AEE INTEC

Ammonia recovery from liquid waste streams by means of Vacuum-Membrane Distillation and its use as an energy vector

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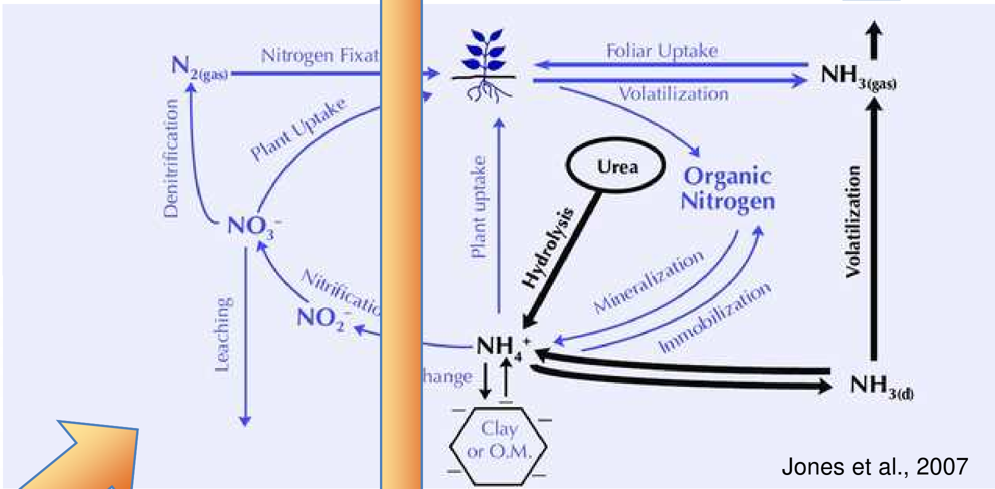
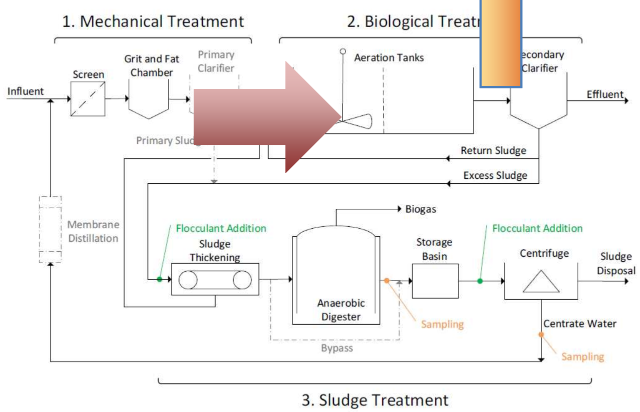
„Industrial“ Ammonia Cycle

178 Mt/a NH3
Haber Bosch = 1-2% of world final energy demand; 1,44% of CO2 emissions
energy losses:
50%

75-90% of NH3 used for fertilizer production (e.g. urea, ammonia-sulfate solutions)
50% of world‘s food production relies on fertilizing



60-80% of ferti er-NH3 is lost to atmosphere
Eutrophication oblems
Climate chang mpact
over depositior xation 60% of this NH3 ends up in water (oc n)



11 Mt/a in livestockwaste /digestate
2-5 Mt/a in selected ind. waste streams

→ Currently treated in WWTP; 16,4 Mt WWTP sludge

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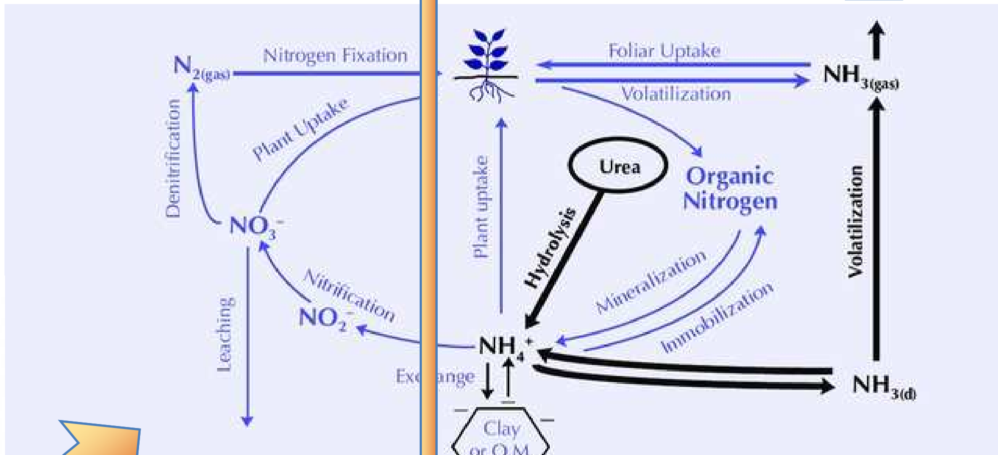
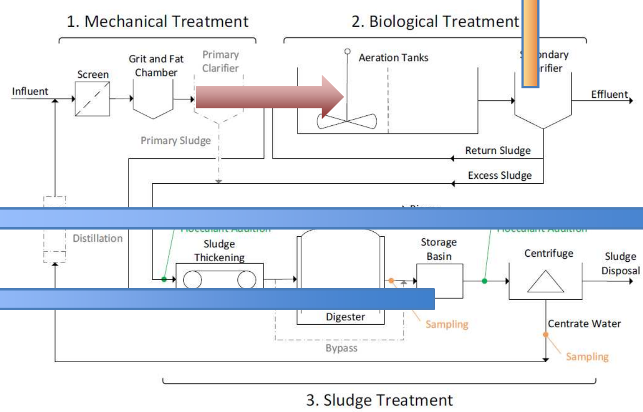


Jones et al., 2007

60-80% of fertilizer-NH3 is lost to atmosphere
Eutrophication problems
Climate change impact
over deposition/fixation 60% of this NH3 ends up in water (ocean)



11 Mt/a in livestockwaste /digestate
2-5 Mt/a in selected ind. waste streams

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NH_3 Problematic vs. Oportunity

Problematic

NH_3 is produced through the energy-intensive, CO_2 emitting HB process

Increasing food demand → excessive production of agricultural, animal and industrial NH_3-rich waste streams

NH_3 has **a high solubility in water** and chemical reactivity

Cause of surface water eutrophication, NO_x emission, acid rain, etc.

To reduce TAN to N_2 via **N/DN (energy intensive) in WWTP** → CO_2 and NO_x emissions

N-pollution costs the EU **between €25 and €115 billion/y** + health and climate change impacts up **to €320 billion/y**

Increasingly stringent legislation for ammonia disposal (Austria < 0,5 mg/l)

Oportunity

NH_3 is a valuable chemical

EU is highly dependent on external fertilizer imports; more than **6 Mt/y of N-based fertilizers + NH_3** are imported from third countries

Only in the EU, between **2 and 5 Mt of N** per year are not being recovered from agriculture, sewage and food chain waste streams.

These quantities represent **18 - 46% of the 11 Mt** of the mineral-N currently applied.

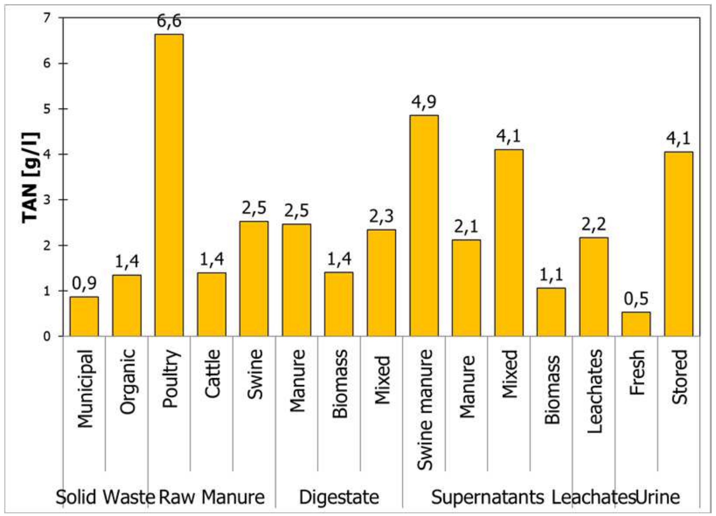
The potentially recovered **NH_3** from these waste streams can be used to produce any of the N-fertilizers in both liquid and solid form

