TYPKI – Nutrient recovery from wastewaters

Vesikemiapäivät
23rd Jan, 2023
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VTT – beyond the obvious

VTT is a visionary research, development and innovation partner
and one of the leading research organisations in Europe.

Our role is to promote the utilisation and commercialisation of research and technology in business and society. Through science and technology, we turn global challenges into sustainable solutions for business and society in a responsible way.

254 M€
turnover and other operating income

2,093
employees

45%
of the net turnover from abroad

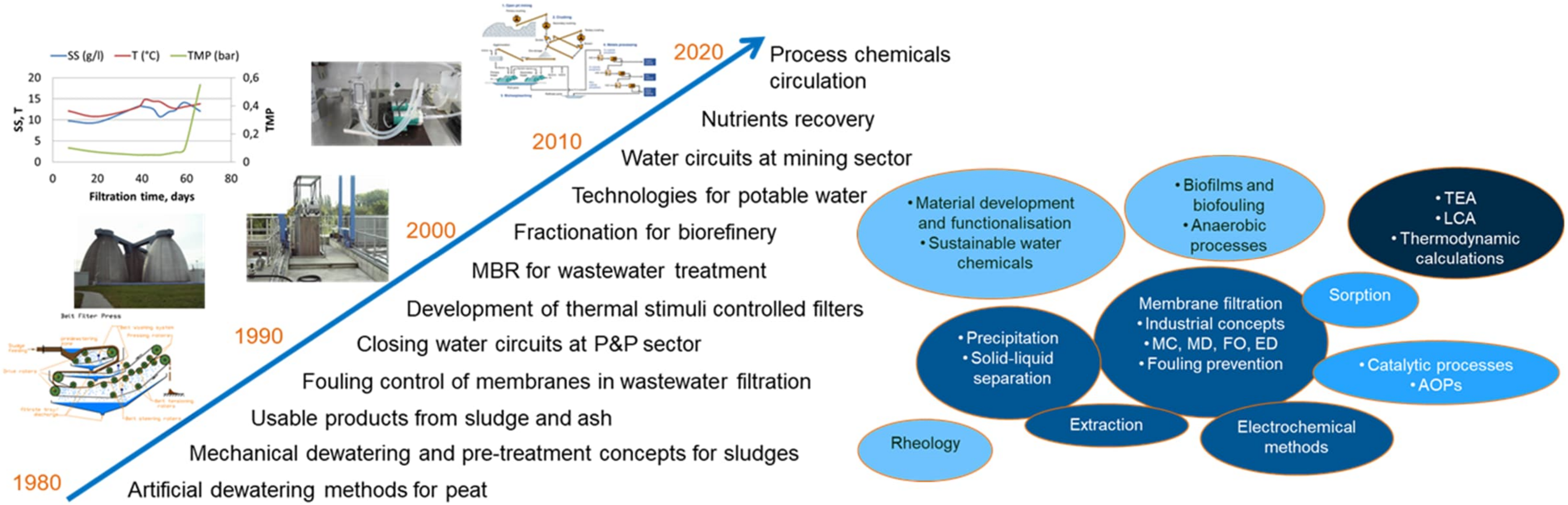
32%
a doctorate or a licentiate's degree

Establishmen year
1942

Steered by Ministry of Economic Affairs and Employment

VTT Separation technology

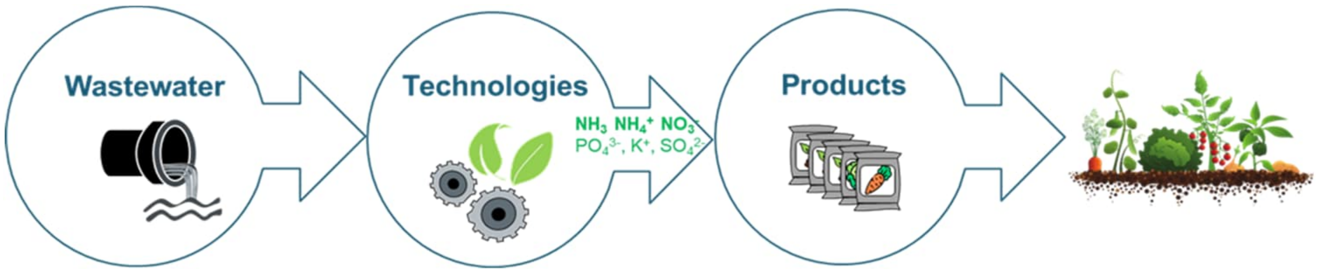
Develops process concepts for industrial water reuse, process/waste liquors purification and chemicals recovery from concentrates



TYPKI - Resource-wise nutrient recovery from industrial wastewater

At VTT we develop feasible solutions for treatment of industrial wastewater and recovery of nutrients hence answering the challenge of ZLD.

