Membrane filtration as a part of nitrogen recovery concept

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Nanofiltration 2022, June

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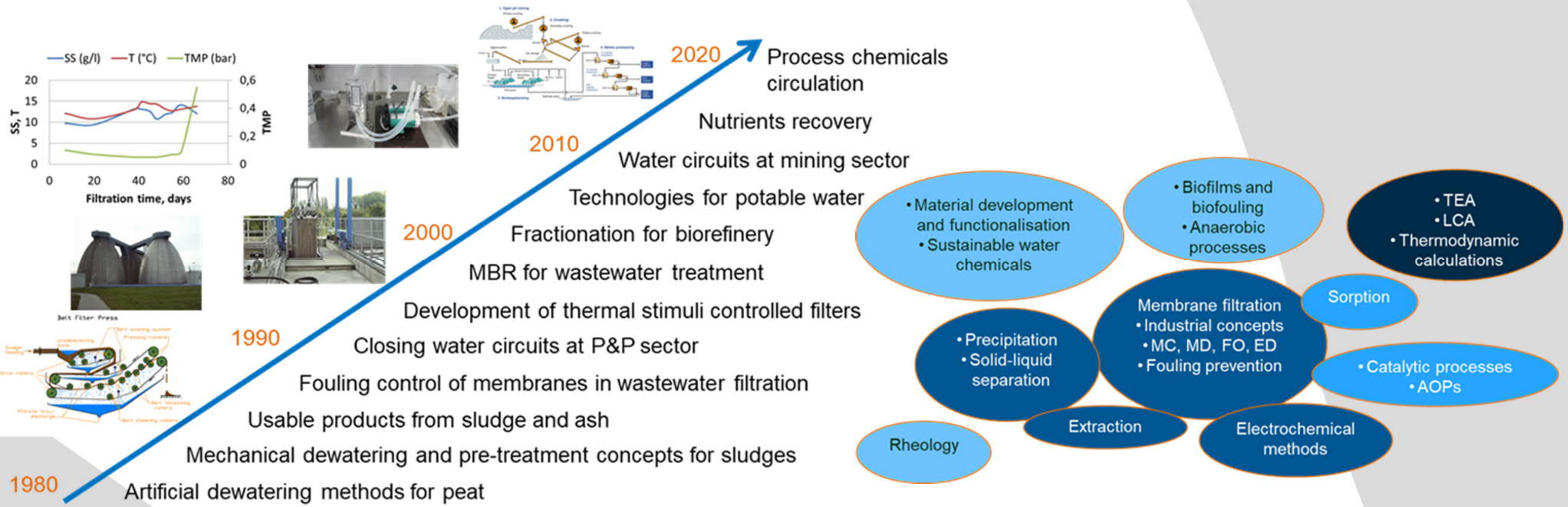
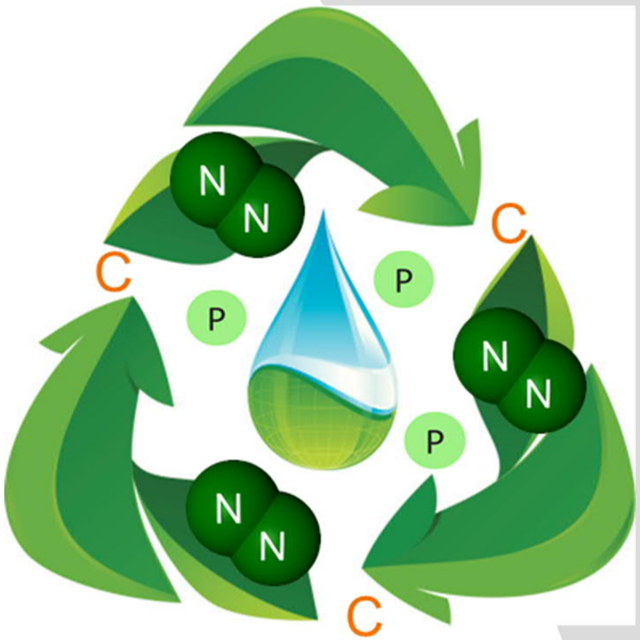
VTT Membrane technology

Develops process concepts for industrial water reuse, process/waste liquors purification and chemicals recovery from concentrates



Content

- Introduction to nitrogen and recovery
- Trends and regulation related to circulated nutrients
- Membrane filtration as a part of
  - Municipal wastewater (WW) concept
    - WW from WWTP
    - Septic WW
  - Industrial water concept
- Conclusions



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Intoduction to nitrogen (N) and recovery

- N can be found e.g. in Earth's atmosphere as N_2, proteins as amino acids, urine as urea or as hydrolysed ammonium/ammonia, industrial chemicals, fertilizers, as an impurity in water systems or flue gases
- Industrial N chemicals are produced by energy intensive Haber-Bosch technology
- **Wastewater nutrient recovery has two-way benefits by removing impurities from usable water as well as by concentrating nutrients to be utilized as recycled chemicals**
- Various N recovery technologies are available, choice depends on phase, composition and concentration:
  - stripping, absorption, adsorption, evaporation, membrane filtration, electrodialysis, precipitation as struvite

Trends of N chemicals

- Nutrient product prices have increased during past year
  - Increased natural gas prices since Jan 2021
  - Effects of Russia-Ukraine conflict
    - Russia exported 11% of the world's urea, and 48% of the ammonium nitrate
    - Russia and Ukraine together exported 28% of nitrogen, phosphorous, potassium fertilizer
  - However, there is an overproduction of ammonium sulphate
    - Target in other products if possible
- New sources for nutrients are needed

