mole/l, such as by providing  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ,  $\text{NH}_4\text{NO}_3$ , or  $\text{NH}_4\text{HCO}_3$ .

**[0028]** In an exemplary embodiment of the present system the first electrode rinse compartment 21 may comprise  $\text{NH}_4^+$  or  $\text{H}^+$ , or wherein the second electrode rinse compartment 22 comprises  $\text{OH}^-$  or  $\text{HCO}_3^-$ , or a combination thereof.

**[0029]** In an exemplary embodiment of the present system the at least one recirculation unit may comprise a membrane 61a, 62a, which typically is hydrophobic, such as a macroporous hydrophobic membrane, a molecular sieve for ammonia or for  $\text{CO}_2$ , respectively, a pervaporation membrane, a pump 82, or a combination thereof.

**[0030]** In an exemplary embodiment of the present system at least one membrane 61a,62a in the stripper may be impermeable to liquids, such as water, and permeable to gases, such as  $\text{CO}_2$  and  $\text{NH}_3$ , respectively. The stripper 61,62 typically comprises a strip chamber 61b,62b,

respectively.

**[0031]** In an exemplary embodiment of the present system the (hydrophobic) membrane 61a, 62a may be macroporous, with an average pore size of 50-500 nm, or microporous, with an average pore size of 0.4-10 nm, preferably 0.5-1 nm (as determined by electron microscopy).

**[0032]** In an exemplary embodiment of the present system the membrane 11a, 11b, 12, 13, 61, 62 may have a size from 50 cm<sup>2</sup> to 10<sup>4</sup> cm<sup>2</sup>, such as 10<sup>2</sup>-10<sup>3</sup> cm<sup>2</sup>, and a thickness of 100-7000 μm, such as 200-900 μm, a compartment 31, 32, 33, 21, 22 may have a width of 0.1-50 mm, such as 1-30 mm, and a flow may be parallel to the membrane. A membrane may comprise a support. Membranes 12 may be polyvinyl chloride based, with sulphonic acid in Na<sup>+</sup> ionic form, membranes 13 may be polyester based, with ammonium in Cl<sup>-</sup> ionic form.

**[0033]** In an exemplary embodiment of the present system the membrane 61a, 62a, may be selected from polymeric material, preferably thermoplastic polymers, such as poly propylene and poly vinylidene fluoride, inorganic material, such as silica, and reinforced silica, and combinations thereof.

**[0034]** In an exemplary embodiment of the present system the exchange unit 30 may comprise a stack of a cation exchange membrane 12, an alkaline compartment 31, a bipolar membrane 11a, an acidic compartment 33, an anion exchange membrane 13, and a wastewater compartment 32, and wherein the second electrode rinse compartment 22 is in fluidic contact with a further cation exchange membrane 12, and wherein the third recirculation unit 74a,b is adapted to receive input from a first electrode rinse compartment 21 to compartment 22, and adapted to provide output to compartment 22 (see fig. 1,2). Therein a cathode 42 may be provided in contact with a compartment 22 and an anode 41 may be provided in contact with compartment 21.

**[0035]** In an exemplary embodiment of the present system the exchange unit 30 may comprise a stack of an anion exchange membrane 13, an acidic compartment 33, a bipolar membrane 11a, an alkaline compartment 31, a cation exchange membrane 12, and a wastewater compartment 32, and wherein the second electrode rinse compartment 22 is in fluidic contact with a further anion exchange membrane 13, and wherein the third recirculation unit 74a,b is adapted to receive input from a first electrode rinse compartment 21 to compartment 22, and adapted to provide output to compartment 21. Therein a cathode 42 may be provided in contact with a compartment 22 and an anode 41 may be provided in contact with compartment 21.

**[0036]** In an exemplary embodiment of the present system the exchange unit 30 may comprise a stack of a bipolar membrane 11a, an alkaline compartment 31, a cation exchange membrane 12, a wastewater compartment 32, an anion exchange membrane 13, and an acidic compartment 33, and wherein the first electrode rinse compartment 21 is in fluidic contact with a further bipolar

membrane 11b, and wherein the third recirculation unit 74a,b is adapted to receive input from a first electrode rinse compartment 21 to compartment 22, and adapted to provide output to compartment 21, and vice versa to compartment 22 (see fig. 3). Therein a cathode 42 may be provided in contact with a compartment 22 and an anode 41 may be provided in contact with compartment 21.

**[0037]** In an exemplary embodiment the present system may comprise 2-2<sup>10</sup> ion exchange units 30 in parallel, preferably 4-2<sup>9</sup> ion exchange units, such as 200-400 ion exchange units.

**[0038]** The system of the invention comprises a tube 72 for removing gaseous ammonia, and a tube 73 for removing gaseous CO<sub>2</sub>.

**[0039]** In an exemplary embodiment of the present system in operation at least one of a voltage of 0.1-5 V per ion exchange unit 30 may be applied, preferably 0.3-3V, more preferably 0.5-2V, such as 0.7-1.5V.

**[0040]** In an exemplary embodiment of the present system in operation a pH in the first alkaline compartment 31 may be from 7-14, preferably from 8-13, such as 9-12.