The on-going **TYPKI project coordinated by VTT promotes recovery and refinement concepts of nutrients into industrial chemicals, construction materials, and fertilizer additives.**



Nutrient sources: wastewater purification produces clean water but also concentrates to be utilized or safely deposited

Recovery and refinement: precipitation, adsorption, membranes, electrochemistry, evaporation

For use: reuse water, alternative process chemicals, adhesives for cementation, and fertilizer additives

Impact: Less nutrient discharge, increased nutrient self-sufficiency and 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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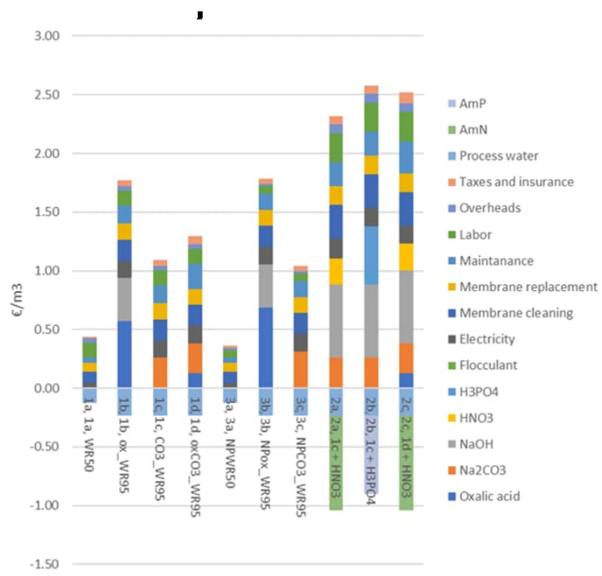
Background to nutrient recovery

- Industrial wastewaters are often in large volumes and low nutrient concentrations
- Nutrient concentration and recovery from wastewaters is the most feasible when it is a part of water purification
  - Concentrate needs to be deposited, thus nutrient recovery is a good option
- Recovery usually requires many steps when targeting to sufficiently concentrated circular economy product
  - As deposition of impurities is costly, low volume matters → makes concentration and recovery more desirable
  - Final concentration requires often additional technologies
  - If many steps are needed, recovery becomes easily costly
  - All streams need to be considered



Techno-economic analysis

Target TYPKI feed waters and products

Process/wastewater	Recoverable component	Product/incredient
Process water from a mine	NH_3, NH_4NO_3, $(NH_4)_2SO_4$, $CaCO_3$ (precipitate)	NH_3 water, NH_4NO_3 fertilizer/chemical, $CaCO_3$ for cementation, acid and base or persulfate from Na_2SO_4 residue
Neutralizing pond water	$CaCO_3$ (precipitate) RO-concentrate: S, Mg, Na, K	$CaCO_3$, $Mg(OH)_2$, $MgSO_4$, K_2SO_4, alternative adhesive for cementation
Pit water containing residuals of explosives	KNO_3, $NaNO_3$, NH_4NO_3,	KNO_3 fertilizer/chemical, $NaNO_3$ chemical
Reject water from biogas production	NH_3, $(NH_4)_2SO_4$, ammonium humate, PO_4^{3-}, NO_3^-	NH_3 water, $(NH_4)_2SO_4$, $Ca_3(PO_4)_2$, humate fertilizers, HNO_3, struvite (NH_4MgPO_4 * 6 H_2O) with Mg from other sources
S, N –scrubber water	NO_3^-, SO_4^{2-}	N product (NO_3-fertilizer/chemical etc.), S product (H_2SO_4, Na_2S etc.)

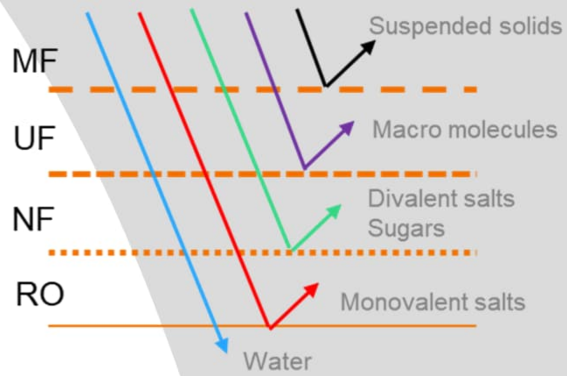
Nitrogen (N)

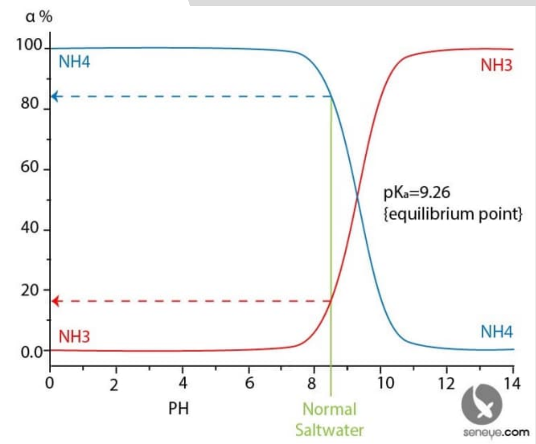
Intoduction to nitrogen (N) and recovery