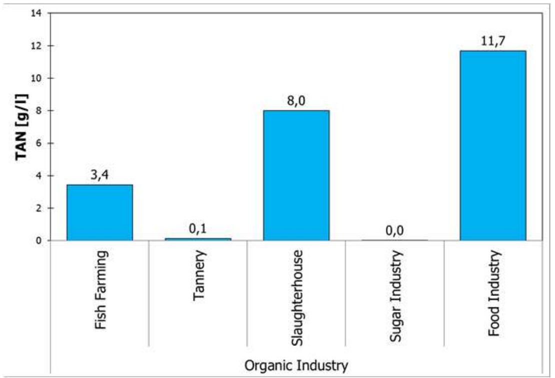
Ammonia recovery from waste streams can **potentially shortcut the anthropogenic N-cycle** in a circular economy scenario

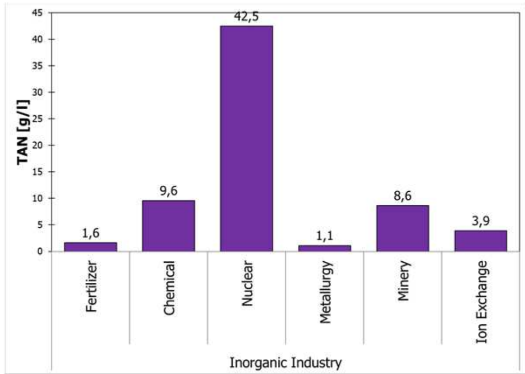
Ammonia in liquid waste streams

Ammonia pollution

- Is partly unavoidable
- Is largely available in high volumes and low concentrations
- Induces environmental costs







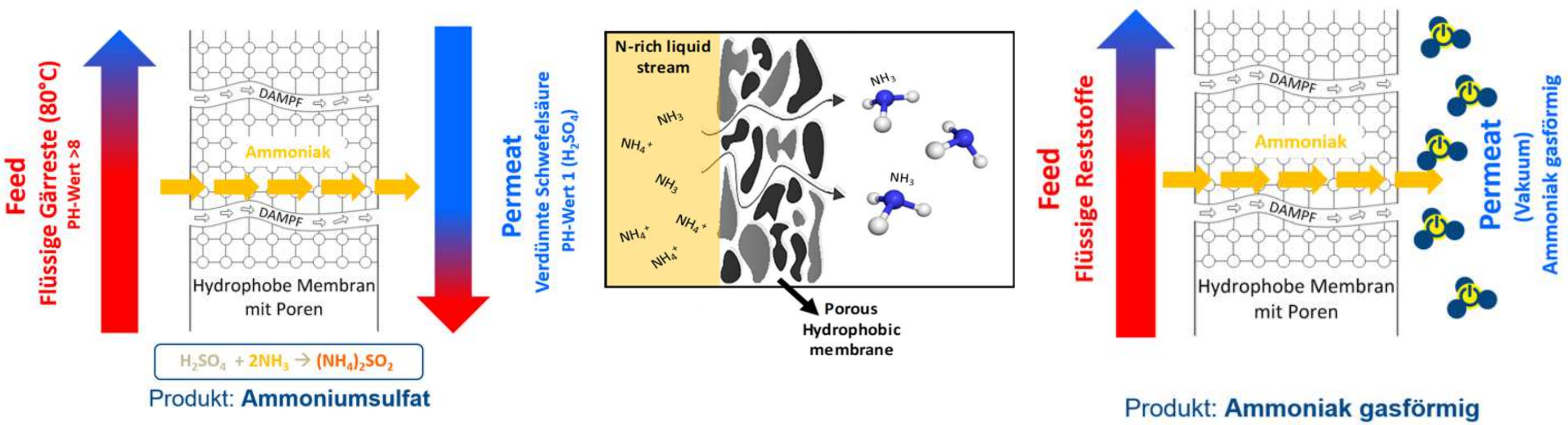
Deng et al, 2021

Ammonia application

Application	Form of NH_3	Concentration	Challenges in the application
Fertiliser	$NH4^+$ (aq.) or $NH4^+$ (s) (AS, AN, Struvite)	**min. of 2 w% N liquid organic, EU regulation >21 % in solid form**	• Pollutants and end product performance (?) • Use in crops is limited regulated by the European nitrates' directive (91/676/EC) • Urea is still the most precious fertilizer
CO_2 and H_2S capture	NH_3 (aq.)	**Absorption columns 5 - 15 w %**	Market dominated by amines Necessity to cool down (10 C)
Chemical industry	NH_3 (aq.)	**Min. 28 w %**	**High purity needed**
Pre-treatment processes (bio industries)	NH_3 (aq.)	~ **0.7 %**	Small market
NOx abatement (flue gas)	NH_3 (aq.) AS (aq.)	**(32,5 w %) (20 w %)**	High purity needed. Big market. **Water ammonia is preferred**
Energy Generation (SOFC)	NH_3 (g)	**>17% Theoretical >50% Practical**	Impurities fuel cell catalizers (S) → H_2S is common in bio waste streams Low heat capacity of NH_3 → you need a lot of NH_3!!!

Separation principle of NH3 via Membrane Distillation

DCMD | **VMD**



Only ammonia in **free form (NH_3)** passes the membrane → **pH > 8 + temperature**

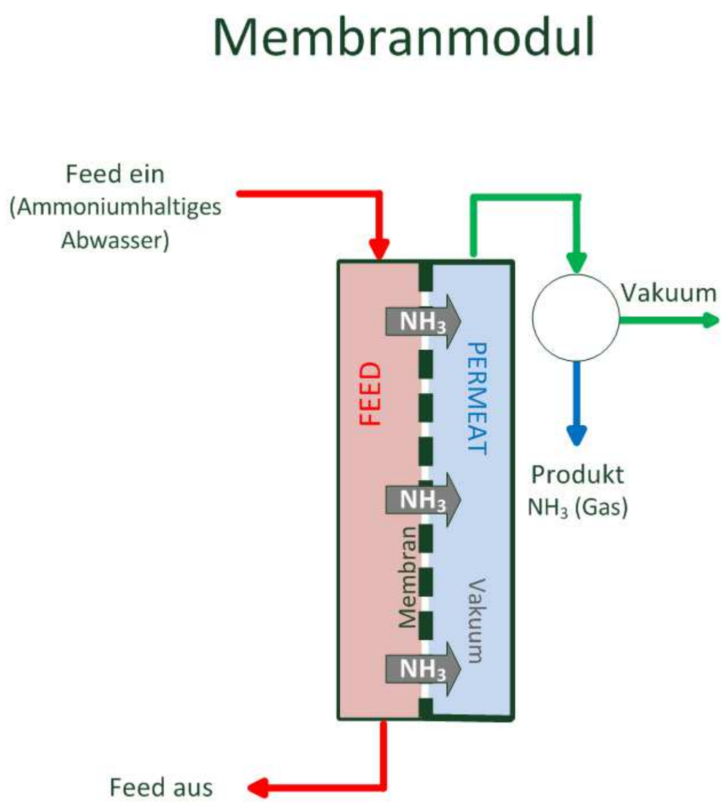
- Ammonia is condensed/reacted in a liquid solution
  - **Water → ammonia water** (other uses)
  - **Acid →** AS, AN, Urea, etc. (**fertilizer**)