**[0041]** In an exemplary embodiment of the present system in operation a pH in the third acidic compartment 33 may be from 1-7, preferably 2-6.5, such as 2-6.

**[0042]** In an exemplary embodiment of the present system in operation a current density may be from 15-500 A/m<sup>2</sup>, such as 50-100 A/m<sup>2</sup>.

**[0043]** In an exemplary embodiment of the present system in operation a flow parallel to a membrane may each individually be from 0.01-0.20 m/s, such as 0.05-0.10 m/s.

**[0044]** In an exemplary embodiment of the present system in operation a NH<sub>4</sub><sup>+</sup> flux over a membrane may each individually be 0.2-20 mole/m<sup>2</sup>/h, preferably 0.5-5 mole/m<sup>2</sup>/h, such as 1-2 mole/m<sup>2</sup>/h.

**[0045]** In an exemplary embodiment of the present system in operation a HCO<sub>3</sub><sup>-</sup> flux over a membrane may each individually be 0.2-20 mole/m<sup>2</sup>/h, preferably 0.5-5 mole/m<sup>2</sup>/h, such as 1-2 mole/m<sup>2</sup>/h.

**[0046]** In an exemplary embodiment of the present system in operation an operating temperature may be from 10-80 °C.

**[0047]** In an exemplary embodiment of the present system in operation the [NH<sub>4</sub><sup>+</sup>] and [HCO<sub>3</sub><sup>-</sup>] in the second compartment 32 may each individually be 10<sup>-3</sup>-2 mole/l, preferably 10<sup>-2</sup>-1 mole/l, such as 10<sup>-1</sup>-0.5 mole/l.

**[0048]** In an exemplary embodiment of the present system in operation an NH<sub>3</sub> flux and a CO<sub>2</sub> flux in recirculation units 51, 52 may each individually be 50-5000 g/m<sup>2</sup>/h, preferably 70-2500 g/m<sup>2</sup>/h, such as 100-1000 g/m<sup>2</sup>/h.

**[0049]** In an exemplary embodiment of the present system membranes 11a,b, 12 and 13 are separated by spacers 2 and the membranes 11a,b, 12 and electrodes are also separated by spacers.

**[0050]** In an exemplary embodiment of the present method transferring NH<sub>4</sub><sup>+</sup> from the wastewater 70 to an alkaline recirculation solution 51 may be through a first

compartment 31.

**[0051]** In an exemplary embodiment of the present method transferring  $\text{HCO}_3^-$  from the wastewater to an acidic recirculation solution 52 may be through a third compartment 33.

**[0052]** In an exemplary embodiment of the present method  $\text{NH}_4^+$  may be converted into  $\text{NH}_3$  in the presence of  $\text{OH}^-$  in the first compartment 31, and wherein  $\text{HCO}_3^-$  may be converted into  $\text{CO}_2$  in the presence of  $\text{H}^+$  in the third compartment 33.

**[0053]** In an exemplary embodiment of the present method  $\text{NH}_3$  may be stripped in ammonia stripper 61, and wherein  $\text{CO}_2$  may be stripped in  $\text{CO}_2$  stripper 62.

**[0054]** In an exemplary embodiment of the present method at a gaseous side of stripper 61,62 an under pressure may be applied, such as of 0.1-90 kPa, preferably 1.5-75 kPa, such as 5-50 kPa.

**[0055]** In an exemplary embodiment the present method may comprise forming  $\text{NH}_4\text{HCO}_3$ .

**[0056]** In an exemplary embodiment of the present method wastewater may be provided by at least one of a domestic sewage treatment plant, a manure treatment facility, a fertilizer production plant, food and beverage industry, and an industry producing nitrogen loaded wastewater.

**[0057]** In the present method an electrical potential difference over the cathode 42/anode 41 in electrodialysis with bipolar membranes 11a,11b is applied. Therewith decomposition of water is established. The wastewater fed into the second compartment of the at least one exchange unit.  $\text{NH}_4^+$  is transferred from the wastewater 70 to an alkaline recirculation solution 51, and simultaneously,  $\text{HCO}_3^-$  is transferred from the wastewater to an acidic recirculation solution 52, over the respective membranes.  $\text{NH}_4\text{HCO}_3$  is depleted in the wastewater, typically in a continuous or semi-continuous mode. However the present system may also be operated batch wise. Water is split over bipolar membranes 11a,11b thereby providing  $\text{H}^+$  to the third compartment 33 and alkaline recycling compartment 21, respectively, and thereby providing  $\text{OH}^-$  to the first compartment 31 and acidic recycling compartment 22, respectively.

**[0058]** The one or more of the above examples and embodiments may be combined, falling within the scope of the invention.

