Progress Update

Nitrogen Extraction from Water

NEWBIES

by an Innovative Electrochemical System

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29 April 2020

Update last weeks (January-February 2020)

Main targeted issues:

1. **Ionic shortcut** → glass beads on cation concentrate side.
2. **Low NH_4^+ Feed concentration (0.2-0.3 g N-NH_4/L)** → increased in March to 450-500 mg/L probably due to maintenance of the centrifuges (February)
3. **Relatively high concentration of cations in Feed solution** → Donnan
   (in mg/L):
   - Na^+ = 90
   - K^+ =110
   - Mg^{2+} =26
   - Ca^{2+} =90
   - Fe=? (Ferric Chloride used in the WWTP as coagulant, Fe not possible to measure via IC)
4. **Low temperature of feed solution** → pre-heating of feed Heater placed in Feed ED Recirculation vessel to keep temperature at 30 °C → **24 °C max reached temperature**

Update last weeks (January-February 2020)

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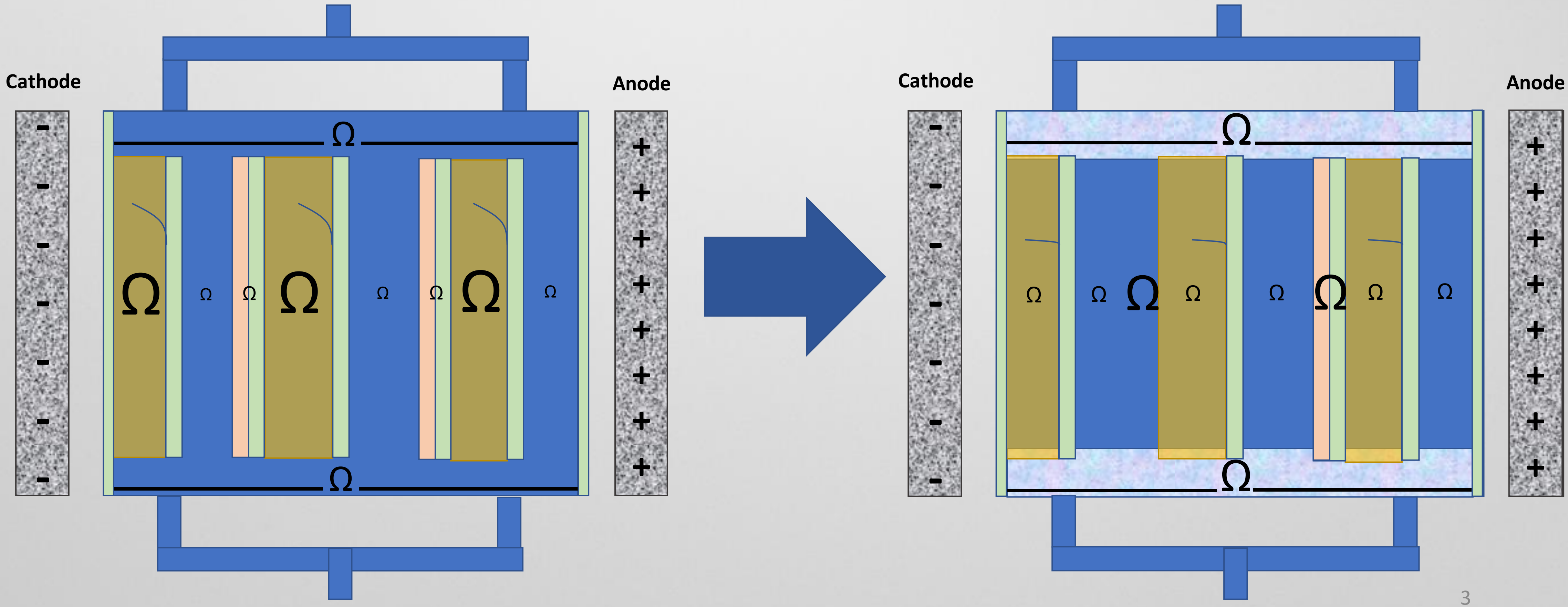
- Ionic shortcut. → **Glass beads**



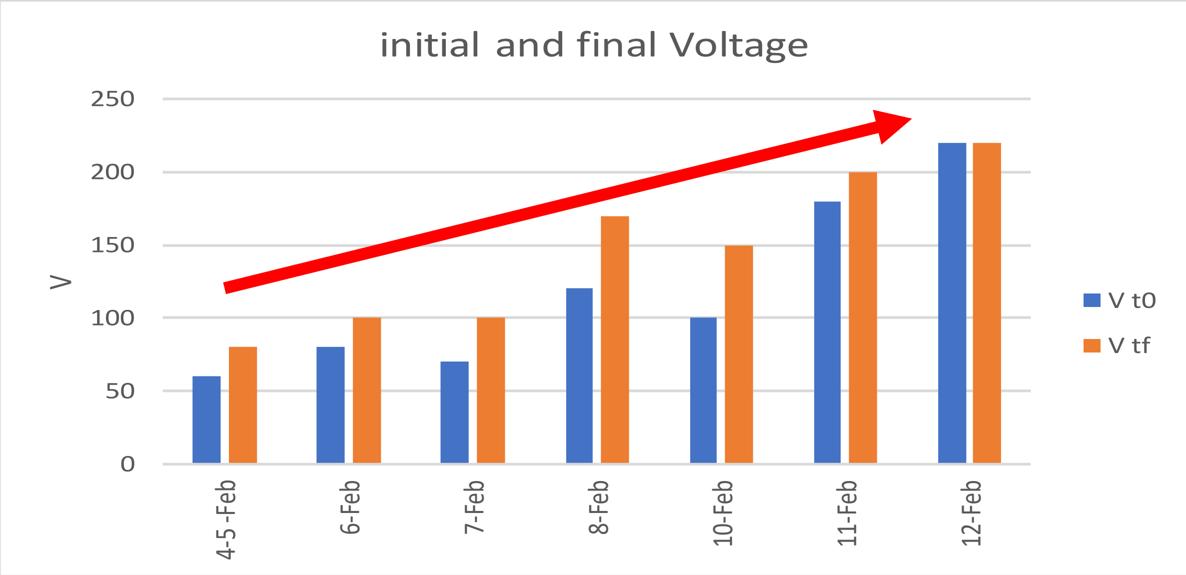
Where were we? Conclusions after last joint meeting (13 February 2020)