- 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

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

Ammonium from a mine effluent

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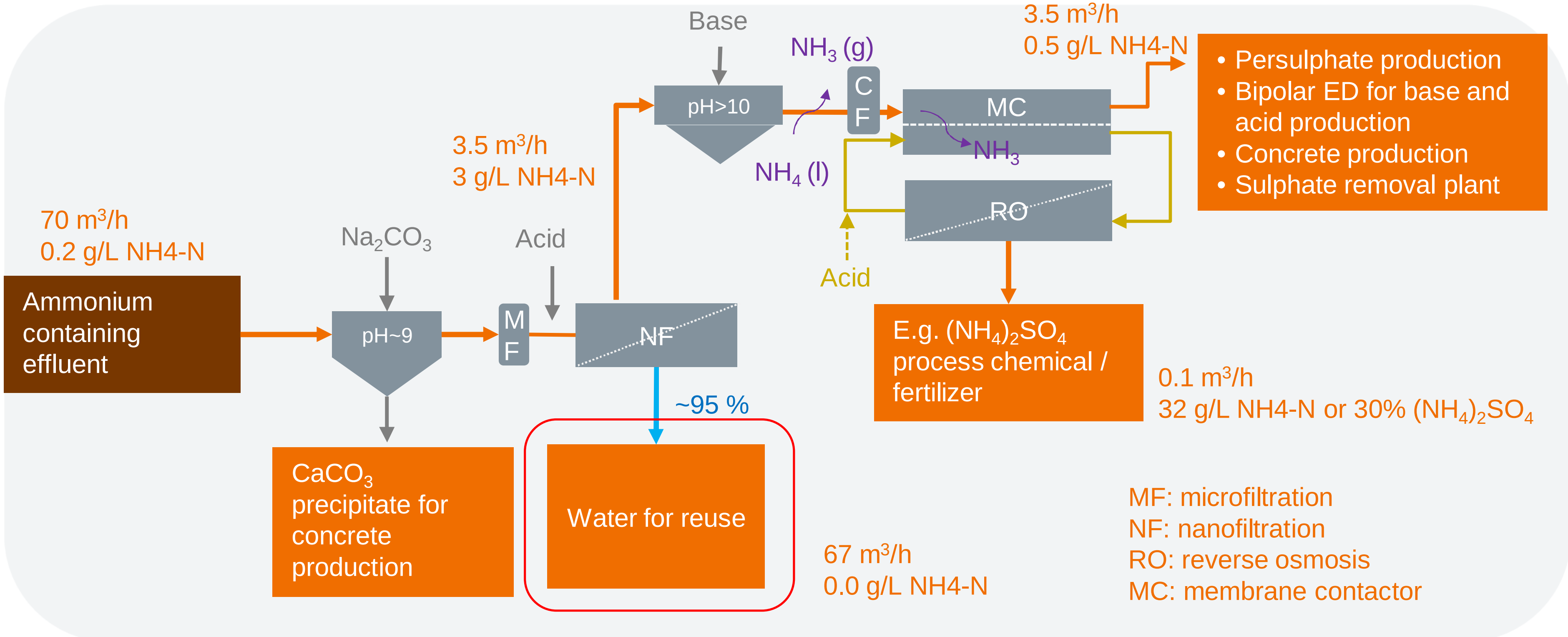
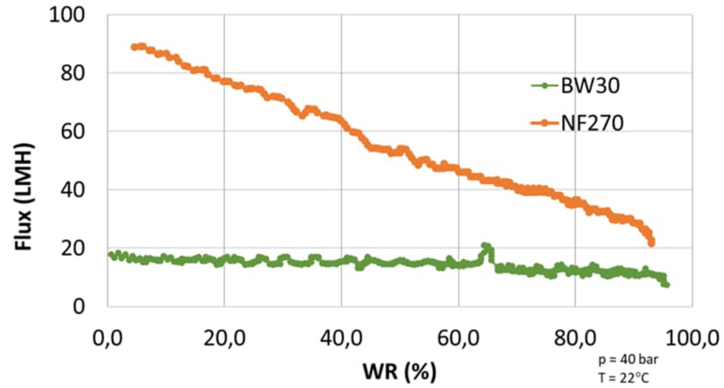
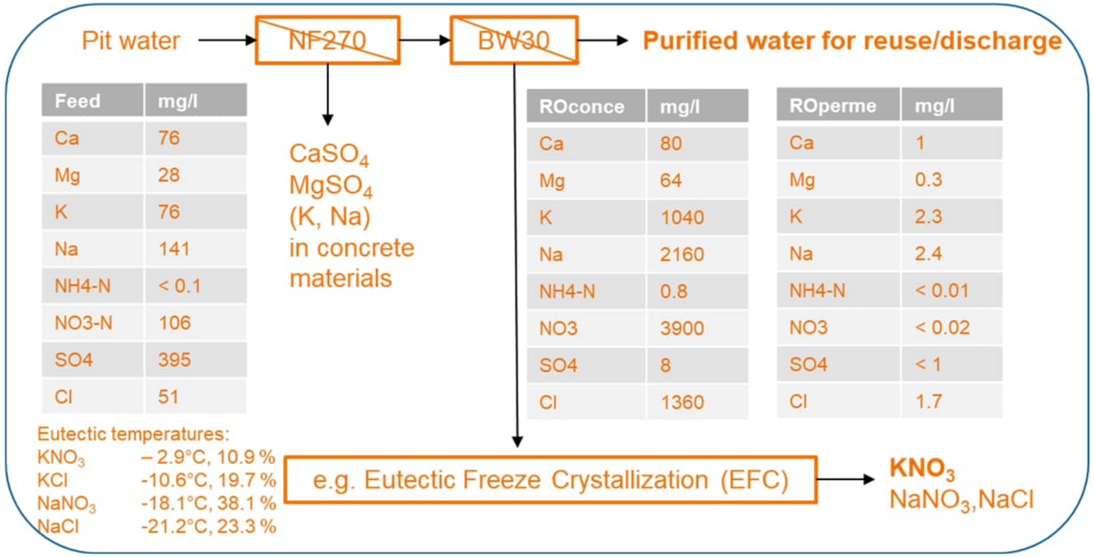
- Goal: Minimise surface water intake, decrease the volume of N in liquid
- TYPKI result: Purified water by membranes, 20-times decrease of volume of N containing water, reuse options for impurities/nutrients