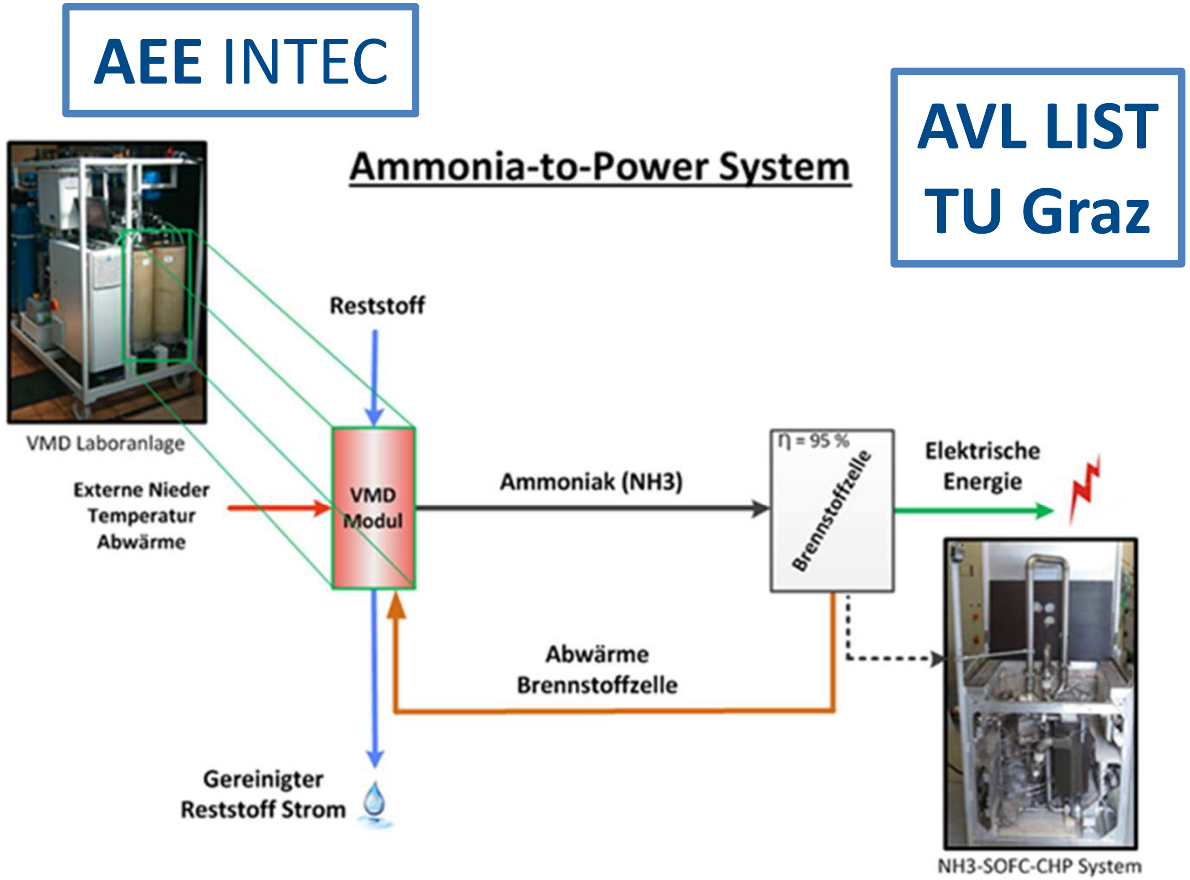
- Vacuum in permeate side
- Ammonia is collected in **gaseous form** (‚wet‘) → **fuel**

The „Ammonia-to-Power“ - Concept

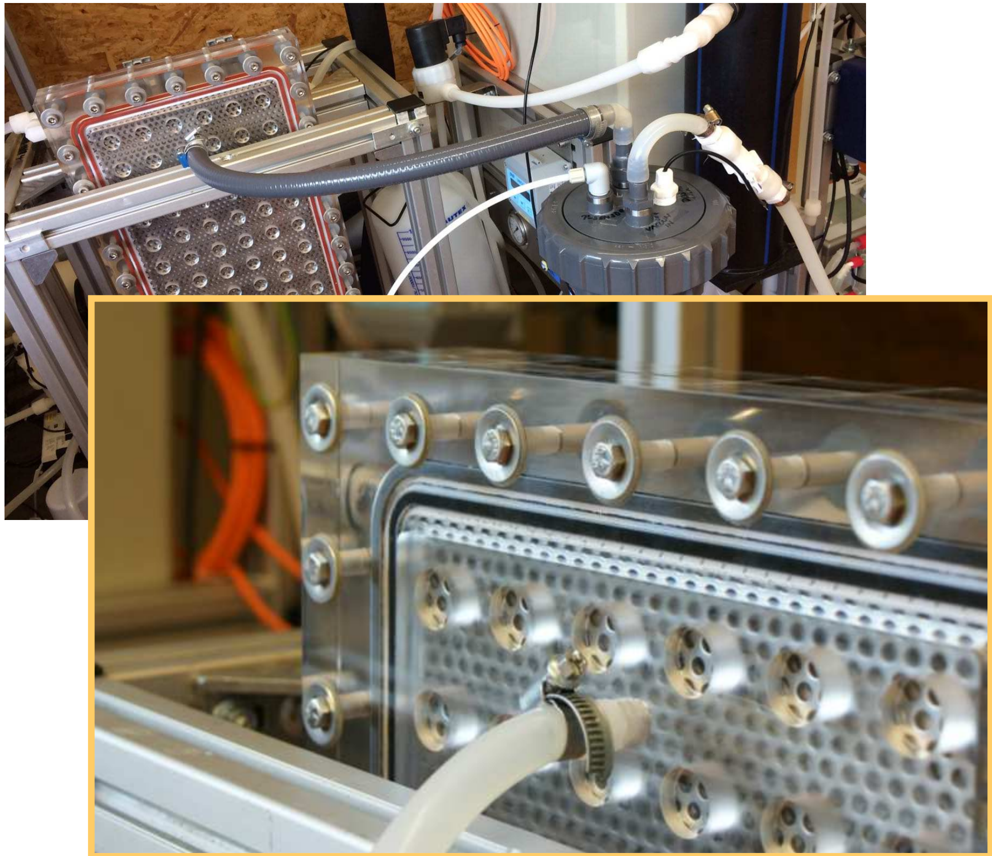
NH3 in gaseous form via MD for use in SOFC

„low temperature heat pump“ → re-valorize N-NH4 water pollution as NH3 energy vector to produce high temperature