Part 1: Recent pilot progress

- Pilot made good progress, with stable CEs, appreciable RE and energy consumptions
- Improvements were partially ascribed to the method of Donnan exchange, and mainly to the addition of glass beads to the concentrate compartments
- However during latest experiments voltage of the stack had gradually gone up, decreasing the energy efficiency of the progress. Cleaning methods used so far had not been able to tackle this
- A brainstorm was kept regarding what is the cause and possible ways to deal with this

Donnan 25%, 75 A/m² (*Feed Flow 50 L/h*)

	Name	Wastewater	Current and Donnan frequency	Feed Flow rate	Load Ratio	Date
1	Donnan Low Flow	Reject WW	75A/m2 (18%)	136 L/h (18%)	LR=3.6	31.01
2	Donnan Mid Flow	Reject WW	75A/m2 (18%)	200 L/h (18%)	LR=2.5	3.02
3	Donnan High Flow	Reject WW	75A/m2 (25%)	200 L/h (25%)	LR=2.5	5.02
4	Donnan High Flow (2)	Reject WW	75A/m2 (25%)	200 L/h (25%)	LR=2.5	7.02
5	Donnan High Flow (3)	Reject WW	75A/m2 (25%)	200 L/h (25%)	LR=2.5	10.02
6	Donnan High Flow (4)	Reject WW	75A/m2 (25%)	200 L/h (25%)	LR=2.5	11.02
7	Donnan High Flow (5)	Reject WW	75A/m2 (25%)	200 L/h (25%)	LR=2.5	12.02



Part 1: Update on pilot progress since February 13th

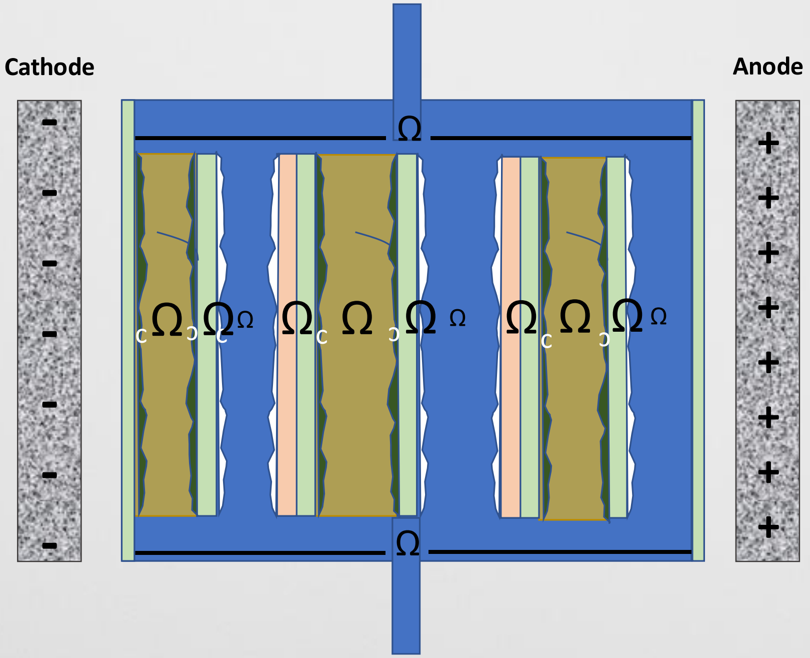
The following recommended practice has resulted:

1. Sample the visually present coagulates from the feed compartment first, so it can be analysed, first visually, maybe with SEM, then analytically
2. The tap water used for cation concentrate refill should be tested for TOC

	Na	N-NH4	K	Mg	Ca	IC	TOC
Tap Water WWTP	111,6	5,7	20,2	12,7	82,7	60.5	10.8

3. In attempt to restore the cell performance, systematically give each process compartment an acid/base wash. See whether this solves the issue
4. A leakage in 2 membranes was evident from bubbles forming during membrane cleaning routine (stack aeration)

Donnan 25%, 75 A/m^2 (*Feed Flow 50 L/h*)



After rinsing the feed side with acid it was possible to replicate the test lowering the voltage back to 80 Volts. :

- The increase in voltage was attributed to increased membrane resistance due to scaling formation in the feed compartment due to a leak in one or more membranes (as suggested by air bubbles passing from concentrate to feed side)

Characterization scheme NEWBIES plant

Investigated operational parameters:

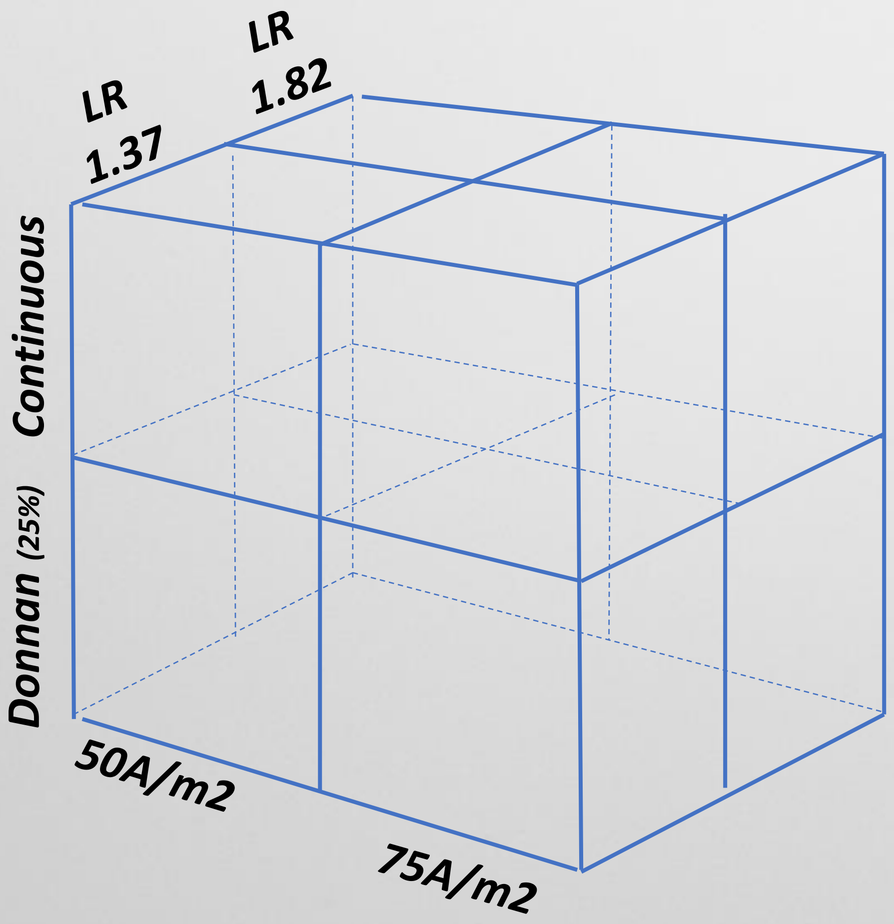
- Current density
- Loading ratio
- Continuous vs Donnan mode