Nitrate from explosive residues in water

- Goal: Decrease the content of nitrate in discharge/reuse water, nitrate concentrate for usage
- TYPKI result: 95% purified water with low impurity content, defined concepts for nitrates

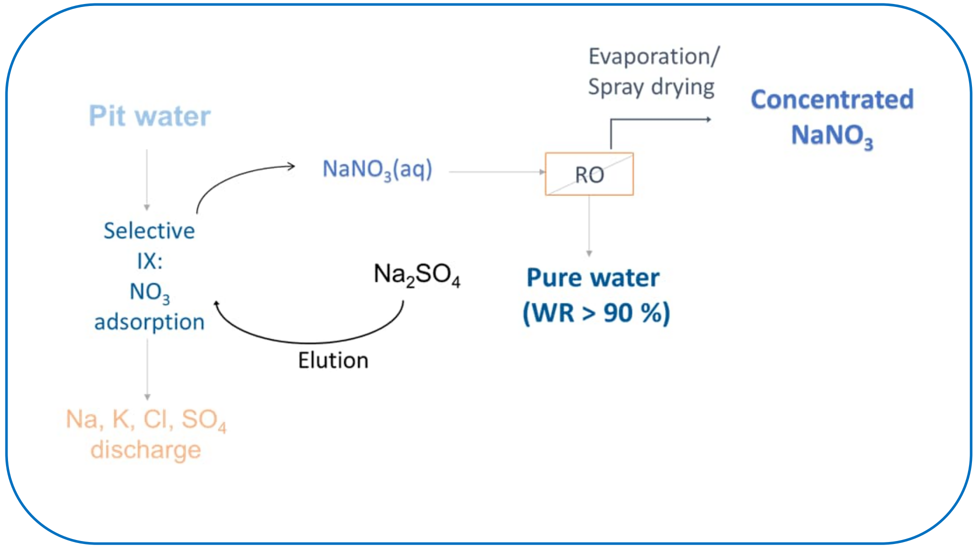




Feed	mg/l
Ca	76
Mg	28
K	76
Na	141
NH4-N	< 0.1
NO3-N	106
SO4	395
Cl	51

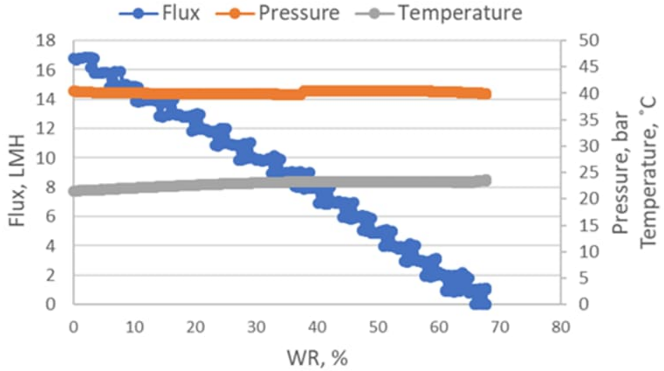
ROconce	mg/l
Ca	80
Mg	64
K	1040
Na	2160
NH4-N	0.8
NO3	3900
SO4	8
Cl	1360