→ Increased interest in recycled nutrients
  - From waste to products

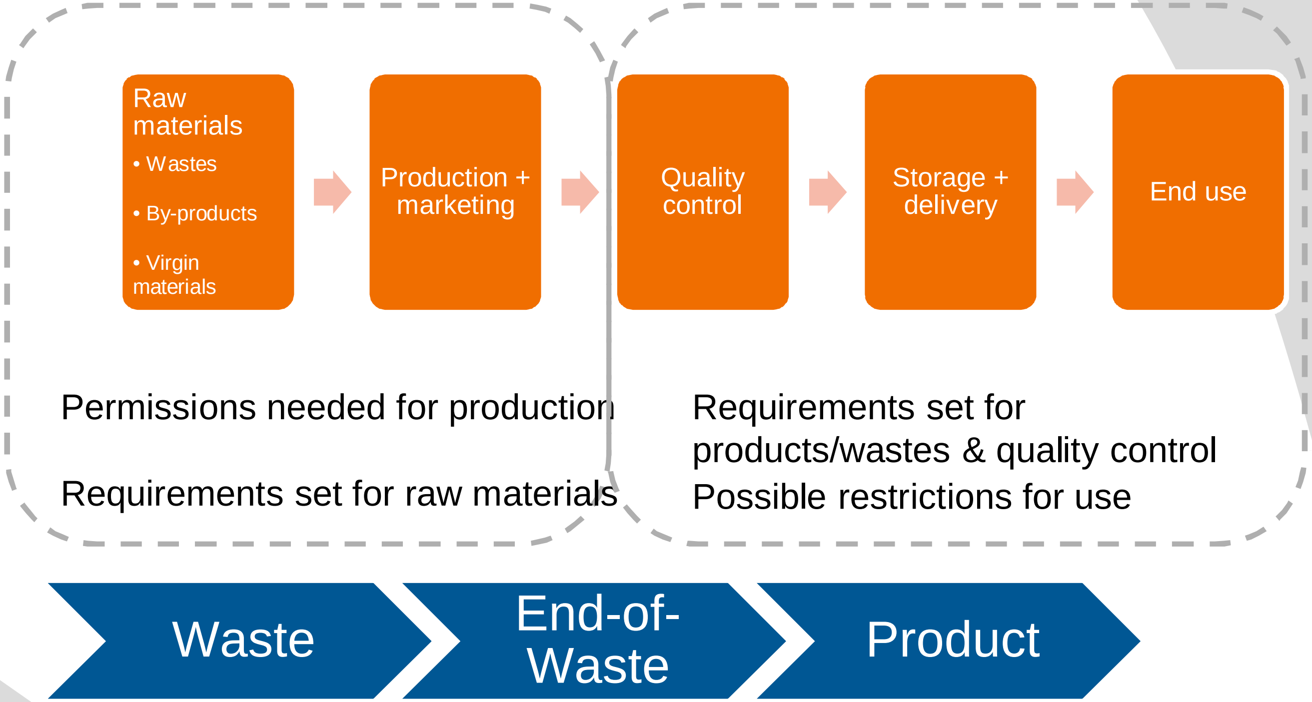
Product	USD/ton March 2022	USD/ton Nov 2021
Ammonium nitrate	1110	730
Ammonium sulphate	240	440
Diammonium phosphate	940	730
Urea	910	420
Nitric acid	620	500

https://m.echemi.com/searchGoods
https://www.indexmundi.com/commodities
https://advisor.morganstanley.com

Possible N chemical/fertilizer ingredients

Chemical product	Examples for utilization
Nitric acid, HNO_3	Raw material for nitrogen chemicals, cleaning chemical, fertilizer
Ammonia water, NH_4OH	Fertilizer, nitrogen chemical, energy product
Ammonium sulphate, $(NH_4)_2SO_4$	Fertilizer, emission reduction chemical for incinerators
Ammonium nitrate, NH_4NO_3	Fertilizer, explosive, energy product (N_2O)
Ammonium phosphate, $(NH_4)_3PO_4$	Fertilizer
Sodium nitrate, $NaNO_3$	Component in explosives, glass
Sodium (hydrogen) sulphide, Na_2S and NaHS	Metal precipitation chemical
Potassium nitrate, KNO_3, K_2SO_4	Fertilizer
Calcium nitrate, $Ca(NO_3)_2$	Fertilizer, concrete additive, foul odours preventing chemical
Struvite, $NH_4MgPO_4 \cdot 6H_2O$	Fertilizer

From wastes to products



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Designation of Component Material Categories (CMCs)

CMC 1: Virgin material substances and mixtures
CMC 2: Plants, plant parts or plant extracts
CMC 3: Compost
CMC 4: Fresh crop digestate
CMC 5: Digestate other than fresh crop digestate
CMC 6: Food industry by-products
CMC 7: Micro-organisms
CMC 8: Nutrient polymers
CMC 9: Polymers other than nutrient polymers
CMC 10: Derived products within the meaning of Regulation (EC) No 1069/2009
CMC 11: By-products within the meaning of Directive 2008/98/EC
CMC 12: Precipitated phosphate salts and derivates
CMC 13: Thermal oxidation materials or derivates
CMC 14: Pyrolysis and gasification materials

New Regulation on EU Fertilizer products 2019/1009 16.7.2022 →

Product function categories (PFCs) of EU fertiliser products

1. Fertilizer
2. Liming material
3. Soil improver
4. Growing medium
5. Inhibitor
6. Plant biostimulant
7. Fertilising product blend

Example: Inorganic macronutrient fertilizer

Contaminants must not exceed the following limits:

(a) **cadmium (Cd):**

(i) where an inorganic macronutrient fertiliser has a total phosphorus (P) content of less than 5 % P_2O_5-equivalent by mass: 3 mg/kg dry matter, or

(ii) where an inorganic macronutrient fertiliser has a total phosphorus (P) content of 5 % P_2O_5-equivalent or more by mass (‘phosphate fertiliser’): 60 mg/kg P_2O_5

(b) **hexavalent chromium (Cr VI):** 2 mg/kg dry matter,

(c) **mercury (Hg):** 1 mg/kg dry matter,

(d) **nickel (Ni):** 100 mg/kg dry matter,

(e) **lead (Pb):** 120 mg/kg dry matter,

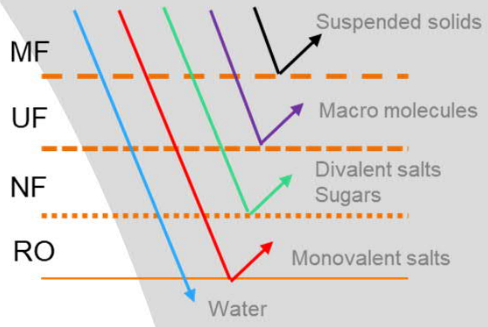
(f) **arsenic (As):** 40 mg/kg dry matter

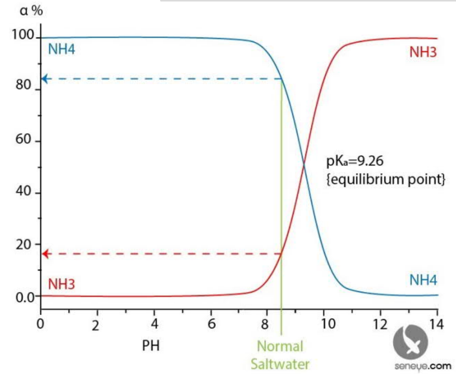
(g) **biuret (C2H5N3O2):** 12 g/kg dry matter,