New experimental plan

	description	PSU	Feed pump	Load ratio	Status	Analytical results
Test 1	Donnan 75A/m2 (20 sec ON, 60 OFF)	75A/m2 (25%)	200 L/h (25%)	1.37	✓ 02,05 March	✓
Test 2	Donnan 100 A/m2 (20 sec ON, 60 OFF)	100 A/m2 (25%)	200 L/h (25%)	1.82	✓ 10,12 March	Partial
Test 3	Donnan 75A/m2 (20 sec ON, 60 OFF) high initial Cat conc pH	75A/m2 (25%)	200 L/h (25%)	1.37	✓ 26 Feb, 09 March	Partial
Test 4	Continuous 75A/m2	75A/m2	150 L/h	1.82		
Test 5	Donnan 50A/m2 (20 sec ON, 60 sec OFF)	50A/m2 (25%)	132 L/h (25%)	1.37		
Test 6	Donnan 50A/m2 (20 sec On, 60 sec OFF)	50A/m2 (25%)	100 L/h (25%)	1.82		
Test 7	Continuos 50A/m2	50A/m2	132 L/h	1.37		
Test 8	Continuos 50A/m2	50A/m2	100 L/h	1.82		

- Tests were run in duplicate,
- Each run had a duration of one day (unless the TMCS or cation concentrate recirculation pump stopped working due to scaling deposition).
- Change of the cleaning procedure: before each test, an acid rinse of the cation concentrate and an acid+base rinse of the feed ED line was operated

New experimental plan – multifactorial design



- *8 tests*
- *2 not possible due to feed flow rate limitations (max flow rate 200L/h) and impossibility to uncouple feeding time with PSU working time. (PRO-Control)*

Data acquisition and processing plan

Real-time monitored variables:

- Voltage
- pH / Conductivity
- Sulfuric Acid Dosing
- Recirculation flow rates
- Process water levels and fluxes

Chemical composition analysis:

- All common anions and cations
- At 3 points in time per run
- For all process waters

Calculated KPIs (i.e. measured performance):

- (net) transport numbers/coulombic efficiencies
  - for all ion species
  - per process water/compartment
- Product flux / concentration / purity
- N Removal/Recovery Efficiency
- Specific energy consumption (kWh/kg N recovered)

Results: *Test 1, Test 2 and Test 3*

	description	NH_4 conc	PSU	Feed pump	Load ratio	Status	Analytical results
Test 1	Donnan 75A/m2 (20 sec ON, 60 OFF)	0.45 g/L	75A/m2 (25%)	200 L/h (25%)	1.37	Done 02,05 March	✓
Test 2	Donnan 100 A/m2 (20 sec ON, 60 OFF)	0.45 g/L	100 A/m2 (25%)	200 L/h (25%)	1.82	Done 10,12 March	Partial
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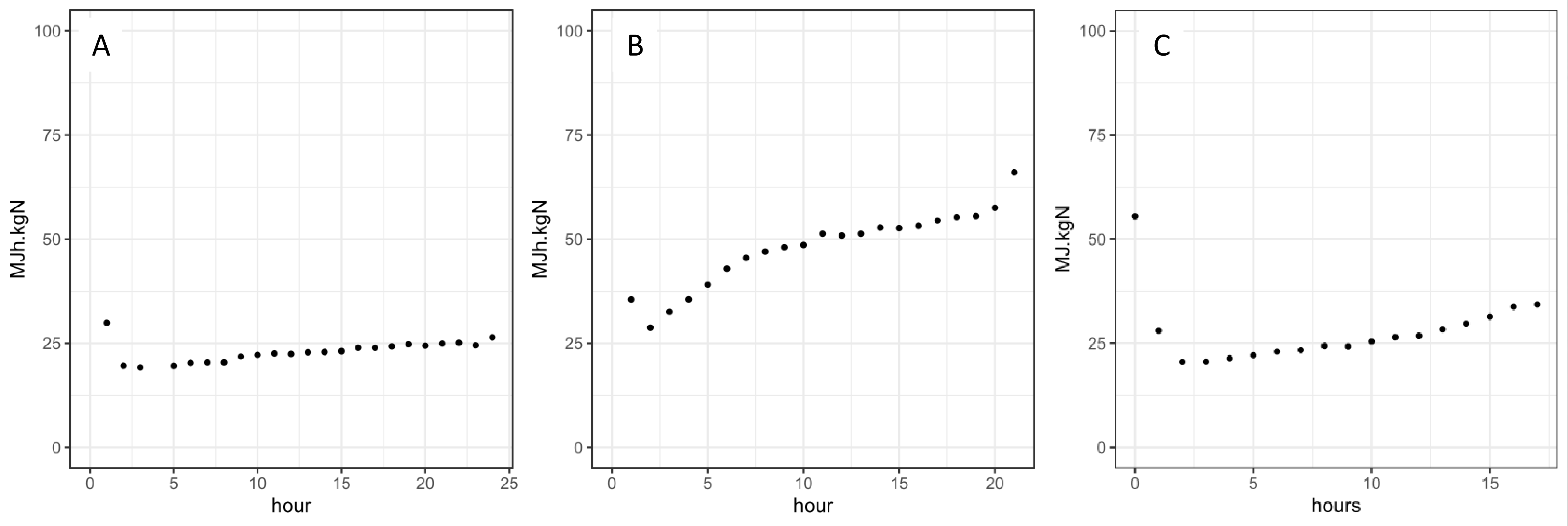
Results– *Energy consumption per kg of N recovered*