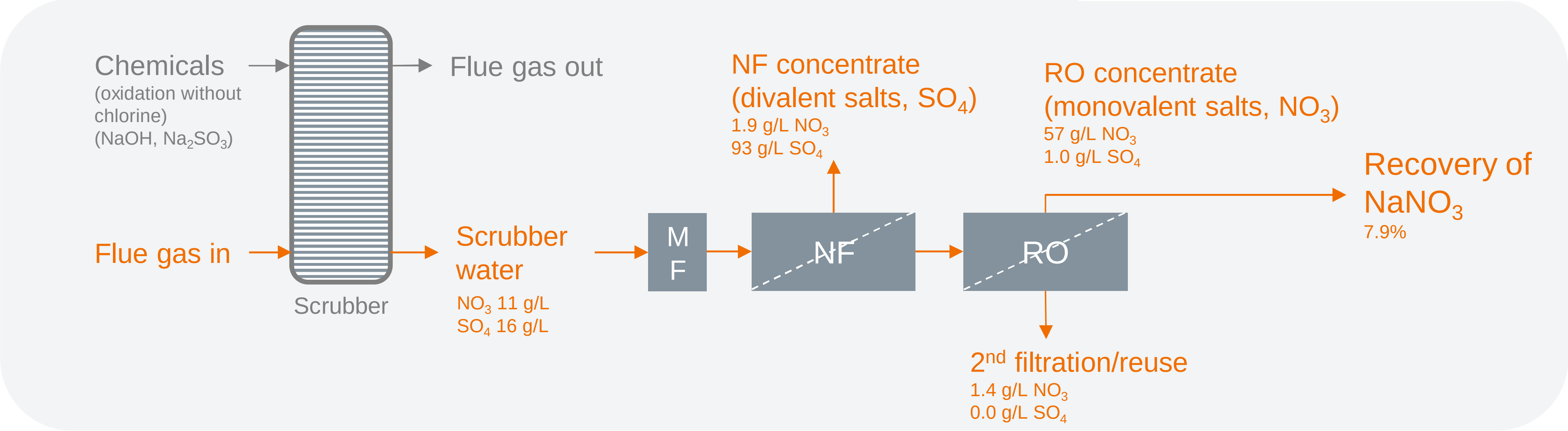
ROperme	mg/l
Ca	1
Mg	0.3
K	2.3
Na	2.4
NH4-N	< 0.01
NO3	< 0.02
SO4	< 1
Cl	1.7



Nitrate from NO_x scrubber water

- Goal: Minimise discharges, increase the concentration of nitrate for usage
- TYPKI result with synthetic water: 87% rejection of nitrate in purified water with 1-pass RO, 5-times concentrated nitrate having 16-times less sulphate

