Nitrogen Extraction from Water By an Innovative Electrochemical System

Deliverable for action B3

Report on operational experience and performance of NEWBIES on leachate

Dec 2021

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Abbreviations

BPM: Bipolar Membranes

CEM: Cation Exchange Membranes

CIP: Clean in Place

EC: Electrical Conductivity

ED: Electro Dialysis

EIW: Evides Industriewater

KPI: Key Performance Indicator

LR: Load Ratio

N.E.W.B.I.E.S.: Nitrogen Extraction from Water By an Innovative Electrochemical System

NMZ: Noord Midden Zeeland

OCD: Operational Current Density

PWZI: Percolaat Water Zuivering Installatie

PSU: Power Supply Unit

SHE: Safety, Health, and Environment

STR: Stripper

TMCS: Trans Membrane ChemiSorption

TIC: Total Inorganic Carbon

TOC: Total Organic Carbon

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1. Introduction

This report covers the progress made and scientific results obtained in the third operational phase of the Nitrogen (N) Extraction from Water By an Innovative Electrochemical System (N.E.W.B.I.E.S.) pilot treatment of landfill leachate water from the solid waste landfill of Indaver located in Nieuwdorp, the Netherlands.

The primary aim of this third pilot phase was to evaluate the operation of the pilot when treating landfill leachate, with respect to the project proposal defined key performance indicators. There were most notably (1) mass recovered (kg N recovered /day), (2) removal/recovery efficiency (percentage of N removed from the leachate and recovered in the product), and (3) energy efficiency (kWh spent per kg N removed/recovered).

In the second phase of the N.E.W.B.I.E.S. pilot research (Urine case), a second stack, referred to as "spider-stack", was implemented in the system to reduce the phenomenon called ionic shortcuts and therefore to lower the energy efficiency losses. In the third pilot phase, the spider-stack was initially used for the treatment of the landfill leachate. However, energy efficiency losses were still detected and therefore a third stack, referred to as "third generation stack", was commissioned to further reduce the ionic shortcuts. The performance of the system with the two tested stacks during the third phase is discussed in this report.

To allow for a complete and structured analysis and exploration of the abovementioned issues, the research goals in this third pilot phase were as follows:

1. Wastewater characterization
2. Short-term process optimizations (within a Clean in Place (CIP) cycle)
3. Long-term process characterization and analysis
4. Influence of pH control

2. Background Information

Leachate Origin

The landfill leachate wastewater from the solid waste landfill of Indaver located in Nieuwdorp is collected with a drainage system and treated in the Percolaat Water Zuivering Installatie Noord Midden Zeeland (PWZI NMZ) of Evides Industriewater (EIW). A top view of the landfill and the PWZI located nearby is given in Figure 1. The landfill area consists of seven segments that are drained independently resulting in 7 different water streams of leachate that are then combined in one waste stream and treated together in the PWZI. The solid waste in each segment has different age and in many cases origin. Some segments are full and thus covered permanently and some are still in use. From all segments waste water is drained. But, the segments that are still in use/open, since they accept higher amounts of rainfall, have the highest contribution in the overall leachate flow (approximately 200 m^3/d).

Figure 1: Top view of the landfill of Indaver and PWZI of EIW at Nieuwdorp

Leachate Water Quality

The ammonium (NH_4^+) concentration in leachate ranges between 1000 to 1800 mg NH_4^+/L. This high ammonium content was the factor that made this stream interesting to be tested within the N.E.W.B.I.E.S. pilot project for NH_4^+ recovery. However, leachate is a complex stream that contains in high concentration other constituents such as sodium (Na^+), chloride (Cl^-), potassium (K^+), calcium (Ca^{2+}) and more. Also, leachates contain in significant concentrations inorganic and organic carbon (IC and TOC). In Table 1 the average concentrations of several water quality parameters of the leachate is given.

Table 1: Nieuwdorp leachate water quality (average of 19 samples)

Parameter	Symbol	Average	SD	Unit
pH	-	7.5	0.3	-
Ammonium	NH_4^+	1500	100	mg/L
Sodium	Na^+	5700	550	mg/L
Potassium	K^+	950	70	mg/L
Calcium	Ca^{2+}	180	20	mg/L
Magnesium	Mg^{2+}	150	10	mg/L
Chloride	Cl^-	8500	900	mg/L
Sulphate	SO_4^{2-}	360	100	mg/L
Phosphate	HPO_4^{2-}	50	30	mg/L
Total Carbon	TC	1250	1000	mg/L
Inorganic Carbon	IC	700	500	mg/L
Total Organic Carbon	TOC	550	400	mg/L

Comparison to Water Quality of Other Leachate Streams in Literature

In Table 11 and

Table 12 of Appendix A the average concentrations of several water quality parameters in leachates from landfills spread throughout the world available in the literature are gathered. An interesting observation is that the average values for many parameters fluctuate between the different cases. This results in a wide concentration range for the different parameters as can be seen in Table 1Table 2, where the lowest and highest average values noted in the leachate landfills from different countries are given.