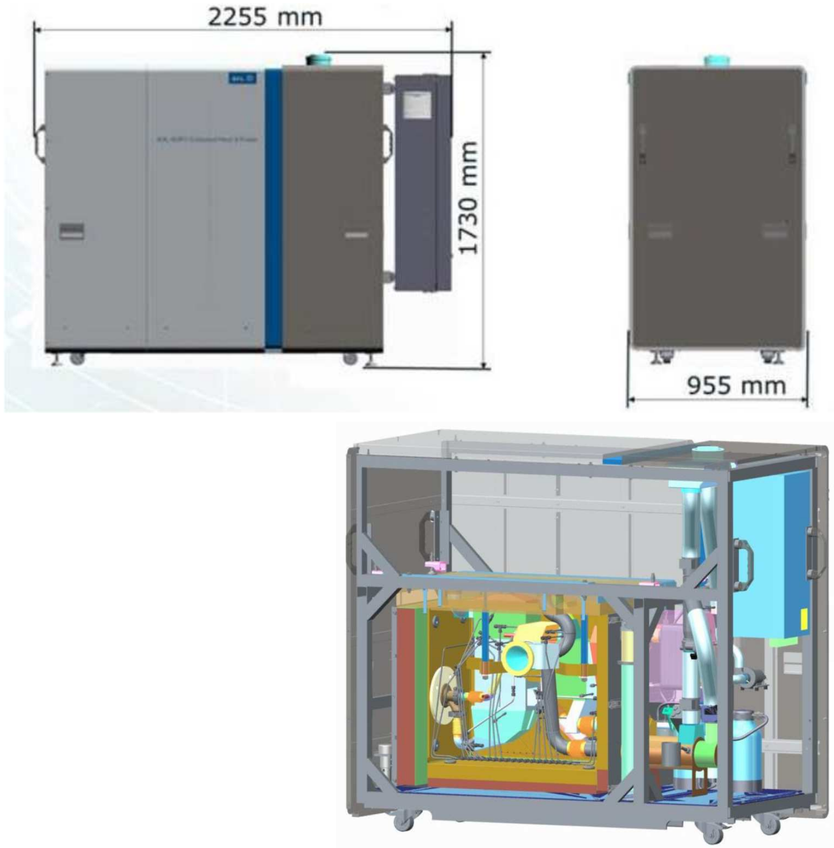


Project activities



Quelle: AEE INTEC

Lab experiments with VMD test cell



Quelle: AVL LIST AG

Ammonia SOFC Fuel Cell Stack Tests

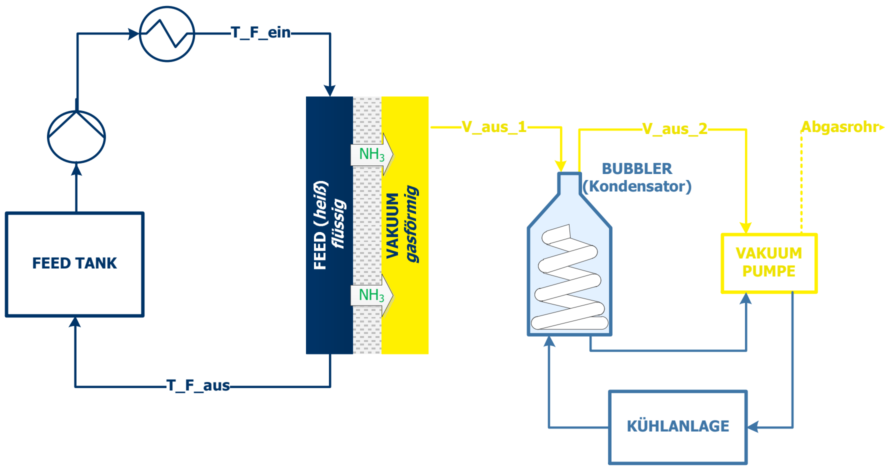
5kW units

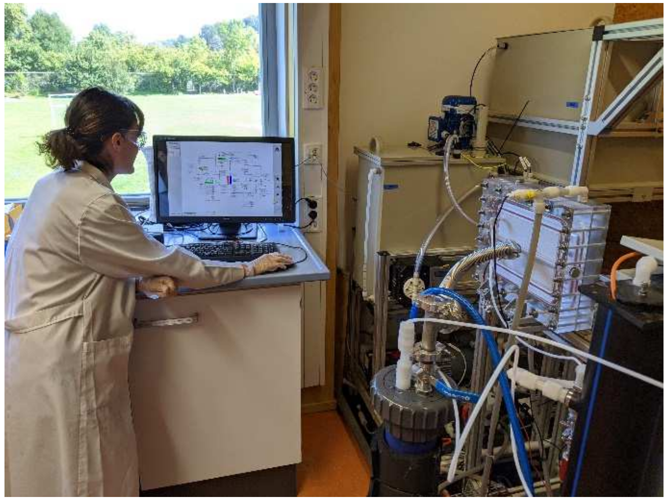
Experiments

Various samples tested:

- Centrate Water from WWTP (< 1g/l)
- Digestate (Slaughterhouse Biogas Plant) (5-7 g/l)
- Urine (motorway services) (< 10 g/l)

- Temperature 40-60°C
- Varying permeate pressure
- Varying feed flow ….



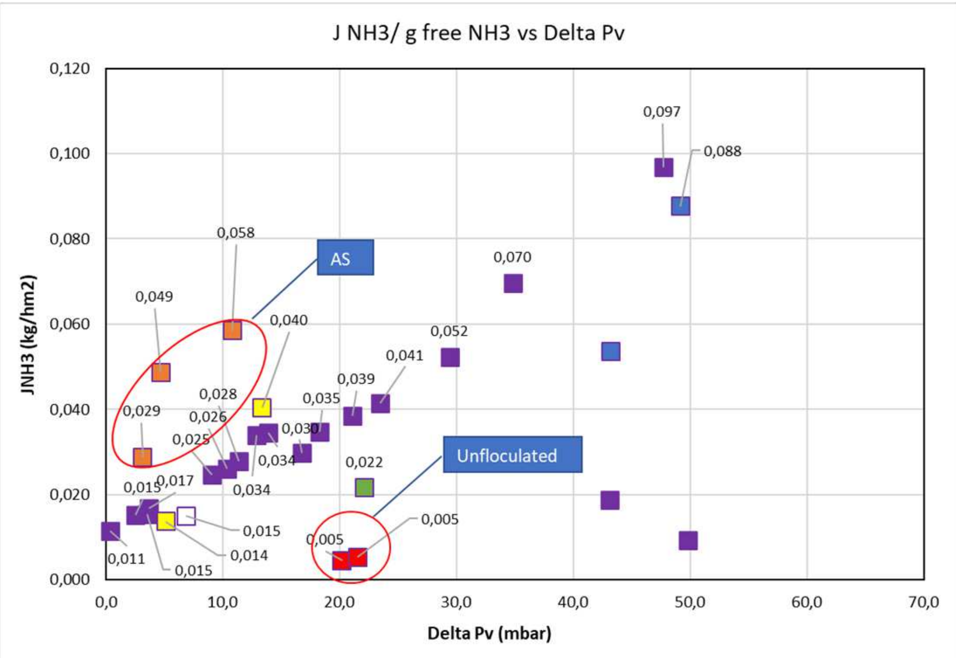


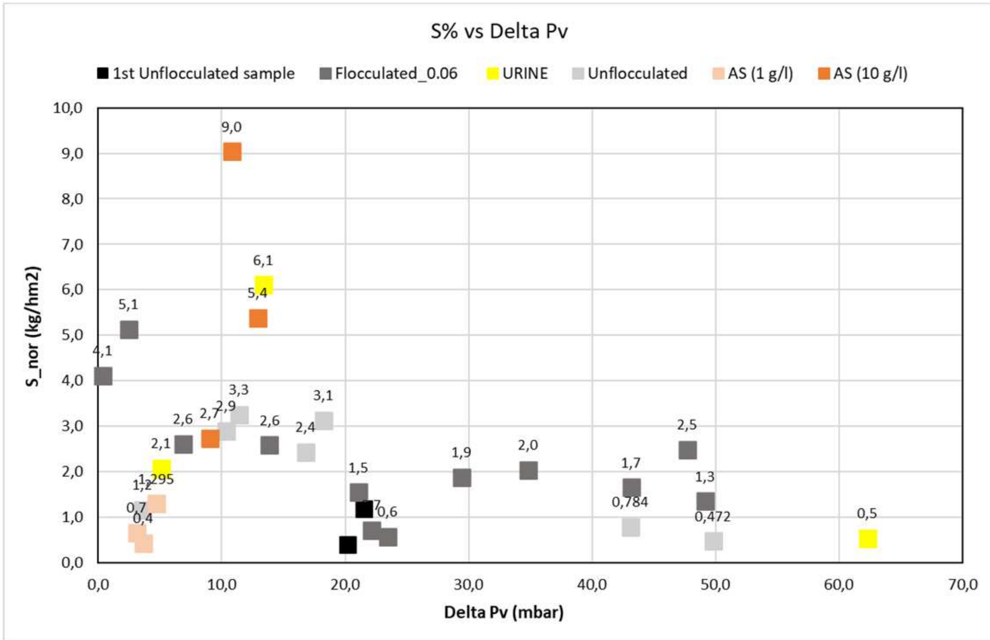
Experimental Results

Main Conlusions:

- Pre-treatment required for digestate samples
- **High concentrations** give best results
- Low vapor pressure differences increase **S** but at the cost of the **Ammonia flux**
- Big trade-off between **Selectivity** and **Ammonia flux**
- **Concentration < 10% NH3 in NH3/H2O**