(h) **perchlorate (ClO4-):** 50 mg/kg dry matter

Background to N recovery by membranes

- Microfiltration (MF) pre-treatment removes solid nitrogen
- Ultrafiltration (UF) rejects e.g. soluble proteins
- Ionic nitrogen, such as ammonium or nitrate, can be rejected by nanofiltration (NF) or reverse osmosis (RO)
- Gaseous forms of nitrogen, such as ammonia, permeate even through RO membranes
  - Depends on pH, temperature, salinity, ionic strength
- Gasous nitrogen can be separated from liquid by hydrophobic microfiltration membranes, *i.e.* membrane contactor (MC) technology
- Electrodialysis (ED) can be used e.g. for valorization of nitrogen compounds and water purification



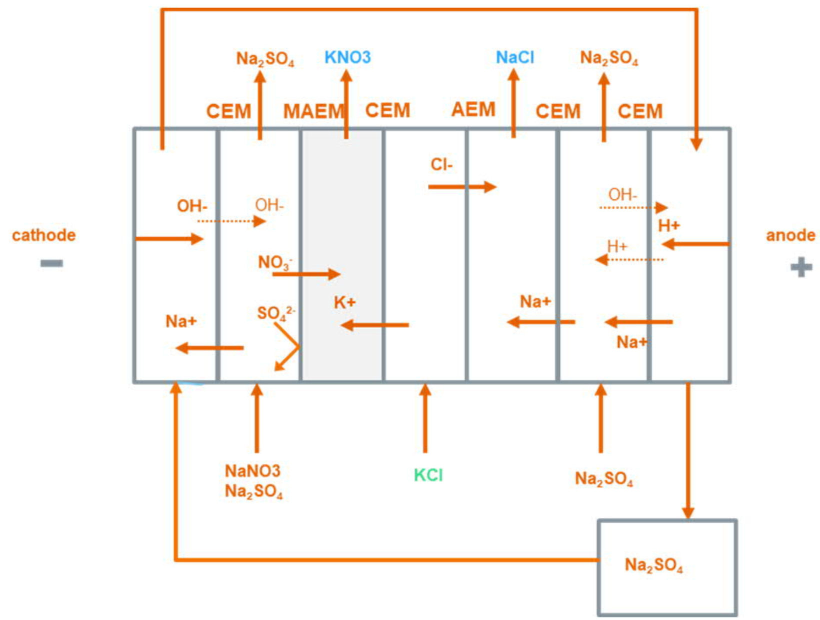


https://answers.seneye.com/en/water_chemistry/what_is_ammonia_NH3_NH4

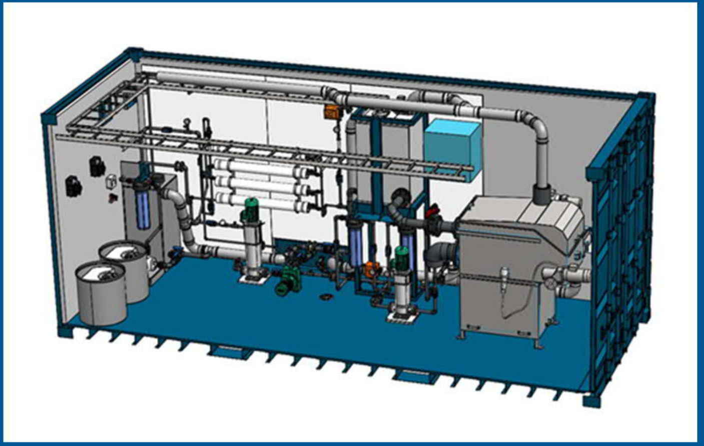
Example of future work using EDR

- Electrodialysis reversal (EDR)
  - Periodic change of electrodes polarity to keep membranes clean
  - Reduced requirements for pre-treatment
  - Cannot be used with bipolar membranes
- Valorizing recovered chemical by switching sodium to potassium or ammonium
  - Increased weight and price:

	M/(g/mol)	ton	USD/ton	USD
KCl	75	1	562	560
KNO_3	101	**1.4**	1072	**1500**
$(NH_4)_2SO_4$	132	1	241	240
NH_4NO_3	80	**1.2**	1107	**1330**



Membrane filtration as a part of municipal wastewater concept



Technology selection at lab scale

- Municipal wastewater (WW):

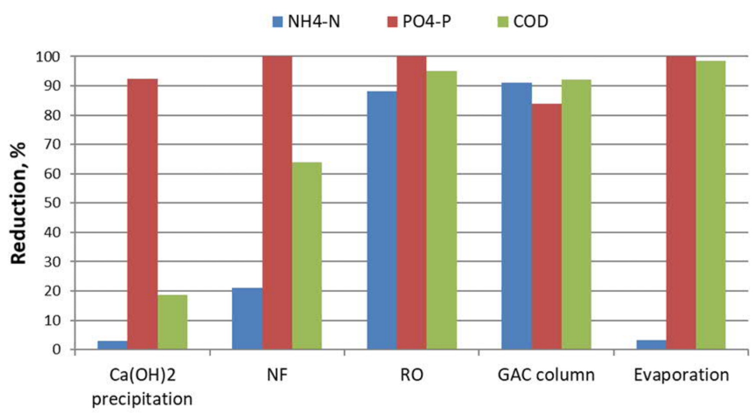
pH	Turbidity NTU	PO4-P mg/l	NH4-N mg/l	COD mg/l	TDS mg/l
7.1	140	16	50	550	650

- Pre-treatment
  - Flocculation aided belt filtration and MF to decrease amount of solid impurities
- Recovery technologies for nutrient recovery
  - Precipitation as calcium phosphate using lime ($Ca(OH)_2$)
  - Concentration by membranes at reasonable water recovery (WR)
    - NF using NF270
    - RO using XLE
  - Concentration by evaporation, T = 80°C
  - Adsorption by GAC
- Piloting decentralised wastewater treatment in a Resource container

Results of technology comparison

For nutrient and carbon products

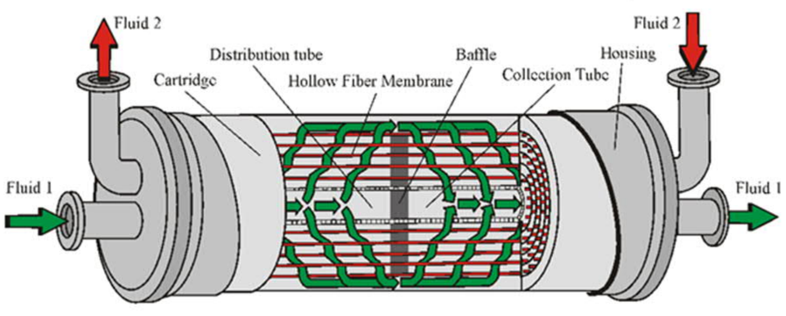
- **Lime** precipitated PO4-P and changed ionic NH4-N to gaseous NH3-N at pH >10
- **NF** did not reject NH4-N or organics measured as COD sufficiently but rejected PO4-P
- **RO** rejected NH4-N, PO4-P and organics well
- **GAC** had pretty similar rejections than RO
- **Evaporation** did not concentrate NH4-N but rejected PO4-P and organics