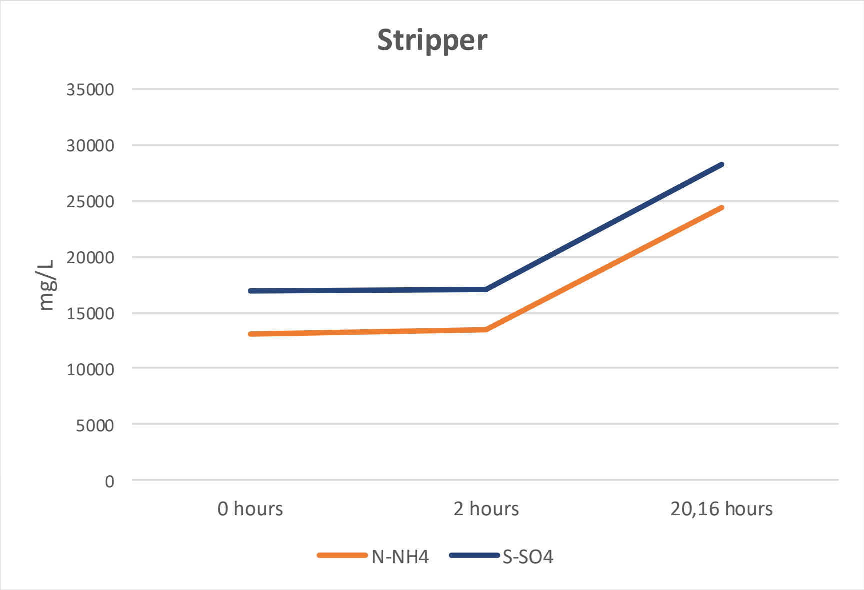
Test 1
Donnan 75 A/m2 (20 sec ON, 60 OFF) LR=1.37

Test 2
Donnan 100 A/m2 (20 sec ON, 60 OFF) LR=1.82

Test 3
Donnan 75A/m2 (20 sec ON, 60 OFF) LR=1.37, high initial Cat conc pH

Results– *Product characteristics*

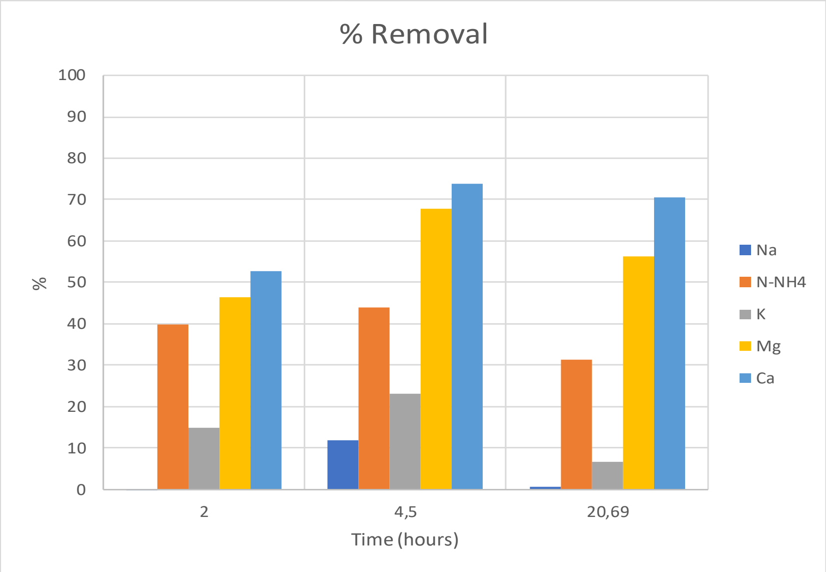
Test 1	Test 2	Test 3
Donnan 75 A/m2 (20 sec ON, 60 OFF) LR=1.37	Donnan 100 A/m2 (20 sec ON, 60 OFF) LR=1.82	Donnan 75A/m2 (20 sec ON, 60 OFF) LR=1.37, high initial Cat conc pH