$$S_{NH3}(\%) = \frac{J_{NH3}}{J_{tot}}$$

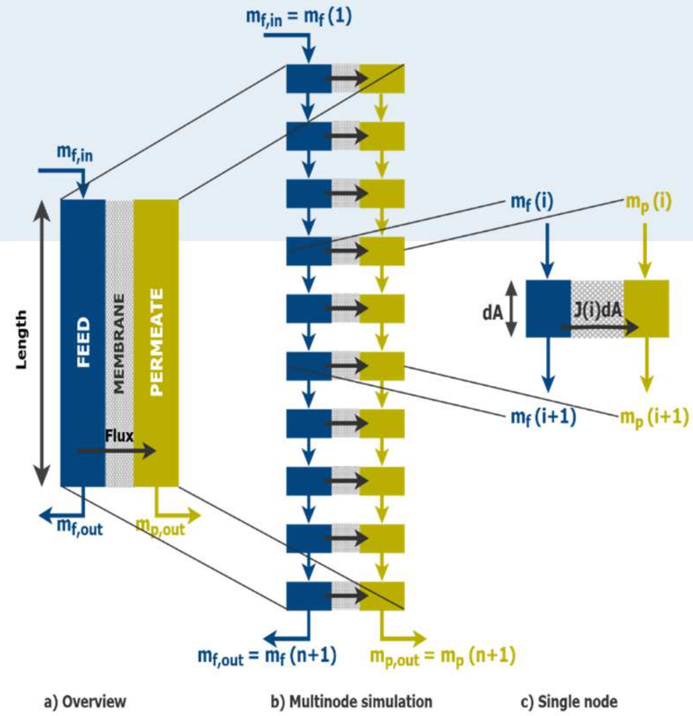


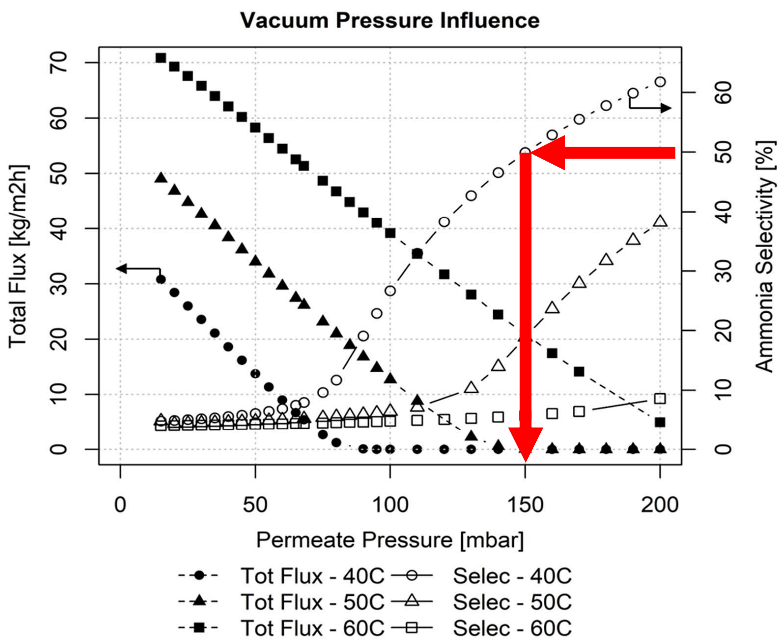


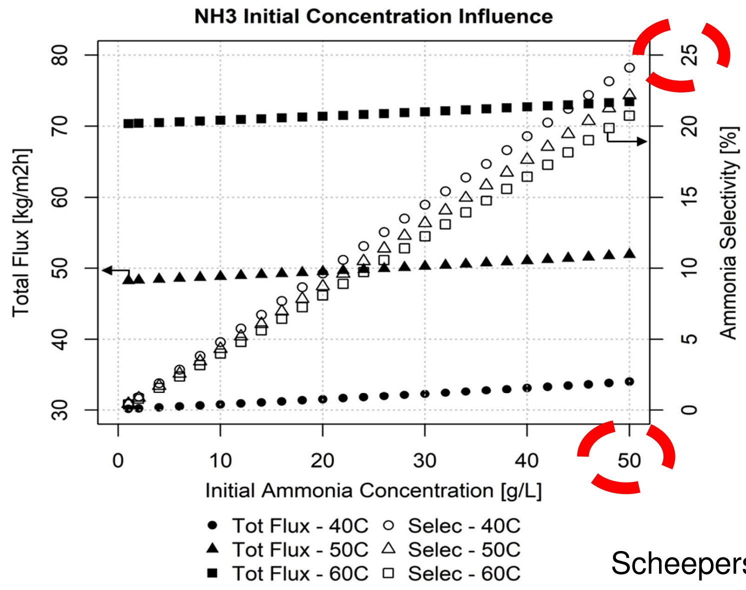
Modelling results

Numerical model validated
→ Good insights towards higher NH3 concentration in gas phase

→ We need to **decouple water and NH3 driving force**







Scheepers et al, 2020

Driving force – vapour pressure difference

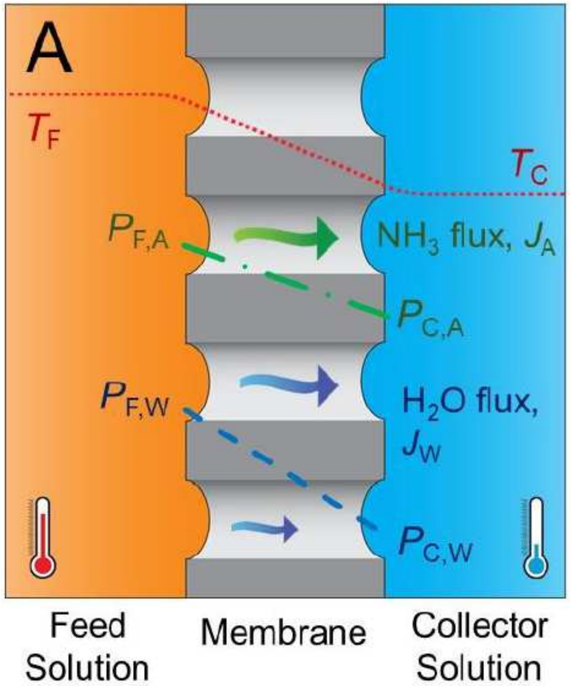
Membrane resistance

FLUX $J_i = L_i (P_{F,i} - P_{C,i})$ DRIVING FORCE

$P_{F,i}$

Vapour pressure FEED

- T_F
- Activity coefficient i (**Concentration i**)
- *pH (ammonia)
- *Henry constant



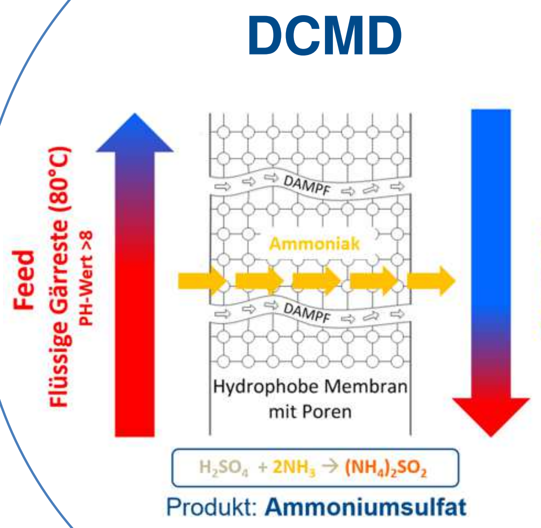
$P_{C,i}$

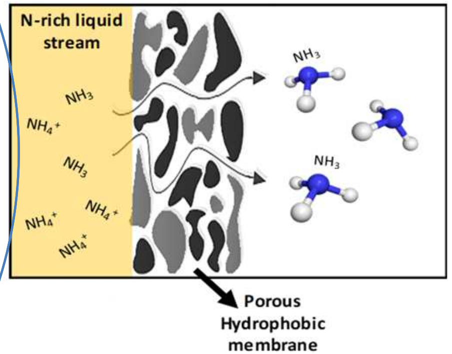
Vapour pressure PERMEATE

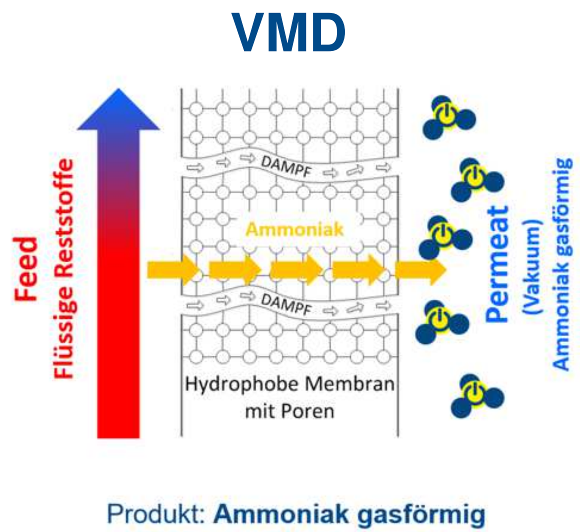
- T_C / Pressure $_C$
- Activity coefficient i (**Concentration i**)
- *pH (ammonia)
- *Henry constant