→ PO4-P precipitation selected treatment technology for RO concentrate to recover NH3-N by MC

NH4-N recovery using MC

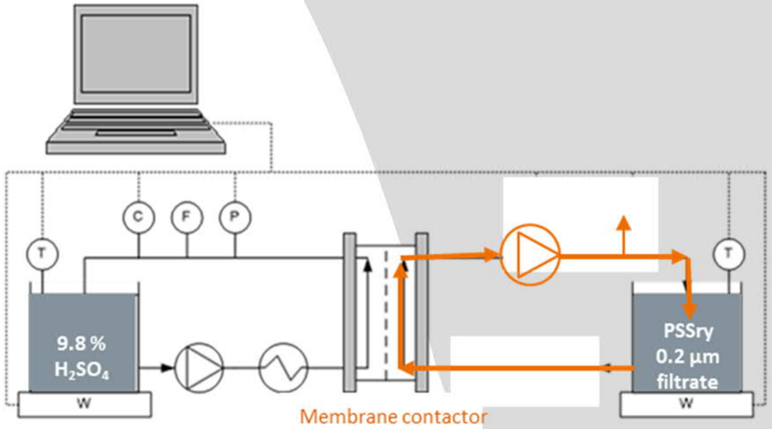
- Hydrophobic MF membrane to separate gas from liquid
- Recovery chain: $NH_4^+ \rightarrow NH_3 \rightarrow (NH_4)_2SO_4$
  - pH increase of WW to ~10 to make alkaline gas
  - Absorption of alkaline gas to acid solution, like sulphuric acid
- Ideal parameters for MC
  - NH_3 inlet conc. > 500 ppm
  - Pre-filtration < 10 µm
  - Temperature 40 - 55°C
  - Feed stream pH > 10
  - Acid stream pH < 2



http://sschi.chtf.stuba.sk/MembraneLab/Pictures/CelgardModulBig.gif

Lab tests for N recovery by MC

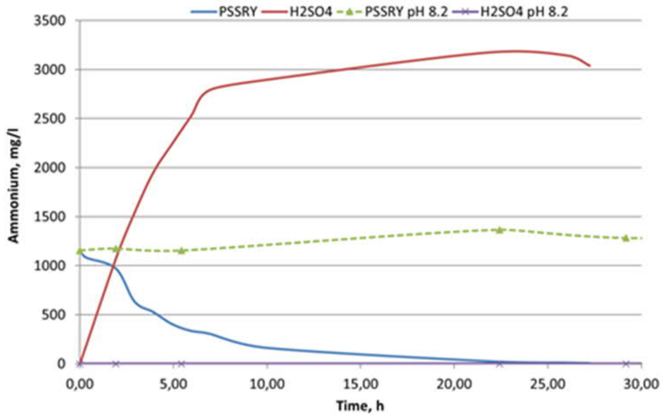
- Feed: Septic WW (PSSry) → flocculation → wire filtration → MF
- Absorption solution 9.8 w-% H_2SO_4
- Membrane: MD QL816, 0.2 µm
- Circumstances during three weeks filtration:
  - Room temperature
  - Process time 7h/day
  - New feed sample faced same absorption solution
- To be studied
  1. Maximum NH4-N concentration in H_2SO_4
  2. Fouling after running 100 hours

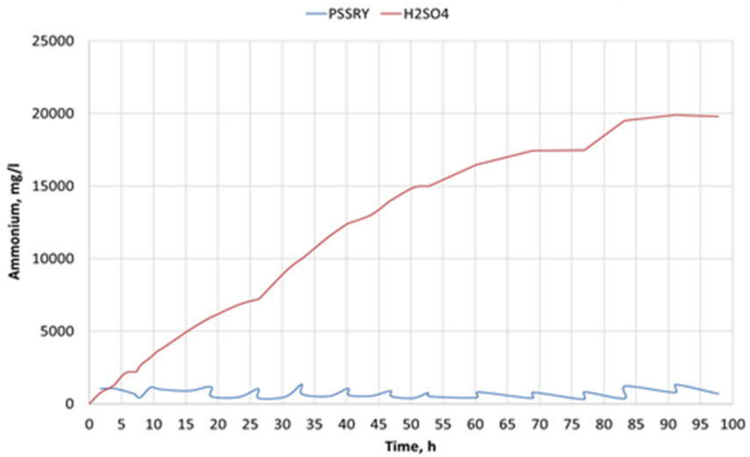


	pH	Turbidity NTU	P total mg/l	NH4-N mg/l	COD mg/l	TDS g/l
Septic WW	8.1	430	14	1450	3700	8.2

Recovery chain $NH_4^+ \rightarrow NH_3 \rightarrow (NH_4)_2SO_4$

- NH_4-N content of septic WW decreased 99 %, from 1150 mg/l to 6.5 mg/l
- Maximum NH_4-N concentration achieved with several steps was 19 900 mg/l
  - Product 10 % $(NH_4)_2SO_4$

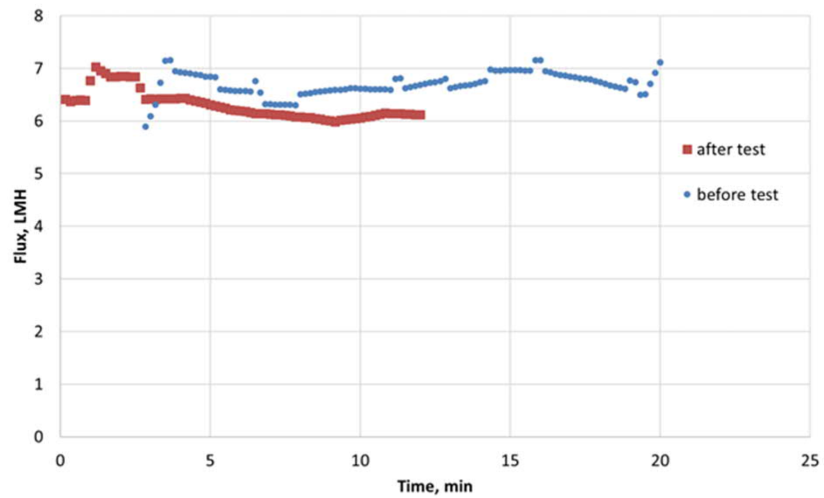




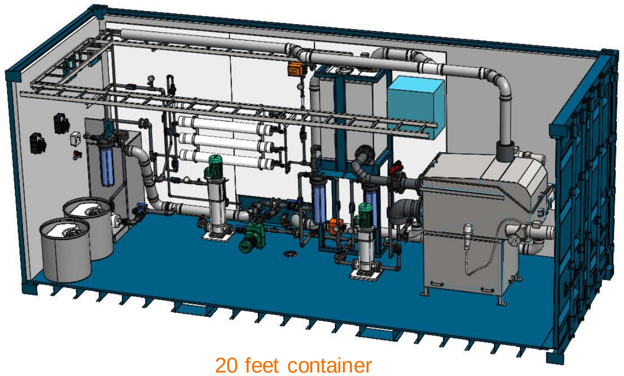
Fouling of the membrane during N recovery