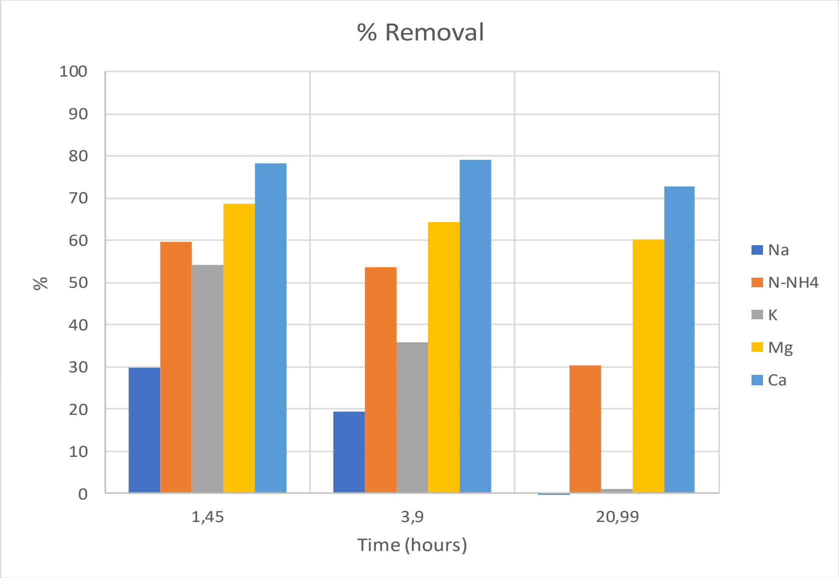


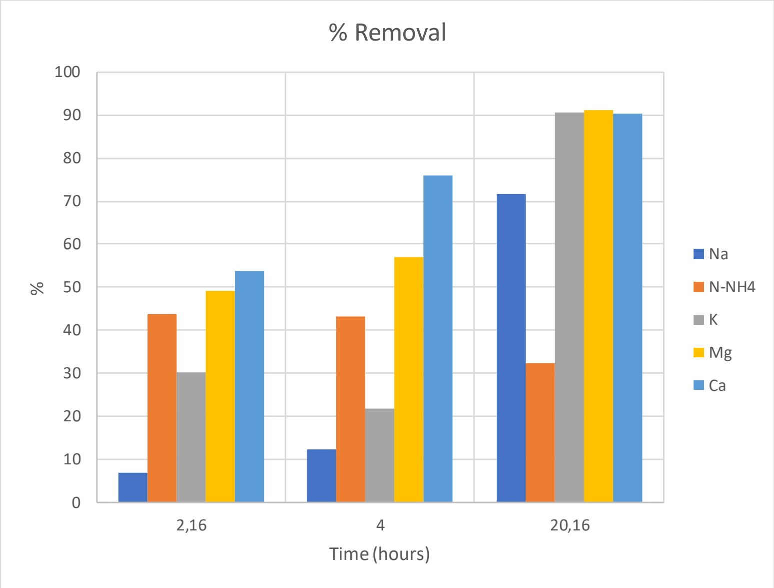
- NH_4^+ concentration in the stripper not higher than 25 g $N\text{-}NH_4$ /L in any test.
- In test 3 initial stripper had to be refilled with DI water

Cations removal efficiencies

Test 1	Test 2	Test 3
Donnan 75 A/m2 (20 sec ON, 60 OFF) LR=1.37	**Donnan 100 A/m2 (20 sec ON, 60 OFF) LR=1.82**	**Donnan 75A/m2 (20 sec ON, 60 OFF) LR=1.37, high initial Cat conc pH**



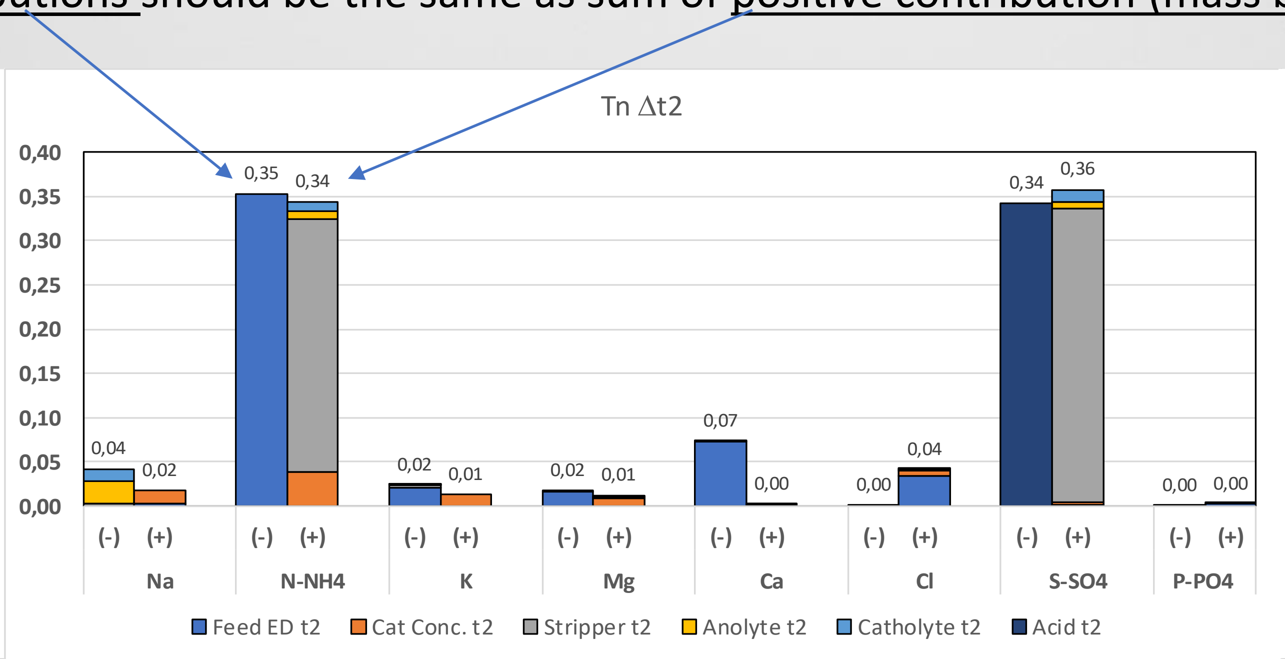




- NH_4: higher for test 2 during the first 2 samples due to the higher current density. And slightly higher for test 3 compared to test 1 probably because of the higher initial pH.
- High removal efficiencies of Ca, Mg