Picture: McCartney S. et al. 2020 ACS Sustainable Chem. Eng

Separation principle of NH3 via Membrane Distillation







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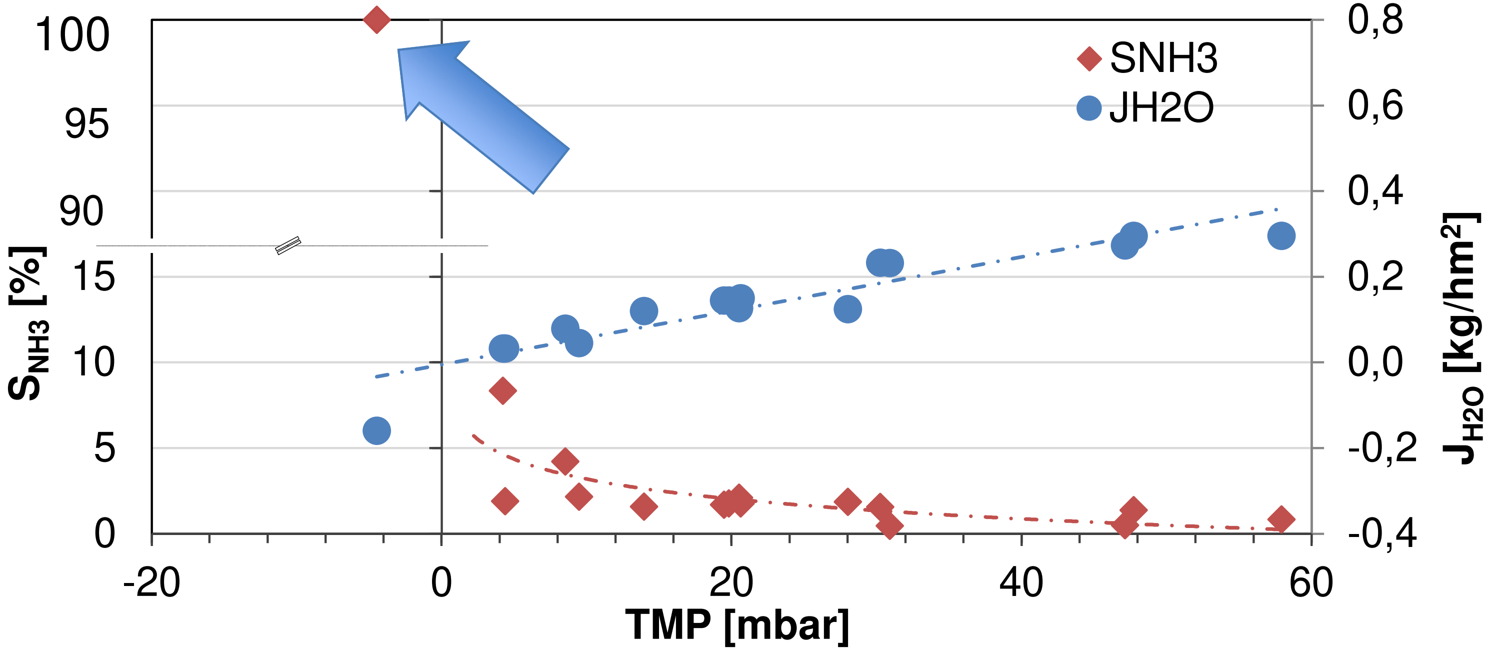
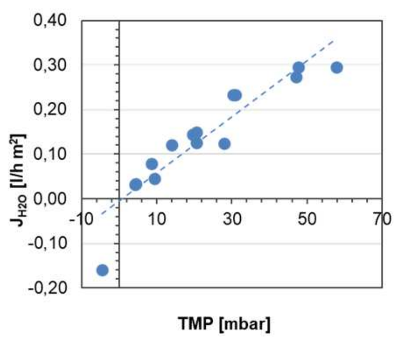
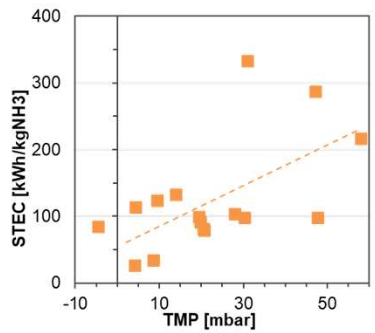
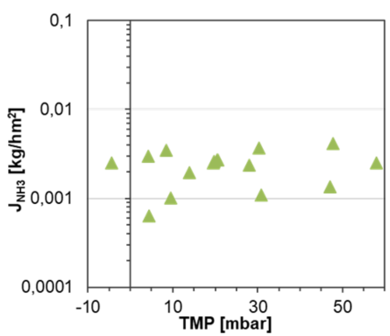
Decoupling of driving forces – achieved in DCMD for AS production

Isothermal operation of MD in DCMD operation leads to pure NH3 flux









Isothermal operation in demo-scale

Pilot plant

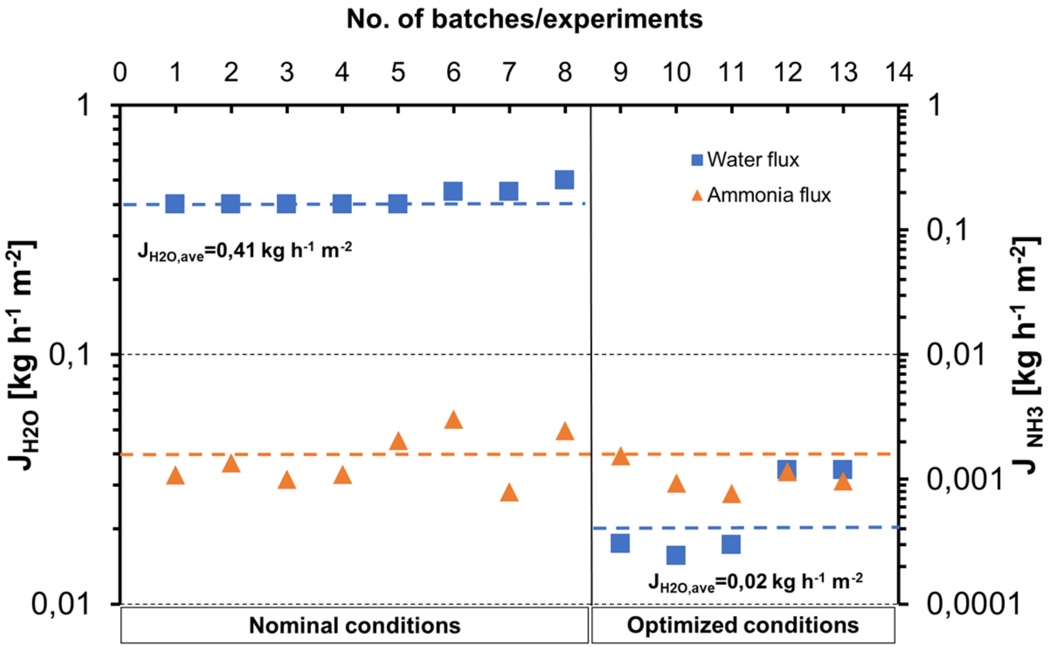
- **14 m²**
- Semi-batch operation (100 l)
- Total treated: ~ **1,5 m³**

Performance values

- **Removal of ammonia > 95%**
- **Recovery of ammonia > 90%**
- **Ammonia in effluent: 4-2 mg/l**

Optimized conditions (T operation < 40°C):

- **Selectivity** from 0,3% to **6-8%**
- **Permeate ~ 10 g/l AS (1% w)**
- **STEC ~15 kWh$_{th}$/kg-N**
- * HB (**19-9** kWh$_{th}$/kg-N)
- * N/DN (**2-6** kWh$_{th}$/kg-N)



	Selectivity [%]	Removal [%]	Recovery [%]	Losses [%]	[AS] / batch [g/l]
Nominal	0,45%	97%	94%	3%	1,04
Improved	8,38%	96%	92%	4%	1,98

Pilot operation 24/7

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Pilot plant

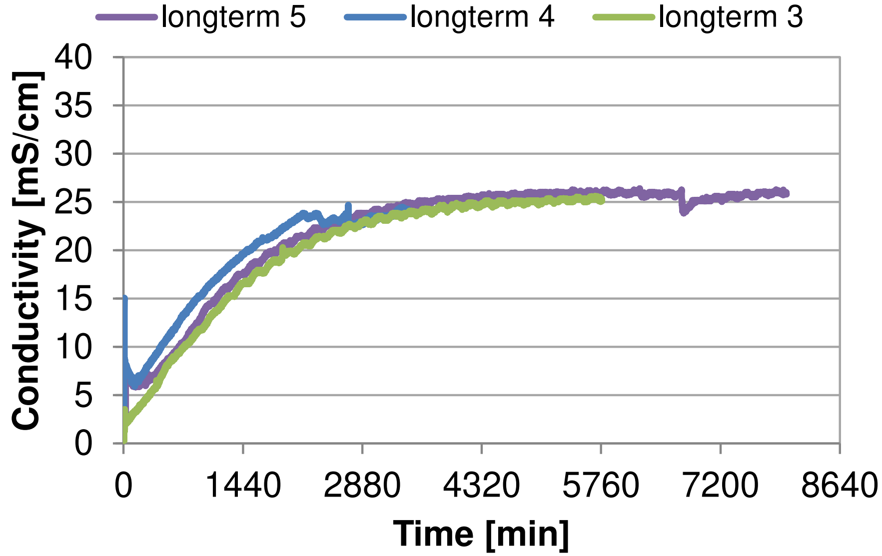
- **14 m²** and capacity of **1 m³/day**
- Semi-batch operation (100 l, 3h)
- Lower pH ~**8,7 (-70% NaOH needs)**
- 24/7