- Negligible transfer of water during test
- Flux of salt rejection tests before and after filtration:
  - DI water 20°C, NaCl solution 60°C
  - Decreased from 6.5 LMH to 6 LMH
  - NaCl rejection 100 % in both tests

→ Only minor fouling

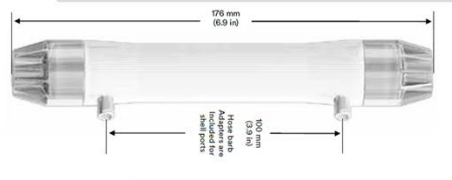


Nutrient recovery as a part of Resource container concept

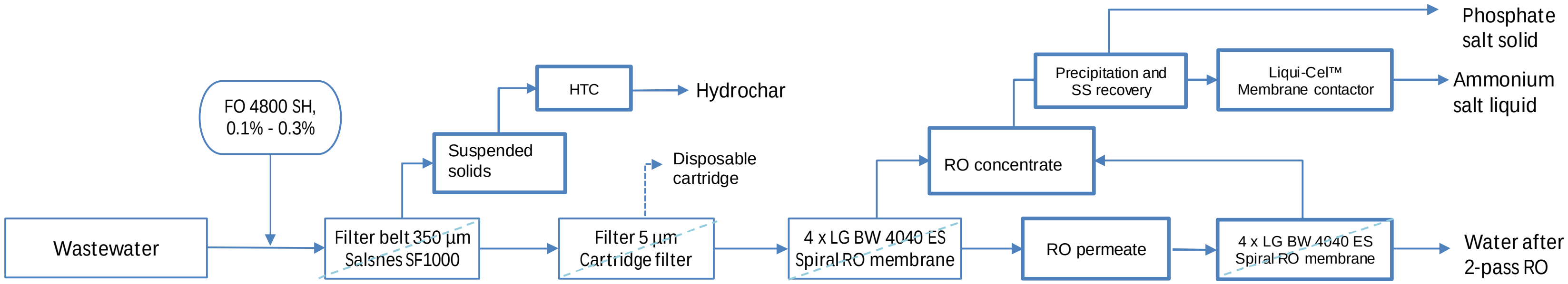


20 feet container

Belt filtration, measurements, RO unit



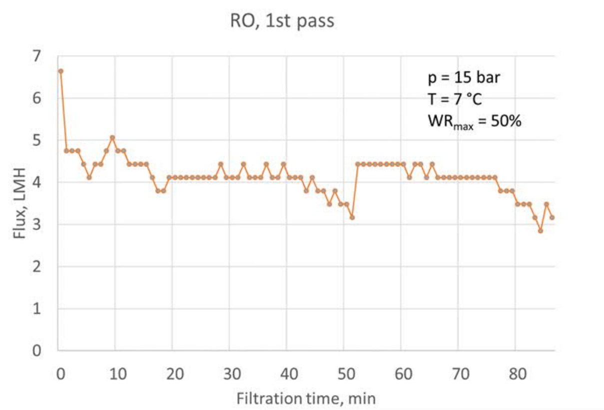
3M™ Liqui-Cel™ MM-1x5.5 Series

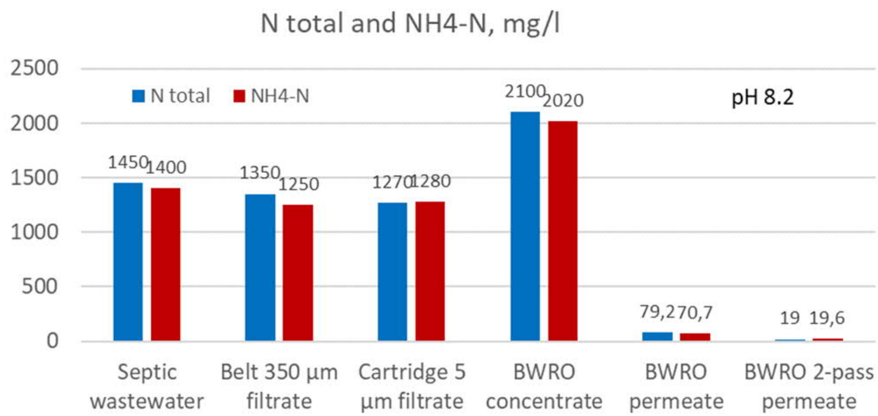


Kyllönen et al., Membranes 2021, 11, 975

Septic WW, concentration by pilot RO

	pH	λ mS/cm	TDS g/l	Turbidity NTU	COD mg/l	P total mg/l
Septic WW	8.1	18	8.2	430	3700	14
Belt filtrate	8.2	16	5.0	140	1900	9.3
Cartridge filtrate	8.2	16	4.8	35	1800	9.3

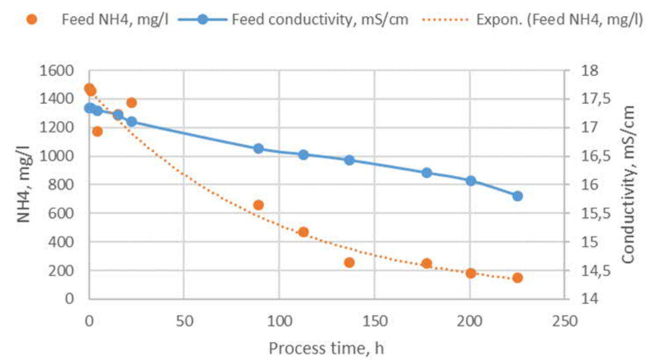


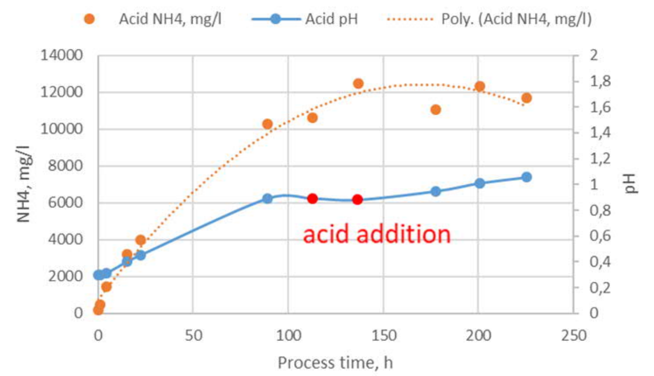


- Concentrated WW for RO
- NO3-N concentration much lower than NH4-N
- Low fluxes in 1st pass with low temperature, stable flux
- Good rejection for NH4-N
- 2nd pass improved water quality