## EXAMPLES

**[0059]** The below relates to examples, which are not limiting in nature.

**[0060]** In experiments,  $1.6 \cdot 10^{-5}$  kg of  $\text{NH}_4\text{HCO}_3$  was removed from 1 litre synthetic wastewater, equalling 87% of the total  $\text{NH}_4\text{HCO}_3$  initially present. In total,  $3.6 \cdot 10^{-5}$  MJ of electrical energy was used to transfer the ions and generate  $\text{OH}^-$  and  $\text{H}^+$ . This required 2.3 MJ/kg- $\text{NH}_3$  for  $\text{NH}_3$  production in the alkaline solution and 5.9 MJ/kg- $\text{CO}_2$  production in the acidic solution. This includes the pumping energy consumption, accounting for 10% of the

total energy consumption. Also,  $\text{NH}_3$  was stripped from alkaline synthetic solution with various initial  $\text{NH}_3$  concentrations (1.2, 8.5 and 13 g- $\text{NH}_3/\text{L}$ , respectively) at room temperature by vacuum membrane stripping. This resulted in fluxes of 0.10, 0.59 and 0.73 kg/ $\text{m}^2/\text{h}$ , respectively. The permeate content of  $\text{NH}_3$  was 1.2%, 7.9% and 11.5%, respectively. The rest of the permeate was water vapour, making it possible to reuse the  $\text{NH}_3$ .

**[0061]** The invention is further detailed by the accompanying figures, which are exemplary and explanatory of nature and are not limiting the scope of the invention, which is defined by the claims.

## FIGURES

**[0062]** The invention although described in detailed explanatory context may be best understood in conjunction with the accompanying figures.

**[0063]** Fig. 1-5 show schematics of the present system.

## DETAILED DESCRIPTION OF THE FIGURES

**[0064]** In the figures:

25	100	present system
	2	spacer
	11	bipolar membrane
	11a	first bipolar membrane
	11b	second bipolar membrane
30	12	cation exchange membrane
	13	anion exchange membrane
	21	electrode rinse compartment (anodic)
	22	electrode rinse compartment (cathodic)
	30	ion exchange unit
35	31	first alkaline compartment
	32	second salt compartment
	33	third acidic compartment
	41	anode
	42	cathode
40	51	alkaline recirculation unit
	52	acidic recirculation unit
	61	ammonia stripper
	61a	(hydrophobic) membrane
	61b	strip chamber
45	62	gaseous $\text{CO}_2$ stripper
	62a	(hydrophobic) membrane
	62b	strip chamber
	70	wastewater input
	71	treated water output
50	72	tube for removing gaseous ammonia
	73	tube for removing gaseous $\text{CO}_2$
	74a	electrode rinse recirculation unit
	74b	electrode rinse recirculation unit
	81	liquid pump
55	82	vacuum pump

Fig. 1-3 show an exemplary set-ups of the present system.

Fig. 4 shows a stacked variant of the present system.

Fig. 5 shows optional spacers.

**[0065]** The figures have been detailed throughout the description.

**[0066]** Fig. 1 shows a cell triplet provided with cation exchange membranes at the electrodes.

**[0067]** Fig. 2 shows a cell triplet provided with anion exchange membranes at the electrodes.

**[0068]** Fig. 3 shows a cell triplet provided with bipolar membranes at the electrodes.

**[0069]** Fig. 4 represents a plural version of fig. 1.

**[0070]** Fig. 5 shows that all membranes (11,12 and 13) are separated by spacers 2. The spacers are made of polyethylene/silicone material and woven into a mesh. The liquids flow through the void fraction of the spacers, forming the salt, acid and alkaline chambers. The spacers are sealed on the top and bottom, making sure that the liquids are not leaking out of the membrane stack. The electrodes (anode and cathode) and the membranes next to the electrodes are also separated by spacers, forming the electrode rinse chambers.

## Claims

1. Wastewater gas recovery system (100) for recovering  $\text{NH}_3$  and  $\text{CO}_2$  comprising

at least one ion exchange unit (30), each exchange unit comprising at least three ion exchange compartments (31,32,33), each ion exchange compartment being in contact over a membrane with at least one adjacent compartment,

a first alkaline ion exchange compartment (31) being in fluidic contact with a positive side of first bipolar membrane (11a) and with a cation exchange membrane (12) and comprising aqueous  $\text{NH}_4^+$  and  $\text{OH}^-$ ,  
 a second ion exchange compartment (32) being in fluidic contact with an anion exchange membrane (13) and with a cation exchange membrane (12) and comprising water,  $\text{NH}_4^+$ , and  $\text{HCO}_3^-$ , and  
 a third acidic ion exchange compartment (33) being in fluidic contact with a negative side of a bipolar membrane (11a) and with an anion exchange membrane (13) and comprising aqueous  $\text{H}^+$  and  $\text{HCO}_3^-$ ,

a wastewater input (70) for providing wastewater to the second compartment,  
 a treated water output (71) adapted to receive output from the second compartment,  
 a cathode (42) and an anode (41) for providing a voltage, at least two electrode rinse compart-

ments (21,22) being in electrical contact with the cathode (42) or with the anode (41) and with a membrane (11a,11b,12,13), and comprising salt,