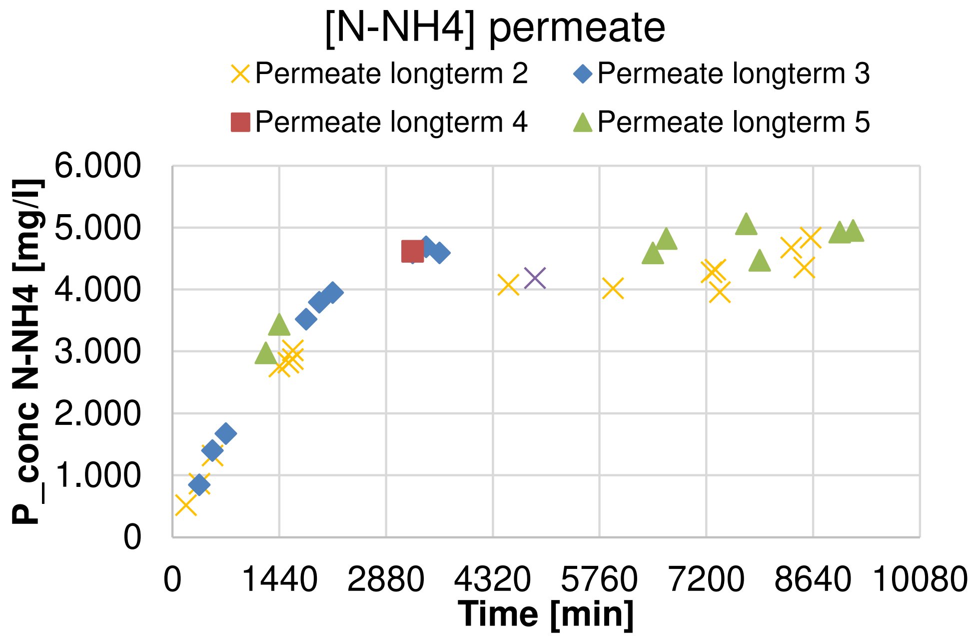
Performance values

- Very stable and reproducible results for days
- Stops, re-starts had no effect on overall performance
- Acid clean (citric) restore pressure in channels
- **Removal of ammonia > 95%**
- **Limited NH_4 concentration ~ 6,4 g/l**

KEY CONCLUSION:

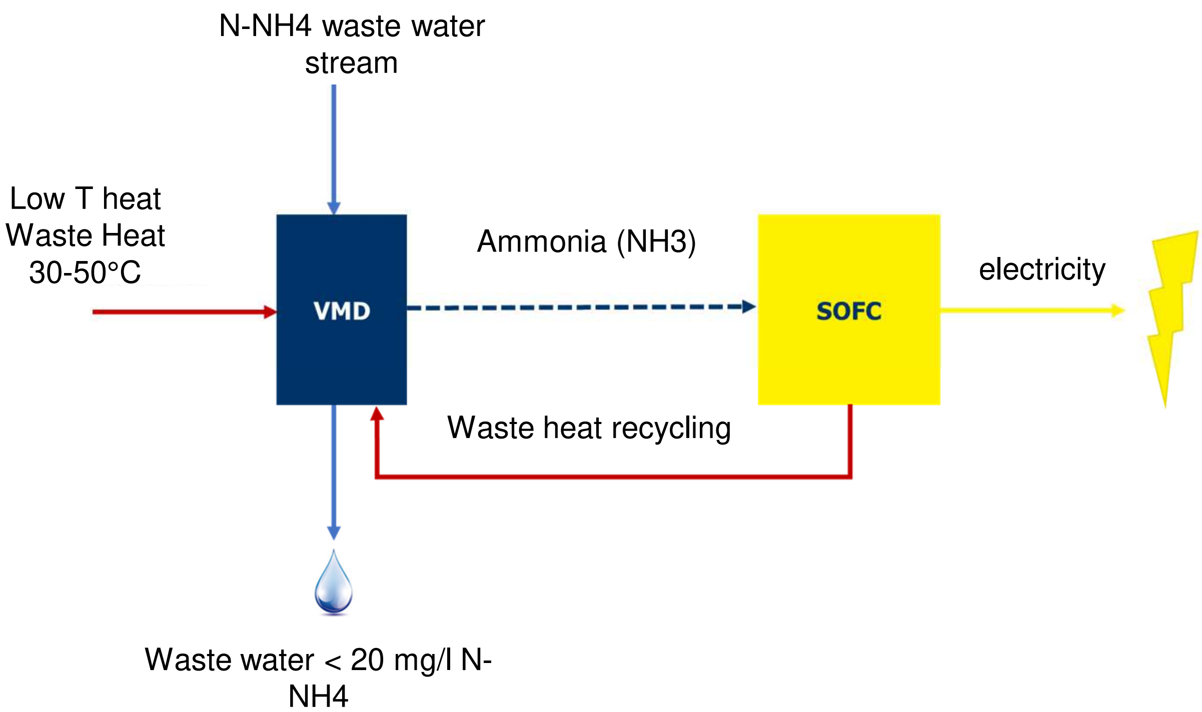
- **Membranes with low H2O transfer coefficient**
- **Appropriate module design**
- **→ transfer results to V-MD "AmmoniaFuel"**





Tecno-Economic Analysis „Ammonia-to-Power System“ for WWTP Gleisdorf

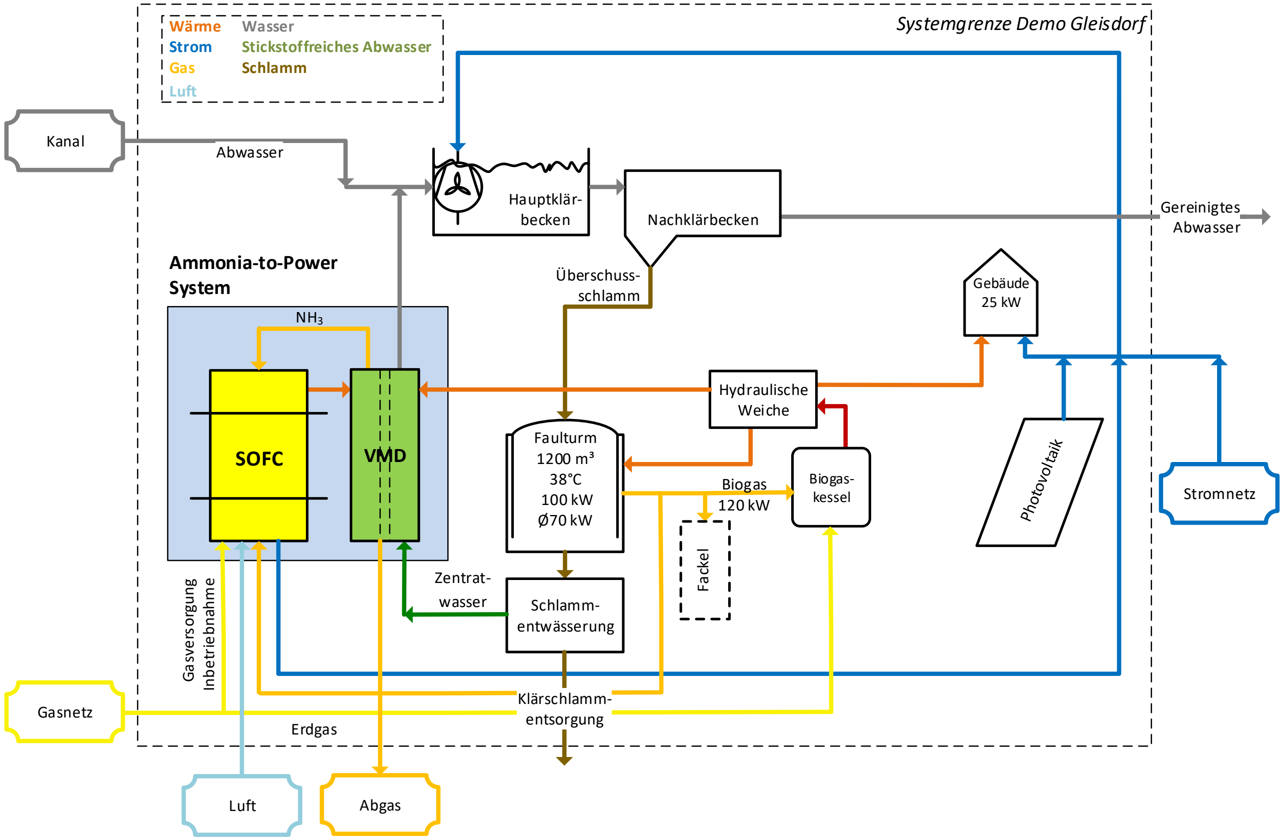
Ammonia-to-Power System:



Water vapour beneficial SOFC operation at 5% NH3

however for high efficiency, target > 30-50% NH3

Business Case - Ammonia-to-Power Integration at WWTP Gleisdorf



European potential:
16,4 Mt/ a sludge
35 kt/a N load

- NH3 heating value of 182 GWh/a
- reduction of ARA energy demand by 140 GWh/a
- Tremendous CO2 savings

Tecno-Economic Analysis

Development of cost scenarios:

- SOFC Stack exchange intervals
- Stack degradation along life-time
- MD-Module life-time
- Serial production investment cost estimation
  Stacks, VMD-Modules…
- 50% NH_3 %
- …

SOFC - Investitions und Betriebskosten

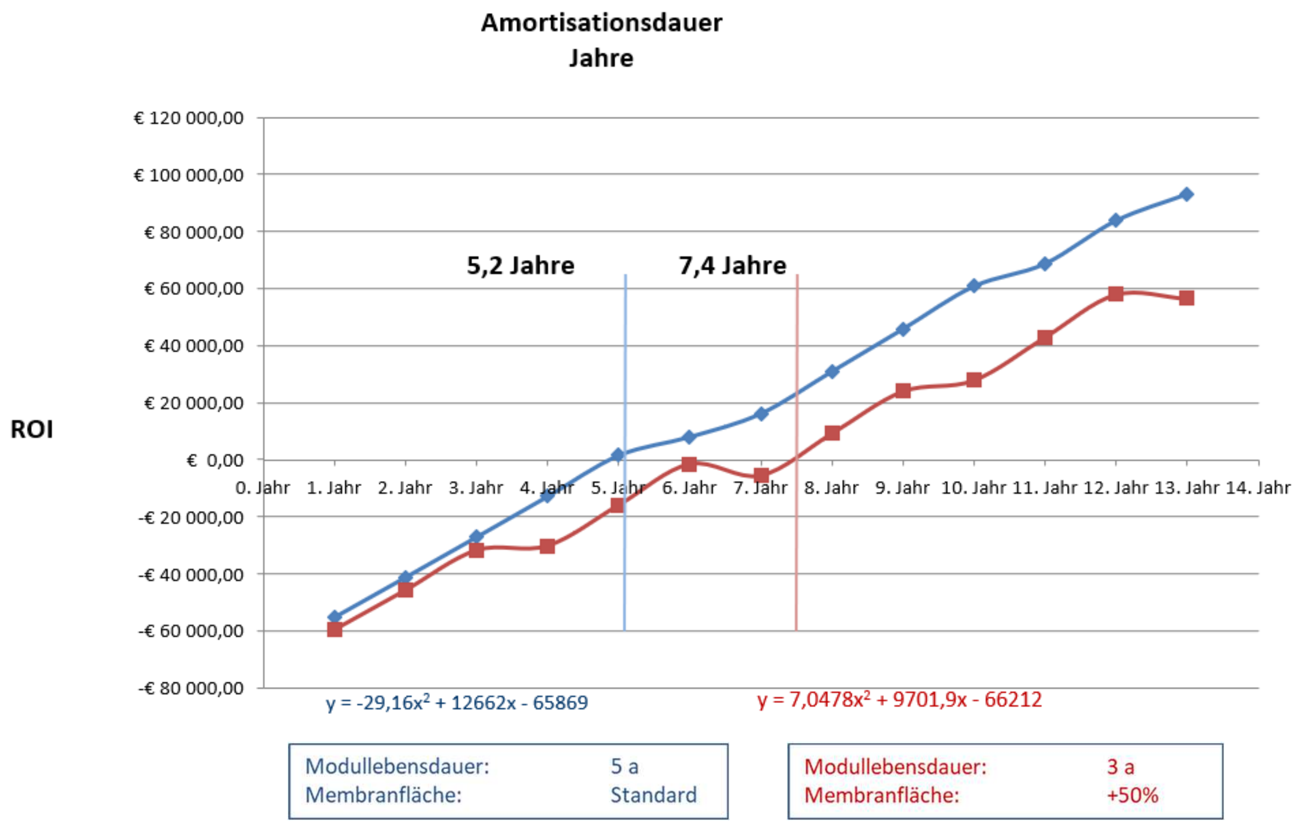
Investionskosten für SOFC System		
Investitionskosten SOFC-Anlage und Peripherie	30 000	€
Bau-, Installation- und Infrastrukturkosten	3 000	€
Overheadkosten Investion	2 000	€
Gesamtinvestitionskosten	**35 000**	**€**
Laufende Kosten für SOFC System		
Brennstoffkosten	-	€ p.a.
Kosten für Energiebereitstellung Gas (Startphase)	5	€ p.a.
Wartungskosten (2% der Investition)	700	€ p.a.
Personalkosten	418	€ p.a.
Gesamte laufende Kosten (im 1. Jahr)	**1 123**	**€ p.a.**
Wiederkehrende Investitionen		
Erneuerung der Stacks	6	a
Kosten pro Stackerneuerung	**7 500**	**€**

VMD - Investitions und Betriebskosten

Investionskosten für Membrandestillationsanlage		
Investitionskosten VMD-Anlage und Peripherie	7 462	€
Bau- und Infrastrukturkosten	1 638	€
Overheadkosten Investition	2 000	€
Module		
spez. Membranpreis	65	€/m²
Fläche pro Modul	140	m²/Modul
Modulanzahl	1	Stk.
Membrangesamtfläche	140	m²
Kosten pro 140 m² Modul	9 100	€
Kosten für Module	9 100	€
Gesamtinvestitionskosten	**20 200**	**€**
Laufende Kosten für Membrandestillationsanlage		
Reinigungsmittelkosten	200	€ p.a.
Kosten für Energiebereitstellung Strom	1 320	€ p.a.
Wartungskosten (1% der Investition)	202	€ p.a.
Personalkosten	418	€ p.a.
Analytikkosten	200	€ p.a.
Gesamte laufende Kosten (im 1. Jahr)	**2 340**	**€ p.a.**
Wiederkehrende Investitionen		
Erneuerung der Module nach	5	a
Kosten pro Modulerneuerung	**9 100**	**€**

Erträge Ammonia-to-Power System		
Erträge aus Stromerzeugung		
Betriebsstunden pro Jahr	8000	h/Jahr
Leistung SOFC el	**15**	kW
Erzeugte Energie SOFC el	120000	kWh/a
Bezugskosten Strom ARA Gleisdorf	0,11	€/kWh
Ertrag Stromerzeugung	**13 200**	**€ p.a.**
Einsparung Belüftungsenergie Hauptklärbecken	135	kWh/d
Einsparung bei Abwasserreinigung	**5 420**	**€ p.a.**
Gesamterträge durch MD Integration (in Jahr 1)	**18 620**	**€ p.a.**

Amortization



Parameter Target Scenario:

- VMD selectivity >50% (ideal 70%)
- VMD system costs 130 EUR/m² membrane area
- Immense CAPEX reduction in comparison to stripping
- u.a.

Outlook

- V-MD low exergy technology to gain NH_3 as chemical/energy vector or storage medium [Ammonia2HeatStorage]
- Huge potential for exploitation, contribution to more sustainable NH_3 handling
- Pure NH_3-water vapour gained from harsh samples
- „Selectivity“ of NH_3 still low in V-MD
- MD technology (DCMD) robust and reliable to remove N-NH_4 effectively > 95% in long-term operation; high selectivity possible

Further work:

- Develop ideal VMD module configuration and operating parameters for decoupling of water and NH_3 flux
- Optimize pre-treatment and module cleaning strategies
- Pilot plant operation of V-MD
- Direct connection to SOFC stacks; further stack development

Special thanks to…

all project partners

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ARA Gleisdorf, Peter Schiefer, Manfred Leber & team

Rochem India and Wolfgang Heinzl from TheVap GmbH

ROTREAT, Robert Gampmayer

all our dedicated students

FFG and Austrian ministries for funding

powered by klima+energie fonds

VORZEIGEREGION ENERGIE

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FFG Promoting Innovation.

ThermaFLEX

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IDEA TO ACTION

Thank you
for your Attention