Septic WW, MC with RO concentrate

- Experiments:
  - 90 l feed: BWRO concentrate, NH4-N ~1500 mg/l
  - 9 kg absorption solution 5.5 w-% H_2SO_4
  - 3M™ Liqui-Cel™ MM-1x5.5 Series:
    - X50 fiber, 0.5 l/min flow rate (30 l/h)
- Results:
  - 82 % of NH4-N could be absorbed in acid, 12 g/l
  - 57 g/l of $(NH_4)_2SO_4$ salt could be obtained
  - When NH4-N content in feed was < 500 mg/l, removal of NH4-N was slow
  - No significant water transportation through membrane
  - Possible process without warming up the liquids



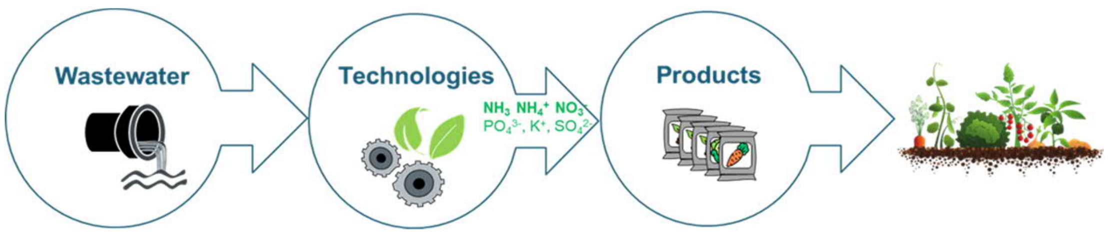


Nanofiltration as a part of industrial water concept

TYPKI - Resource-wise nutrient recovery from industrial wastewater

- Tighter limits on nutrient discharge imposed
- Potential for raw materials lurking in wastewater

→ Solutions for treatment of industrial wastewater and recovery of nutrients from concentrates hence answering the challenge of ZLD



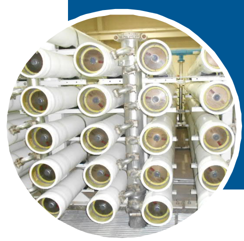
Nutrient sources N, P, K, S, Mg, Ca: Concentrates from wastewater purification to be utilized or safely deposited

Recovery and refinement:
- Precipitation
- Adsorption
- Membranes
- Electrochemistry
- Evaporation

For use:
- Reuse water
- Chemical additives
- Adhesives for cementation
- Fertilizer additives

Impact:
- More usable water
- Less discharge
- Increased nutrient self-sufficiency
- Better business

Schedule:	Feb 2021-Jan 2023
Budget:	EUR 1.03 million
Financer:	Business Finland and the participants
Participants:	VTT, University of Oulu, Tapojärvi, Aquaminerals, BioSO4, Brightplus, Industrial Water, Agnico Eagle, Gasum, Hannukainen Mining, Valmet, Yara Suomi



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N recovery from process water, materials

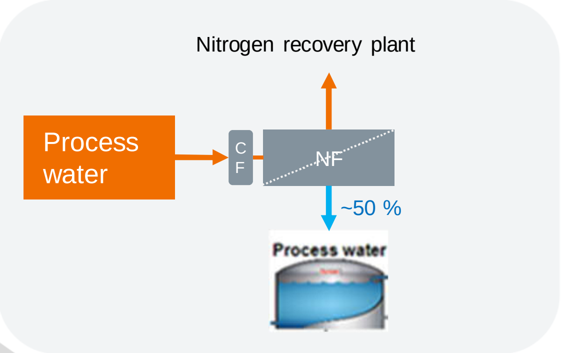
- Scalant removal, *i.e.* calcium precipitation with settling
  - Oxalic acid, dose ~0.8 g/l led to pH ~2
    - At low pH NH_4-N stays in process water
    - Minor effect on osmotic pressure
    - Precipitate calcium oxalate, $CaC_2O_4 \cdot (H_2O)_{0\text{-}3}$
  - Sodium carbonate, high dose 10 g/l to reach pH 10.5
    - Osmotic pressure increases
    - Precipitate calcium carbonate, $CaCO_3$ (also $Mg_2(OH)_2CO_3$)
- Membrane filtration using HP4750X cell, membranes
  - NF270 (FilmTec, DuPont), $MgSO_4$ rej 97.0%, p_{max} 41 bar
  - NF90 (FilmTec, DuPont), $MgSO_4$ rej 98.7%, p_{max} 41 bar
  - LG SW (LG Chem), NaCl rej 99.8%, p_{max} 83 bar

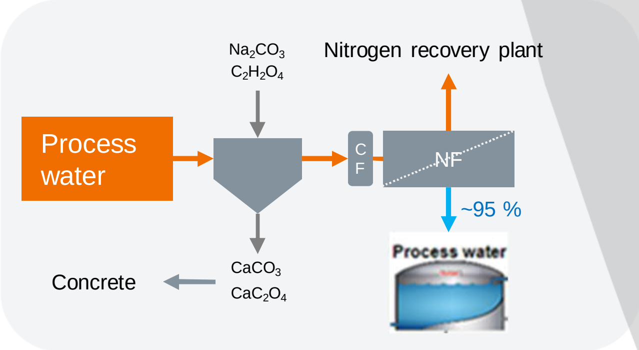
HP4750X Hastelloy Stirred Cell (Sterlitech, USA)

- MF, UF, NF and RO
- High-pressure, chemically resistant stirred cell
- Maximum pressure 172 bar
- Active membrane area 14.6 cm^2
- Maximum processing volume of 300 mL