at least three recirculation units (51,52,74a,74b), including a first alkaline recirculation unit (51) adapted to receive input from the first alkaline compartment (31), comprising a pump (81), a gaseous ammonia stripper (61), and for providing stripped output to the first alkaline compartment (31), a second acidic recirculation unit (52) adapted to receive input from the third acidic compartment (33), comprising a pump (81), a gaseous  $\text{CO}_2$  stripper (62), and for providing stripped output to the third acidic compartment (33), and a third recirculation unit (74a,74b) adapted to receive input from a first electrode rinse compartment (21), in electrical contact with the anode (41), and for providing output to a second electrode rinse compartment (22), in electrical contact with the cathode (42), and vice versa, wherein at least one of the gaseous

ammonia stripper (61) and of the gaseous  $\text{CO}_2$  stripper comprises a hydrophobic membrane (61a,62a), a molecular sieve for ammonia or for  $\text{CO}_2$ , respectively a pervaporation membrane, or a combination thereof, and  
 a tube (72) for removing gaseous ammonia, and a tube (73) for removing gaseous  $\text{CO}_2$ .

2. System according to claim 1, wherein at least one membrane (61a,62a) in the stripper is impermeable to liquids, and permeable to gases.
3. System according to any of claims 1-2, wherein the hydrophobic membrane (61a,62a) is macroporous, with an average pore size of 50-500 nm, or microporous, with an average pore size of 0.4-10 nm (as determined by electron microscopy).
4. System according to any of claims 1-3, wherein the membrane (61a,62a) is selected from polymeric material, inorganic material, and combinations thereof.
5. System according to any of claims 1-4, wherein the exchange unit (30) comprises a stack of a cation exchange membrane (12), an alkaline ion exchange compartment (31), a bipolar membrane (11a), an acidic ion exchange compartment (33), an anion exchange membrane (13), and a wastewater ion exchange compartment (32), and wherein the second electrode rinse compartment (22) is in fluidic contact with a further cation exchange membrane (12), or wherein the exchange unit (30) comprises a

- stack of an anion exchange membrane (13), an acidic ion exchange compartment (33), a bipolar membrane (11a), an alkaline ion exchange compartment (31), a cation exchange membrane (12), and a wastewater ion exchange compartment (32), and wherein the first electrode rinse compartment (21) is in fluidic contact with a further anion exchange membrane (13), or wherein the exchange unit (30) comprises a stack of a bipolar membrane (11a), an alkaline ion exchange compartment (31), a cation exchange membrane (12), a wastewater ion exchange compartment (32), an anion exchange membrane (13), and an acidic ion exchange compartment (33), and wherein the first electrode rinse compartment (21) is in fluidic contact with a further bipolar membrane (11b).
6. System according to any of claims 1-5, comprising 2 - 1024 ion exchange units (30) in parallel.
7. System according to any of claims 1-6, wherein membranes (11a, 11b, 12 and 13) are separated by spacers (2) and the membranes (11a, 11b, 12) and electrodes are separated by spacers (2).
8. System according to any of claims 1-7, wherein in operation at least one of a voltage of 0.1-5 V per ion exchange unit (30) is applied,
- a pH in the first alkaline ion exchange compartment (31) is from 7-14,  
a pH in the third acidic ion exchange compartment (33) is from 1-7,  
a current density is from 5-500 A/m<sup>2</sup>,  
a flow parallel to a membrane is each individually from 0.01-0.20 m/s,  
a NH<sub>4</sub><sup>+</sup> flux over a membrane is each individually 0.2-20 mole/m<sup>2</sup>/h,  
a HCO<sub>3</sub><sup>-</sup> flux over a membrane is each individually 0.2-20 mole/m<sup>2</sup>/h,  
an operating temperature is from 10-80 °C,  
the [NH<sub>4</sub><sup>+</sup>] and [HCO<sub>3</sub><sup>-</sup>] in the second ion exchange compartment (32) is each individually 10<sup>-3</sup> - 2 mole/l,  
a vacuum of 0.1-90 kPa is each individually applied over membranes (61,62),  
a flux of wastewater and recirculation is each individually 0.01-10 kg/m<sup>2</sup>/h, and  
an NH<sub>3</sub> flux and a CO<sub>2</sub> flux in recirculation units (51,52) is each individually 50-5000 g/m<sup>2</sup>/h.
9. Method for treating wastewater comprising providing a system (100) according to any of claims 1-8, applying an electrical potential difference over the anode (41)/cathode (42), providing wastewater in second ion exchange compartment (32) comprising NH<sub>4</sub><sup>+</sup>, and
- HCO<sub>3</sub><sup>-</sup>,  
transferring NH<sub>4</sub><sup>+</sup> from the wastewater (70) to an alkaline recirculation solution (51),  
simultaneously, transferring HCO<sub>3</sub><sup>-</sup> from the wastewater to an acidic recirculation solution (52),  
depleting NH<sub>4</sub>HCO<sub>3</sub> in the wastewater, and  
splitting water over bipolar membranes (11a, 11b) thereby providing H<sup>+</sup> to the third acidic ion exchange compartment (33) and thereby providing OH<sup>-</sup> to the first alkaline ion exchange compartment (31),  
wherein transferring NH<sub>4</sub><sup>+</sup> from the wastewater (70) to an alkaline recirculation solution (51) is through a first alkaline ion exchange compartment (31),  
wherein transferring HCO<sub>3</sub><sup>-</sup> from the wastewater to an acidic recirculation solution (52) is through a third acidic ion exchange compartment (33),  
wherein NH<sub>4</sub><sup>+</sup> is converted into NH<sub>3</sub> in the presence of OH<sup>-</sup> in the first alkaline compartment (31), and wherein HCO<sub>3</sub><sup>-</sup> is converted into CO<sub>2</sub> in the presence of H<sup>+</sup> in the third acidic ion exchange compartment (33),  
wherein NH<sub>3</sub> is stripped in ammonia stripper (61), and wherein CO<sub>2</sub> is stripped in CO<sub>2</sub> stripper (62).
10. Method according to any of claims 9, wherein at a gaseous side of stripper (61,62) an under pressure is applied.
11. Method according to any of claims 9-10, further comprising forming NH<sub>4</sub>HCO<sub>3</sub>.
12. Method according to any of claims 9-11, wherein wastewater is provided by at least one of a domestic sewage treatment plant, a manure treatment facility, a fertilizer production plant, food and beverage industry, and an industry producing nitrogen loaded wastewater.
13. Method according to claim 12, wherein wastewater is provided by a manure treatment facility.
14. Method according to any one of claims 9-13, wherein the NH<sub>3</sub> as stripped in ammonia stripper (61) is used as fuel for a solid oxide fuel cell to recover electrical energy.
15. Method according to claim 14, wherein the recovered electricity is used in the method for treating wastewater.