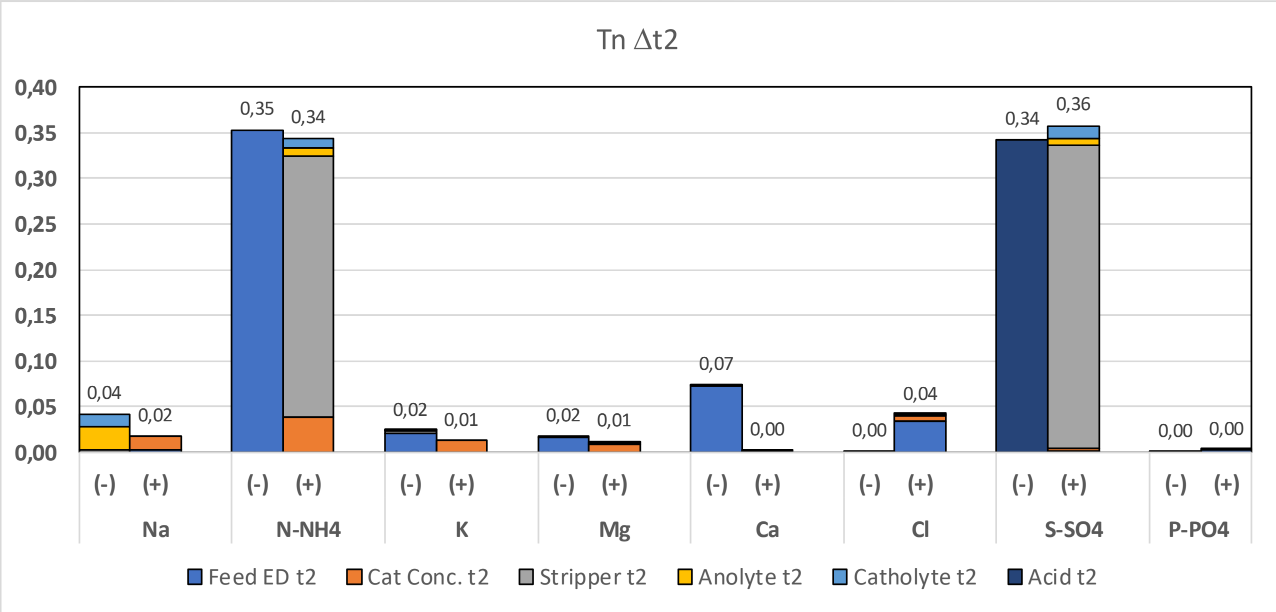
Ion transport number results

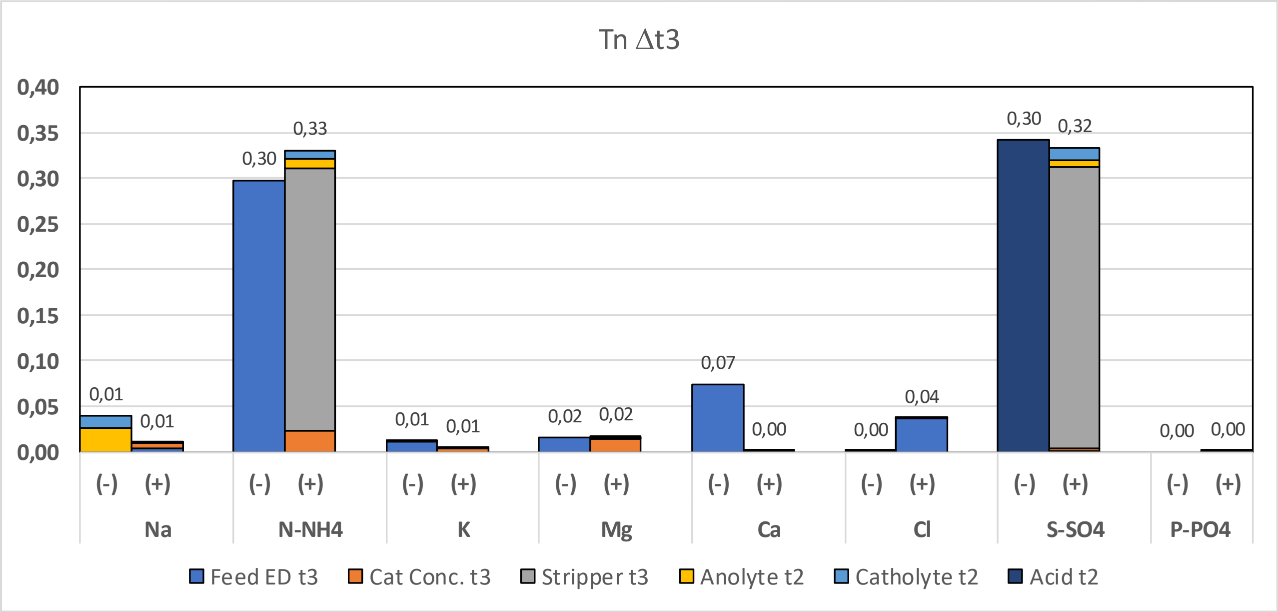
- Ion transport number is the fraction of the total electrical current carried in an electrolyte by a given ionic species.
- 2 results: one for Δt2 (2 hours of maximum CE), the other for Δt3 (from the end of Δt2 till 20th hour since test was started
- Gives information about Coulombic efficiency and mass balance.
- Every ionic species has a negative contribution meaning that ion left the corresponding compartment and a positive contribution meaning that the ion is entering and accumulating in the corresponding compartment.
- Sum of <u>negative contributions</u> should be the same as sum of <u>positive contribution (mass balance)</u>.