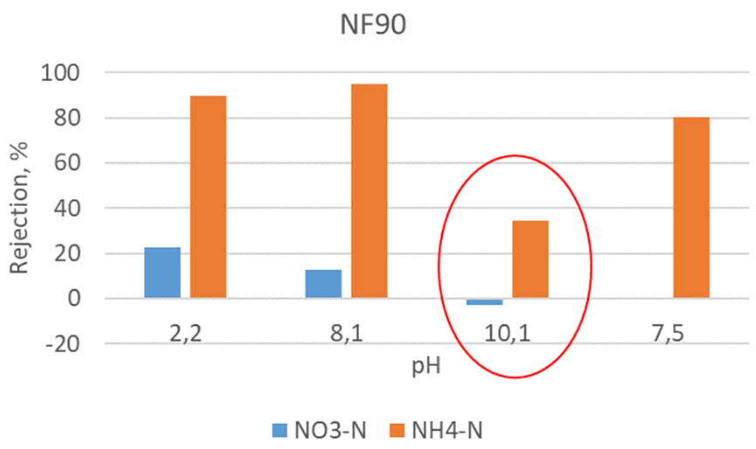
Water qualities in pre-treatment

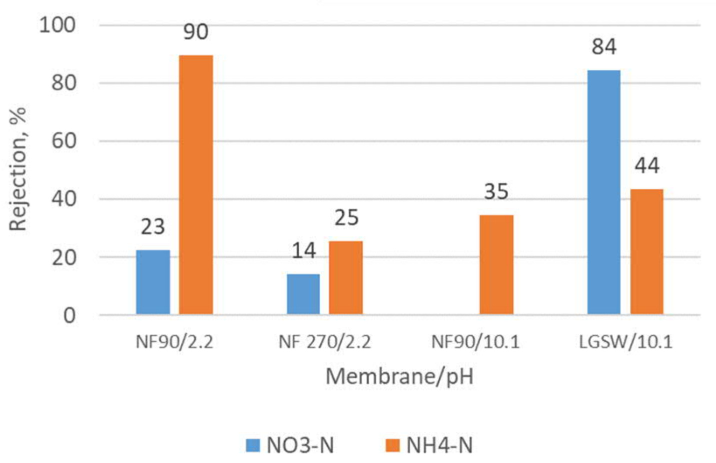
	pH	π bar	NH4-N mg/l	NO3-N mg/l	Ca mg/l	K mg/l	Mg mg/l	SO4 mg/l	COD
Feed with no precipitation	8.1	1.6	170	13	370	69	77	2600	160
Feed after oxalic acid precipitation	2.2	2.0	170	12	81	41	56	2200	240
Feed with carbonate precipitation	10.1	3.5	120	12	7	45	34	2300	na





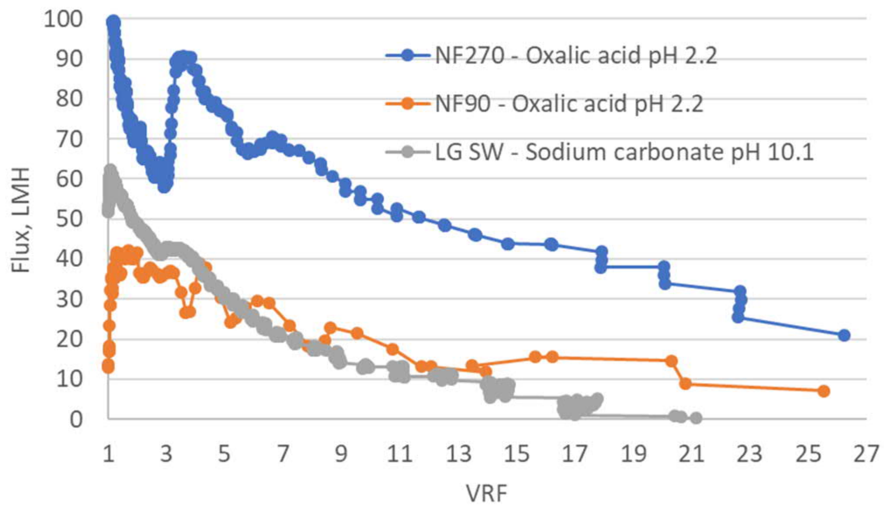
Rejection of N using NF/RO

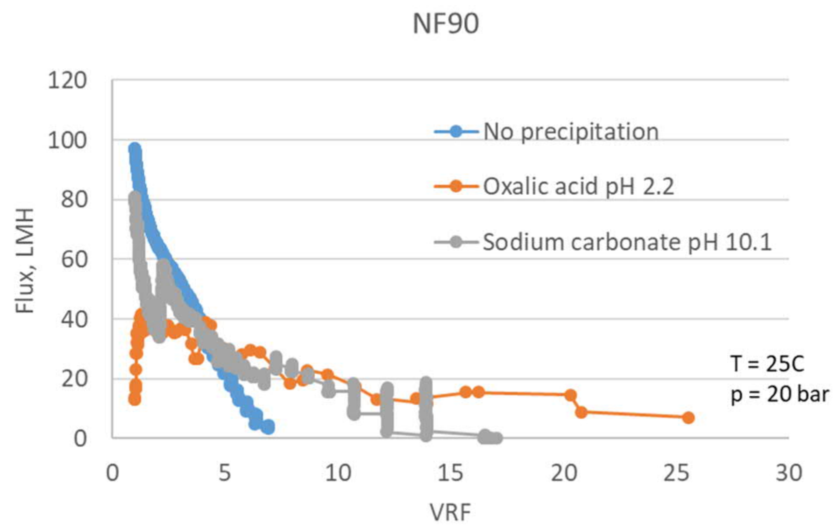




- NF90 produced 90% NH4-N rejection at low pH, NH4-N rejection when using NF270 was only 25% at similar conditions
- Even SWRO at pH > 10 did not sufficiently reject NH4-N
- SWRO rejected NO3-N

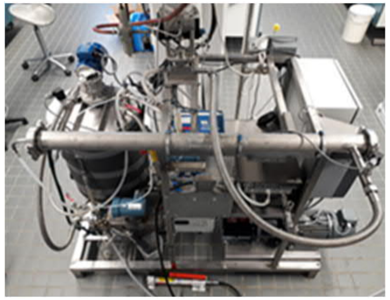
Fluxes using NF/RO membranes

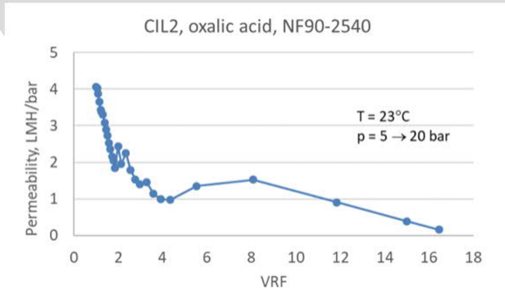




- Higher volume reduction factor (VRF) was obtained when using calcium removal
- SWRO needed double pressure compared to NF (or BWRO), thus NF was selected for further studies due to less energy need
- Best VRF was obtained with NF270 at low pH 2.2 but NH4-N was not rejected, thus NF90 was selected for further studies