Fig. 1

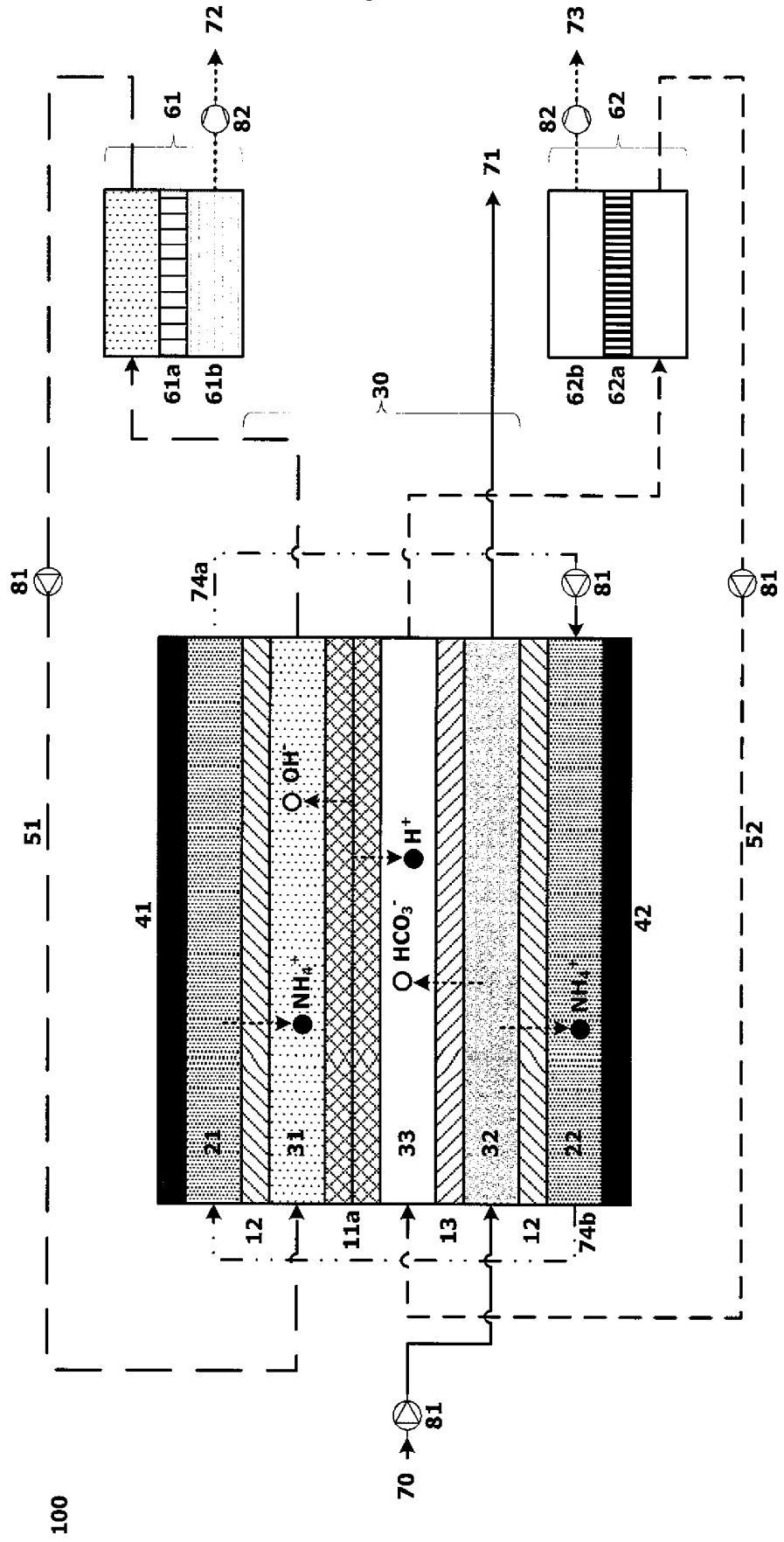




Fig. 2