Test 1– *Ion transport number*

Test 1
Donnan 75 A/m2 (20 sec ON, 60 OFF) LR=1.37

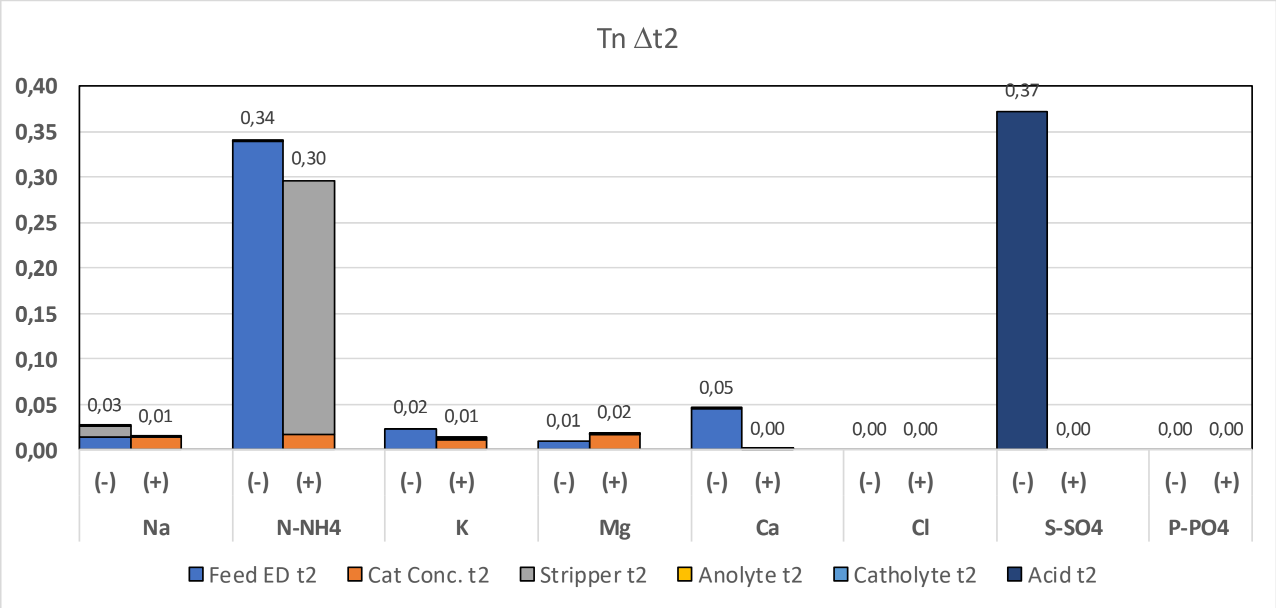


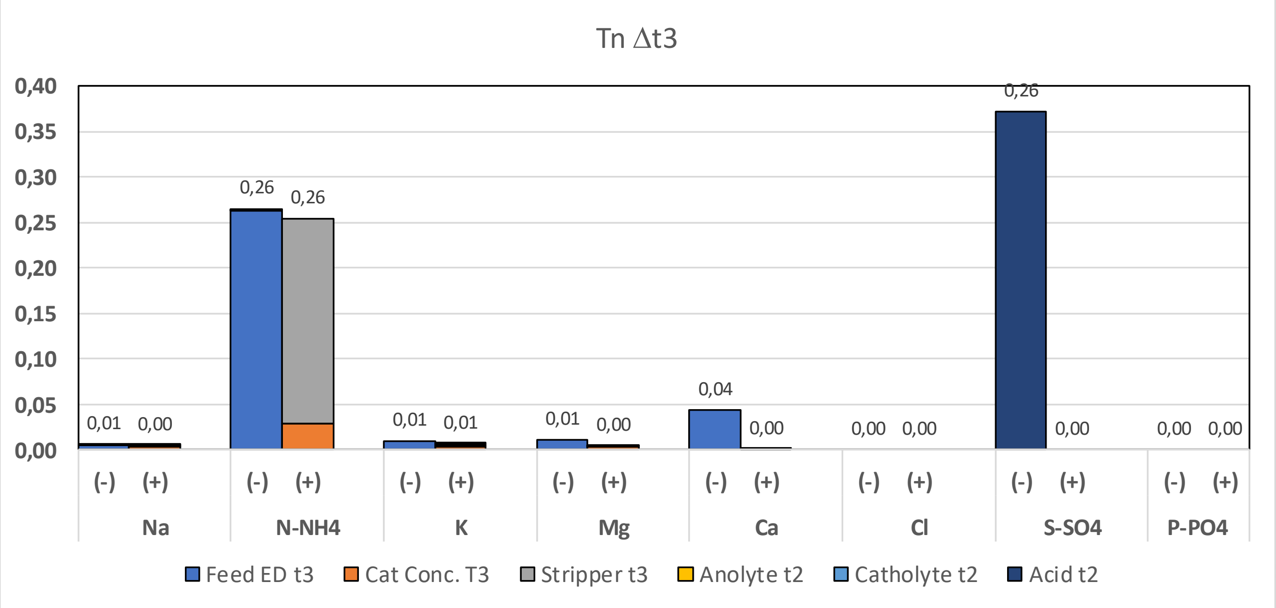


- NH_4: Considering the NH_4 removed from feed, 6% accumulates in the cati. conc. without passing through the TMCS membrane, 5.5 % accumulates in the catholyte/anolyte and the rest 88.5% pass the TMCS and leaves the system with the product.
- Na, K, Mg, Ca: sum of the negative contribution is not equal to the sum of the positive contribution with the first being higher due to scaling formation and cations not more present in dissolved form.
- SO_4: A small fraction diffuses through the TMCS membranes and accumulates in the cat. Conc. and the catholyte/anolyte.