Water qualities using NF90-2540 element



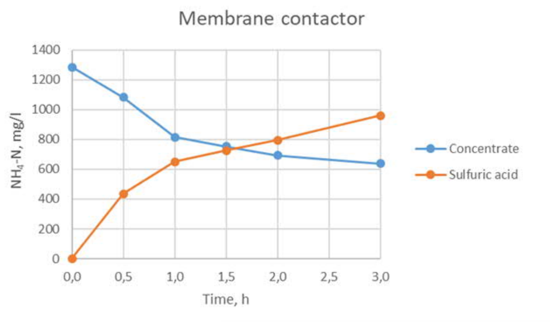


Fraction	pH	Conductivity	Total N	NH_4-N	NO_3-N	Ca	K	Mg	Cl	SO_4	COD
	-	mS/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Process water	7.1	6.1	170	160	12.3	440	58	82	19	1900	160
NF feed with oxalic acid	2.1	8.4	17	160	13.8	110	73	110	21	2990	240
NF concentrate (VRF 16)	1.7	56	1970	**1910**	15.7	540	660	980	5.4	36300	110
NF permeate (WR 94 %)	2.4	1.8	20	4.8	1.9	1	4	2	20	150	160

ICP-MS analysis	Al	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	P	Si	S	Zn
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Process water	<0.03	0.007	390	<0.003	<0.003	<0.05	36	55	0.12	680	0.051	<0.01	8.2	920	<0.005
NF90-2540 concentrate	0.67	0.13	**380**	0.28	5.9	24	**560**	**890**	5.3	**8800**	1.2	<5	76	**13000**	4.5

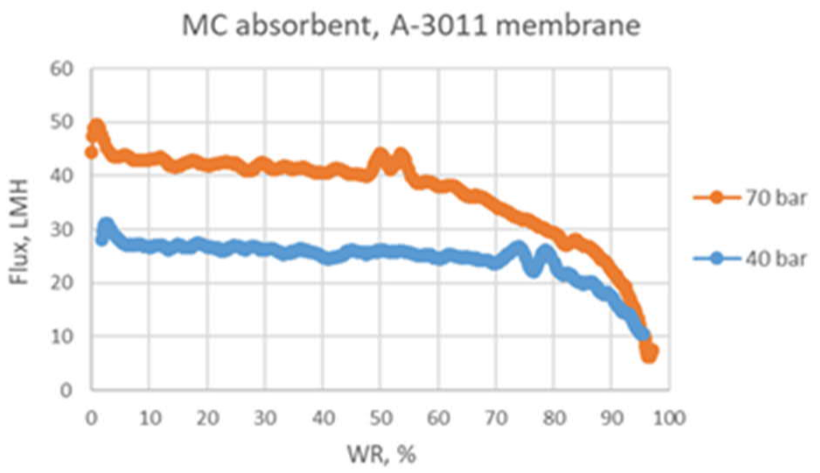
Membrane contactor tests at lab scale

- Process water
  - Feed: NF90-2540 concentrate
  - NH_4-N ~ 1.9 g/l, after pH adjustment ~1.3 g/l
    - Lower NH_4-N concentration than in small scale
- Membrane contactor set-up
  - 3M Liqui-Cel MM-1x5.5 series X50
  - NaOH for feed pH adjustment, pH ~ 10
  - Feed temperature ~25°C
  - Absorbent 0.5 M H_2SO_4
- Product ammonium sulphate salt
  - $2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
  - Work continued to higher product concentration



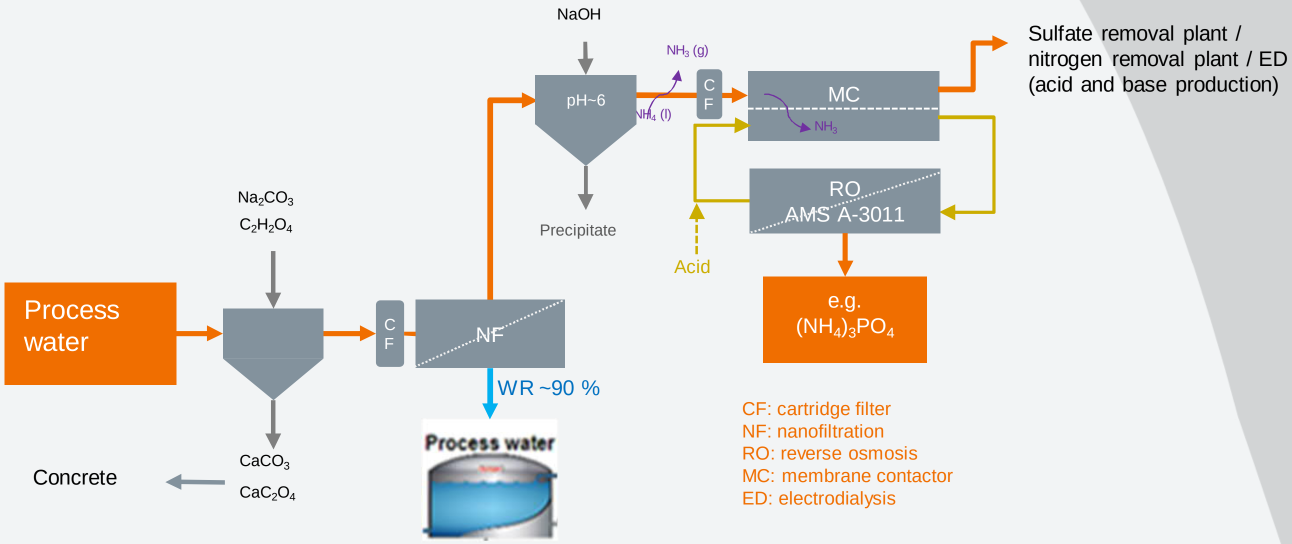
NF concentration at low pH at lab scale

	pH	λ mS/cm	NH4-N mg/l
Feed	1.5	27	610
Concentrate	1.2	230	**32400**
Permeate	1.5	22	380



- Salts were concentrated from acid using AMS NanoPro A3011 membranes
  - Mw 100 Da, pH tolerance 0-12, T_{max} 80°C, p_{max} 70 bar
- It was possible to concentrate NH4-N up to even VRF 50 at low pH and make 15% ammonium sulphate solution
  - stable fluxes obtained using 40 bar

Possible concept for NH4-N recovery in mining industry



CF: cartridge filter
NF: nanofiltration
RO: reverse osmosis
MC: membrane contactor
ED: electrodialysis

Conclusions

What have we learned

- There are increased interest in recycled nutrients in global market. New sources for nutrients are looked for.
- Functional recovery concepts for challenging liquid streams are needed
- Pre-treatment is beneficial for waste/process waters before recovery
  - For purity of nutrient products
  - pH adjustment to obtain NH4-N rejection/permeation when using membranes
  - Calcium removal in the case of high scalant concentrations to obtain high volume reduction factors, thus high concentration of nutrient sources/products
- Purified and concentrated NH4-N salt achievable when using MC and subsequent NF/RO. NF/RO can also act as a pre-concentration method.

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beyond the obvious

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