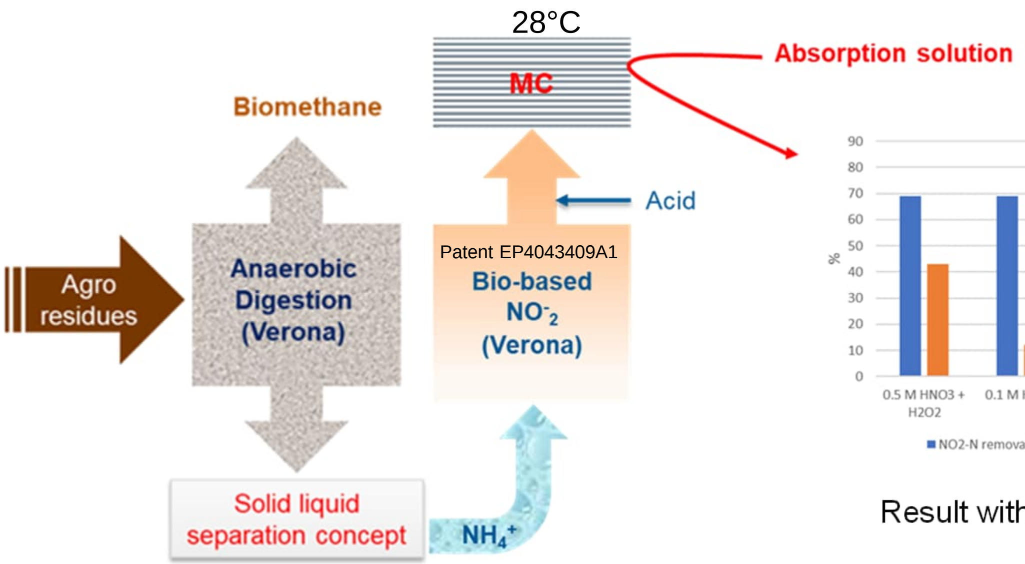


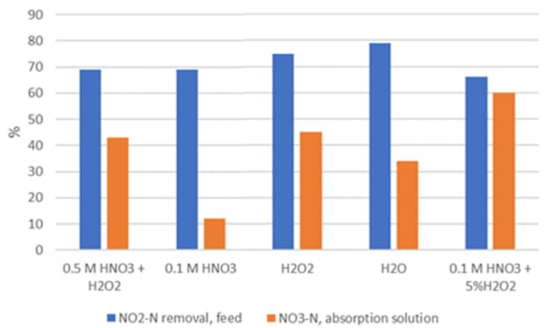


N-products from biogas production

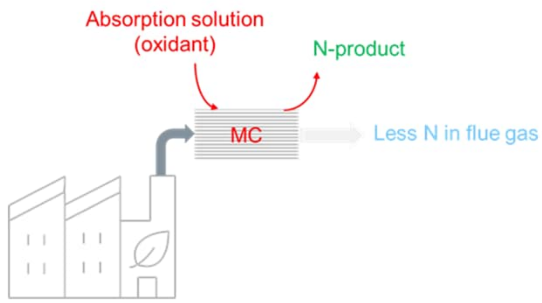
Cooperation with University of Verona/Prof. Nicola Frison

- Goal: Removal of fine suspended solids as a pre-treatment, recovery of N as nitrate from reject water using less chemicals
- Result so far: Ammonium has been biologically converted to nitrite which is chemically vaporized to NOx gas and absorbed as nitrate in oxidizing solution





Result with synthetic waters

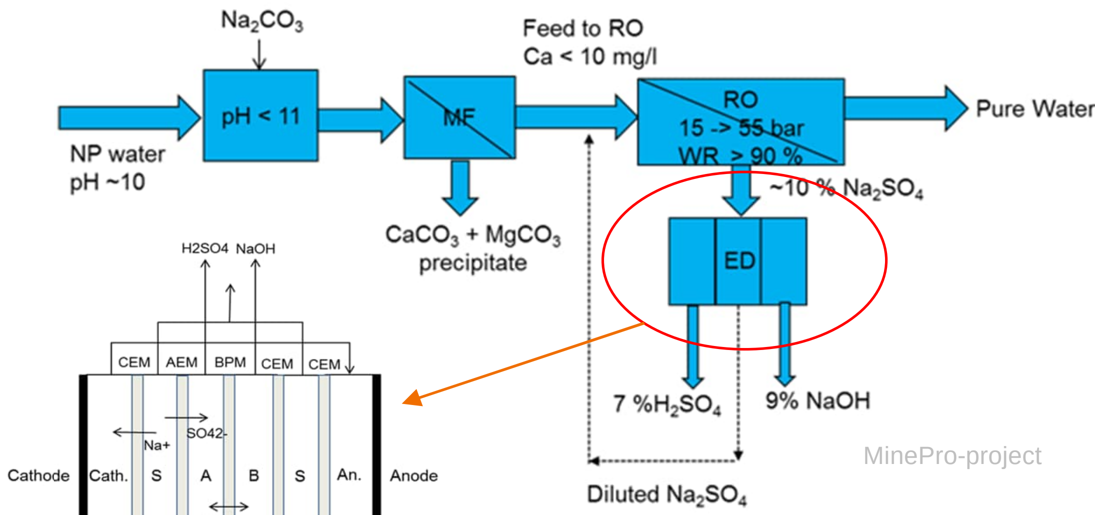


In future?

Sulphate (SO_4^{2-})

Ideas for removal of SO_4 and products recovery

- Precipitation as gypsum, ettringite, barite or Tutton salt
- Membrane technologies for removal and concentration
- Electrodialysis (ED, BPED) for acid and base production
- Biological reduction to sulfide
- Anodic oxidation to persulphate
- Adsorption for removal, Na_2SO_4 as an eluent in desorption
- Ion exchange