Test 2– *Ion transport number*

Test 2
Donnan 100 A/m2 (20 sec ON, 60 OFF) **LR=1.82**



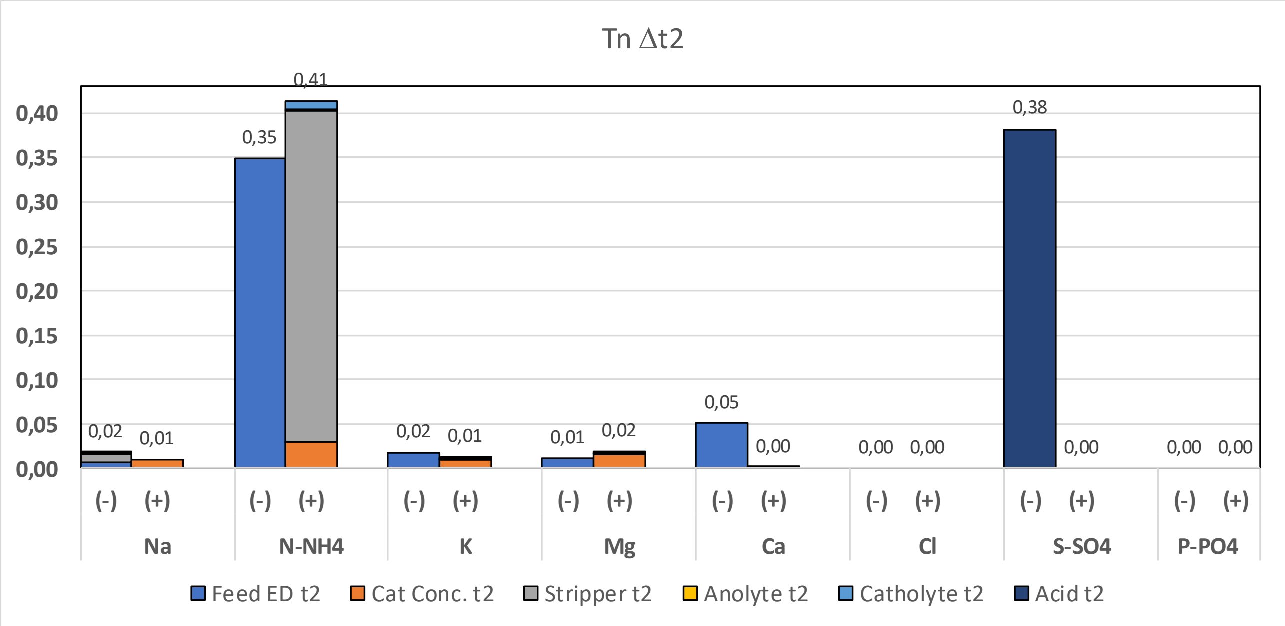


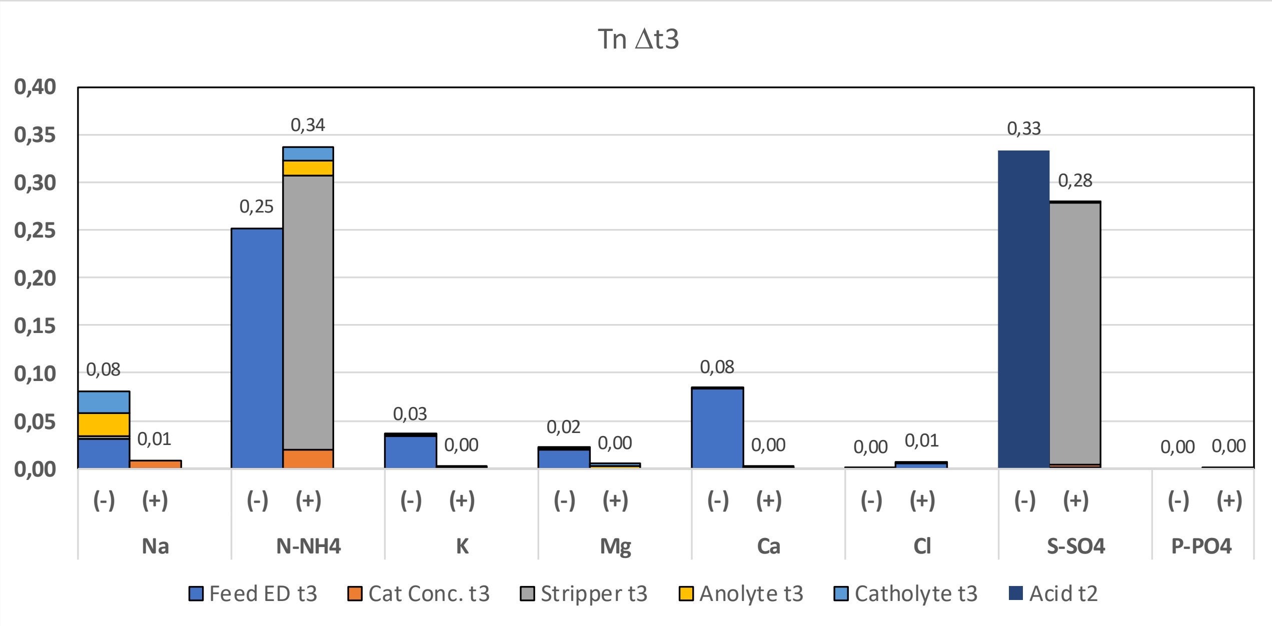
- Lower coulombic efficiency during Δt2
- Higher percentage of NH4 (11%) stays in the cation concentrate. The high presence of NH_4 in the cat concentrate could be due to the relatively low pH of the cation concentrate during the first time interval. AT pH 8.9 and operational temperature (22°C) only 19% of the ammonia is in gas form. During the second interval it can be attributed to the combination of low pH and the increasing scaling problems in the TMCS module that represent a limitation for ammonia to pass from the cation concentrate to the stripper solution.

Test 3– *Ion transport number*

Test 3

Donnan 75A/m2 (20 sec ON, 60 OFF)
LR=1.37, high initial Cat conc pH





Similar results to test 1 but with better results for Δt2 due to the higher pH and lower test duration until TMCS pump stopped working probably due to the higher faster scaling due to the higher pH;

Cl, PO_4: completely washed out by the system in every test confirming the good cation membranes functioning.

Tests– *conclusions*

- Maximum Coulombic efficiencies were 45% for test 1 and 3 while 40% for test 2.
- CE decreased faster for test 2 and 3 because of the quickest scaling deposition due to higher applied current and higher pH respectively.
- TMCS recirculation pump stopped working before 24 hours of operation for test 2 and 3 due to the same reason of the previous point.
- NH_4 removal efficiencies from the feed were up to 40% for test 1, 3 and 60% for test 2
- Average daily NH_4 recovered via product about 160-200 gN-NH_4/day, still far from project target 1kgN/day but probably related to the low concentration of ammonia in reject WW.
- Iron might have a big role in the ion transport number. Iron will be measured in the samples with kits since it is not detectable via IC.
- Energy consumption per Nitrogen recovered was double for test 2. And for test 1 averaged 20 MJ/kgN (not taking into account pump functioning) which is close to the target of 18 MJ/kgN. Operational parameters of test 1 gave the best results in terms of longer test duration, higher energy efficiency
- Results reproducibility (same results for duplicates) suggests that membrane leakage should not represent an issue for one day tests in case it does not get bigger.

Conclusion: Effect of N:Ca ratio

- Ca^{2+} Mg^{2+} K^{+} precipitate when free carbonate is around
- This is always the case when pH>7
- pH needs to be >>8 for ammonia-stripping (pkA=9.26)
- Transported cations will therefore always precipitate
- Calcium gradient will always be more favorable than ammonia, as long as it is not depleted
- Divalents are more strongly transported in potential field
- System can handle x amount of Ca^{2+} Mg^{2+} K^{+} deposits before it needs cleaning
- **Therefore, N:Ca,Mg,K ratio determines amount of cleaning needed per kg of N recovered**

Test 3– *next experiments*

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- 4-5 weeks to complete remaining tests (tests 4-8).
- PhACs analysis to check concentrations in feed, cation concentrate & product.