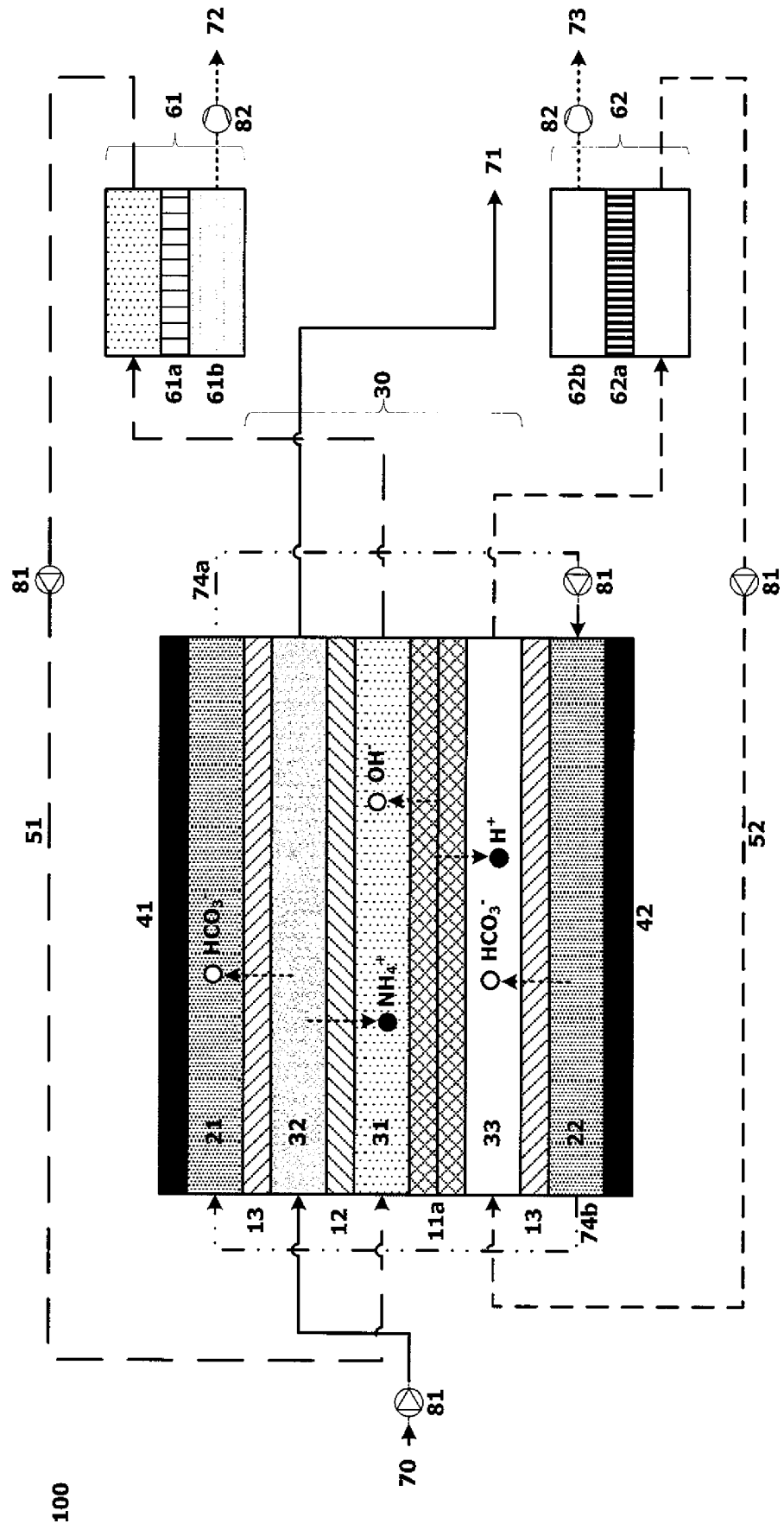
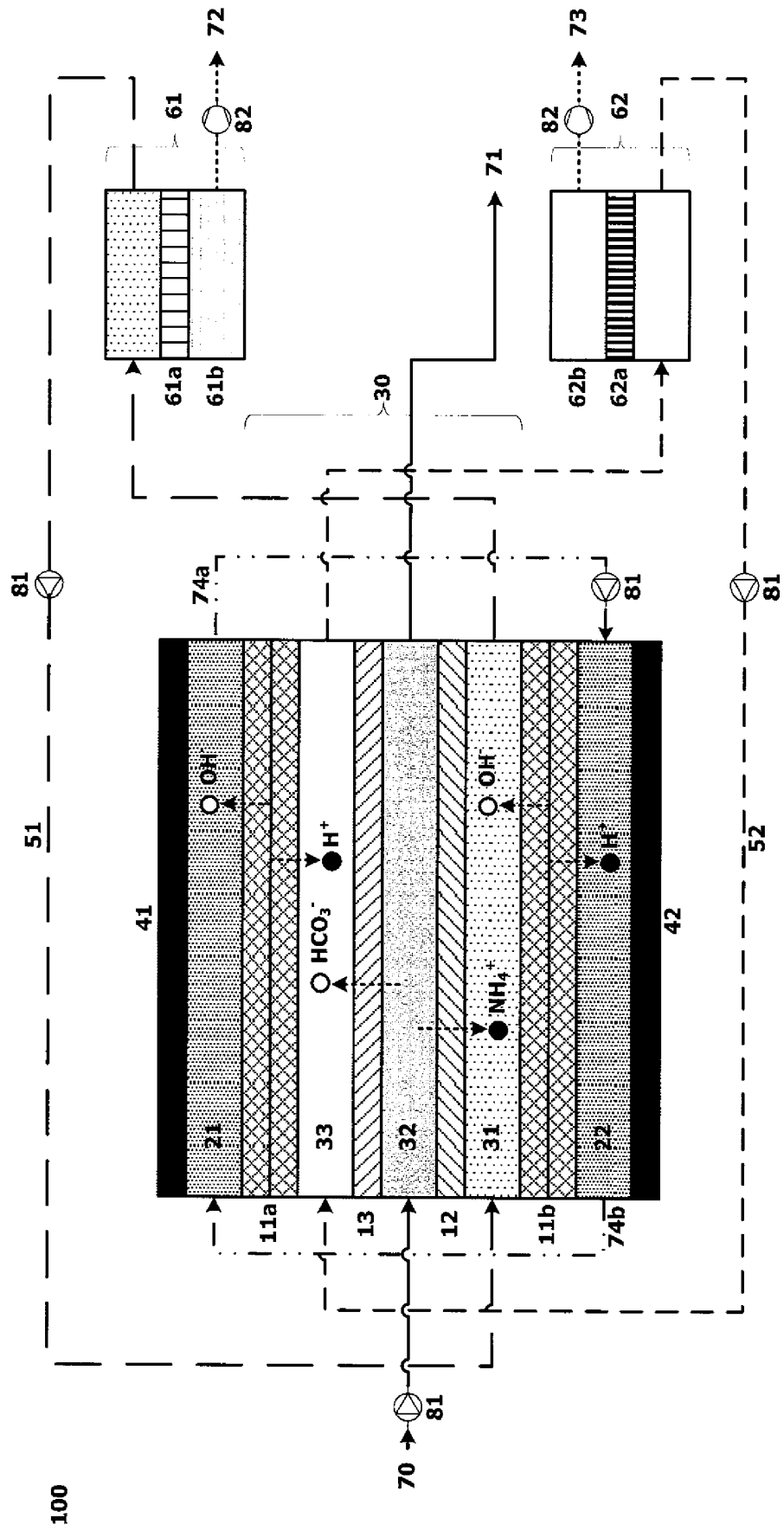