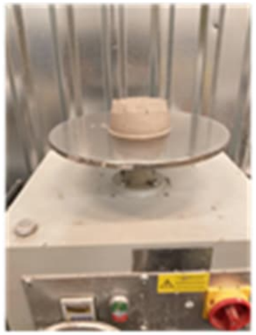


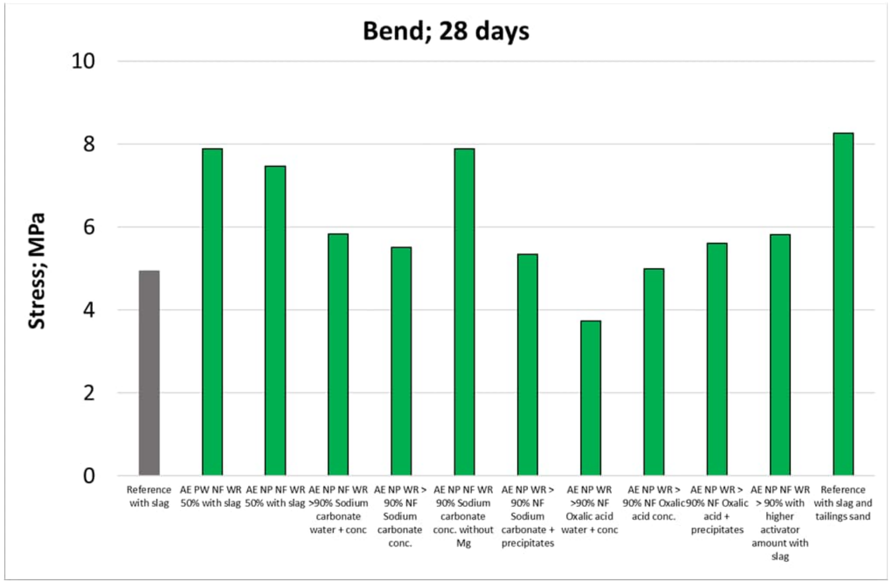
Pajari 2019

g/100 ml, 20°C	Sulphate SO_4^{2-}	Carbonate CO_3^{2-}	Hydroxide OH^-	Sulphide S^{2-}
Na	19.5	21.5	109	18.6
K	11.1	111	112	KOH + KSH
Ca	0.26	$6.2*10^{-4}$	0.17	$Ca(OH)_2$
Mg	35.1	0.039	$9.6*10^{-4}$	0.52
Ba	$2.4*10^{-4}$	$2.4*10^{-3}$	3.86	7.86
Cd	76.6	$3.9*10^{-5}$	$2.6*10^{-4}$	$1.3*10^{-12}$
Al	36.4	$Al(OH)_3$	$2*10^{-8}$	$Al(OH)_3$
Cr	220	insoluble	insoluble	insoluble
Cu	32	$1.5*10^{-4}$	$8.1*10^{-7}$	$1.4*10^{-15}$
Fe	28.8	$6.6*10^{-5}$	$5.3*10^{-5}$	insoluble
Mn	62.9	$4.9*10^{-5}$	$3.2*10^{-4}$	$5*10^{-3}$
Ni	44.4	$9.6*10^{-4}$	0.013	insoluble
Pb	0.004	$7.3*10^{-5}$	$1.6*10^{-4}$	$6.8*10^{-13}$
Zn	53.8	$4.7*10^{-5}$	$4*10^{-5}$	insoluble