Fig. 3



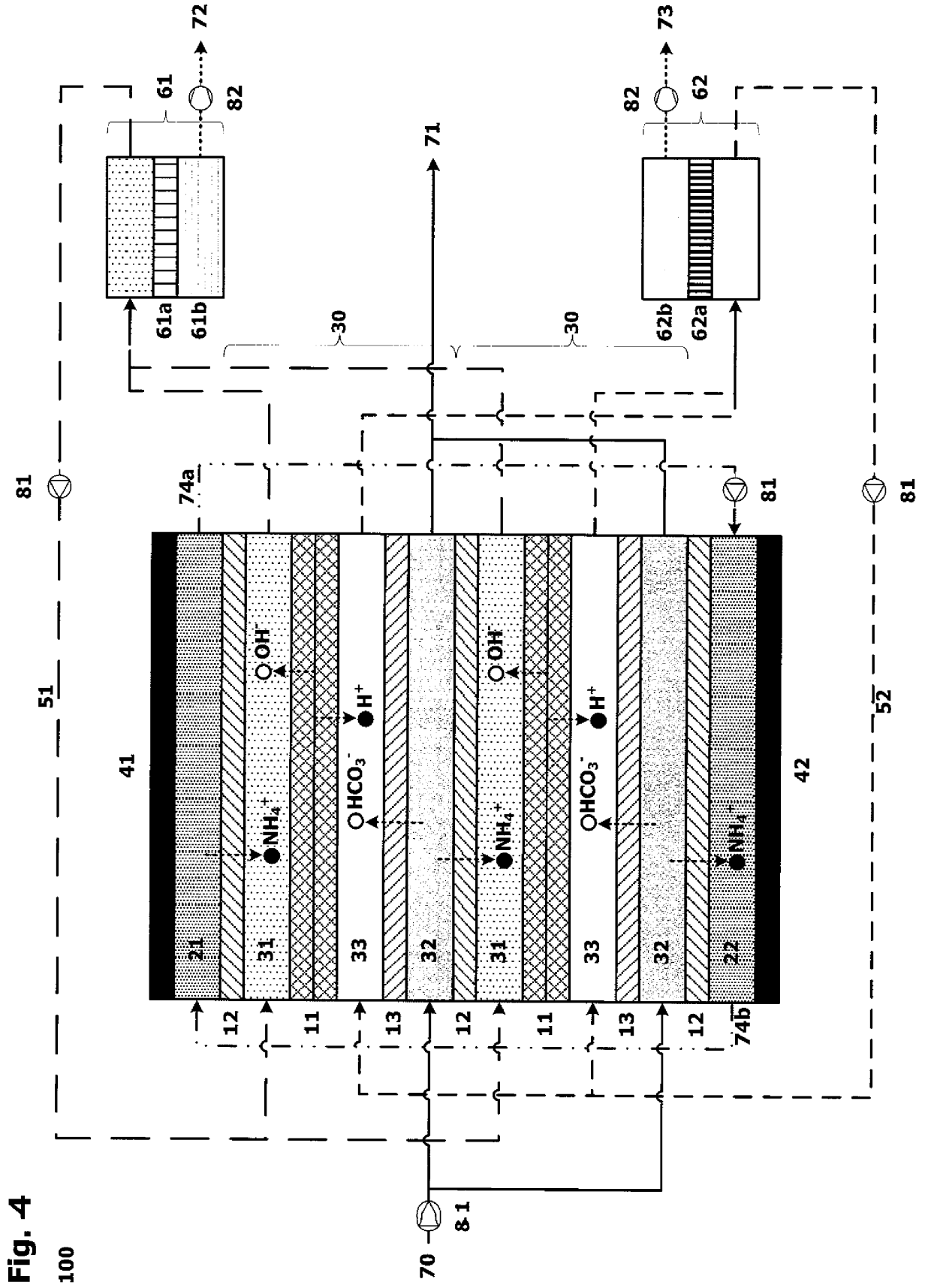


Fig. 4

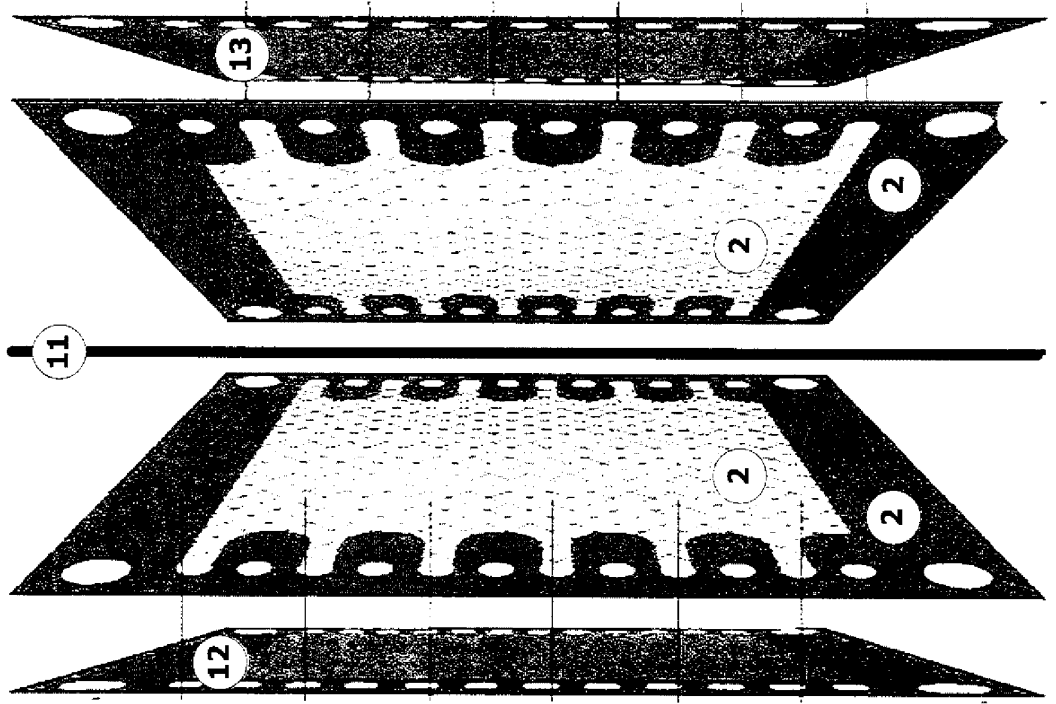


Fig. 5

**REFERENCES CITED IN THE DESCRIPTION**

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**Patent documents cited in the description**

- US 2016271562 A1 [0010]
- US 4969983 A [0011]

**Non-patent literature cited in the description**

- **PRONK et al.** Treatment of source-separated urine by a combination of bipolar electro dialysis and a gas transfer membrane. *Water Science Technology*, 2006, vol. 53 (3), 139-146 [0012]
- Experimental study on desorption of simulated solution after ammonia carbon capture using bipolar membrane electro dialysis. **SHUANGCHEN et al.** *Int. J. Greenhouse Gas Control*. Elsevier, 03 November 2015, vol. 42, 690-698 [0013]
- **ALI et al.** *J. Membrane Science*. Elsevier, 15 November 2004, vol. 244, 89-96 [0014]