Construction products from sulphate containing membrane concentrates

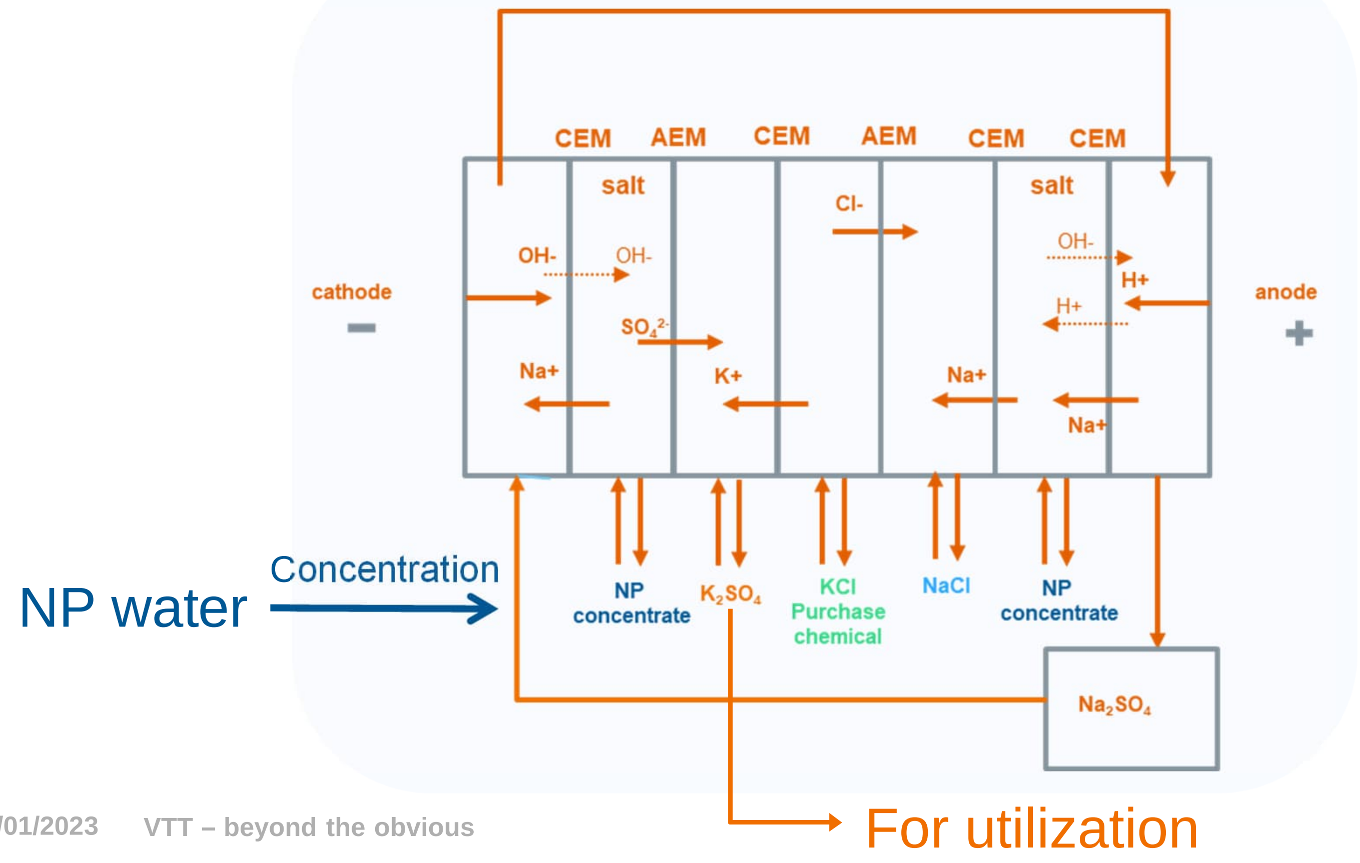
- Goal: Sustainable method for disposal of concentrates after water and nutrients recovery
- TYPKI result: Concentrates have been stabilized into construction products with excellent results; good strength properties; leaching of SO_4^{2-} and Cl^- needs to be taken into account for the tightest MARA limits





Valuable products from waste Na_2SO_4

- Goal: Valorise waste salt to usable product/incredient
- TYPKI result: Conversion of Na_2SO_4 to K_2SO_4 and NaCl by ED

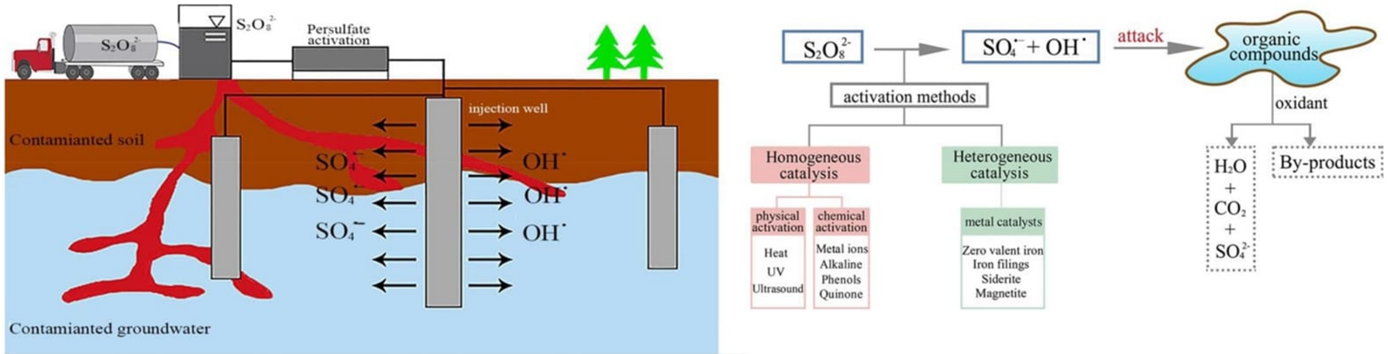


Advantages:
- Higher price
- No limit for NaCl discharge

Disadvantages:
- Dilute product
- Energy consumption

Ideas of utilisation sulphate as persulphate

- Goal: Utilise SO4 -side stream as a usable chemical
- TYPKI result so far based on literature:
  - Manufacturing possible from concentrates by electrolytic way
    - Concentration needs to be high to produce precipitate of persulphates.
    - NH_4SO_4 and K_2SO_4 have higher efficiencies as Na_2SO_4
  - Identified applications:
    - Advanced oxidizing processes (AOP)
    - Cyanide oxidation to less harmful compounds
    - Chloride removal by oxidation to Cl_2 gas
    - Metal leaching



Zhou, Y. et al. (2018). *Journal of hazardous materials*, *359*, 396-407.

TYPKI-project group at VTT

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