The NH_4^+ value in Nieuwdorp leachate is within the range of lowest and highest average from other landfills cases. It should be noted that in the NH_4^+ average values in other leachates, 9 out of the 19 cases of other landfills have a value around 1250 mg NH_4^+/L (see Table 11 and

Table 12) and therefore are in the same range of Nieuwdorp leachate NH_4^+ content. Most of the other parameters mentioned for Nieuwdorp leachate are also within the range of lowest and highest average from other landfill cases, which was expected since the ranges are quite large as mentioned before. The Na^+ and Cl^- concentration in Nieuwdorp leachate is higher than that observed in other landfills, but still in the same order of magnitude.

The main conclusion made when comparing the water quality of Nieuwdorp leachate with leachates from other landfills is that in general leachate streams are unique. This conclusion was also verified by the manager Safety, Health and Environment (SHE) from Indaver (the owner of the Nieuwdorp landfill and therefore leachate stream).

Table 2: Comparison between the water quality of the leachate from Nieuwdorp landfill (Indaver) with the lowest and highest average leachate water quality from other landfills

Parameter	Symbol	Unit	Nieuwdorp Leachate Average	Other landfills Lowest – highest Average
pH	-	-	7.5	6-9
Total Organic Carbon	TOC	mg/L	550	700-12000
Ammonium	NH_4^+	mg/L	1500	100-7000
Nitrate	NO_3^-	mg/L	<10	3-500
Nitrite	NO_2^-	mg/L	<10	1-8
Phosphate	HPO_4^{2-}	mg/L	50	4-500
Chloride	Cl^-	mg/L	8500	800-5500
Sulphate	SO_4^{2-}	mg/L	360	1-3000
Sodium	Na^+	mg/L	5700	200-4000
Potassium	K^+	mg/L	950	350-3500
Magnesium	Mg^{2+}	mg/L	150	15-500
Calcium	Ca^{2+}	mg/L	180	15-2400
Zinc	Zn^{2+}	mg/L	35	0.15-17
Manganese	Mn^{2+}	mg/L	0.4	0.04-33
Iron	Fe^{3+}	mg/L	0.7	0.2-780
Arsenic	As^{5+}	µg/L	<2000	12-160
Cadmium	Cd^{2+}	µg/L	<500	6-100
Chromium	Cr^{2+}	µg/L	300	60-2200
Copper	Cu^+	µg/L	<500	50-390
Nickel	Ni^+	µg/L	<500	100-1350
Lead	Pb^{2+}	µg/L	< 500	4-3500

Comparison of Leachate Water Quality to the Digestate and Urine

The landfill leachate was considered the most challenging stream to treat with the N.E.W.B.I.E.S. pilot compared to digestate and urine due to its complex water composition. In Table 11 the water quality of leachate in comparison to digestate and urine is given. The NH_4^+ content in leachate was higher compared to the other two streams, but at the same time, it contained high concentrations of cations competitive to NH_4^+ (Na^+, K^+, Ca^{2+}, and Mg^{2+}). Figure 2, in which the ratios of the different ion over NH_4^+ content are given, facilitates the comparison between the three streams tested within the N.E.W.B.I.E.S. pilot. Noticeable are the ratios of Na^+ and Cl^- over NH_4^+ that in leachate reached a value as high as 3, while in the other two streams were below 0.5. This means that in the other two streams the main contributor in the overall ion composition was NH_4^+, while in leachate this was salt (NaCl). Also, K^+ and Ca^{2+} ratios over NH_4^+ were higher in the case of leachate compared to the other two streams. Mg^{2+} ratio over NH_4^+ was higher compared to urine and at the same level compared to digestate. The high content of Ca^{2+} and Mg^{2+} can possibly result in scaling issues, as was observed in the digestate phase of the N.E.W.B.I.E.S. pilot. Moreover, the high presence of organics (double compared to digestate and 30-times higher compared to urine) leads to a high membrane fouling potential. Finally, a positive characteristic of the leachate water is that throughout the year daily and seasonal variations of the composition are small, which can allow stable operation with the N.E.W.B.I.E.S. system in contrast to the urine case.

Table 3: Nieuwdorp leachate water quality with Digestate and Urine water qualities

Parameter	Symbol	Unit	Leachate	Digestate	Urine
pH	-	-	7.5	7.6	8.5 – 9
Total Carbon	TC	mg/L	1250	488	41
Total Organic Carbon	TOC	mg/L	550	62	15
Ammonium	NH_4^+	mg/L	1500	592	1022
Phosphate	HPO_4^{2-}	mg/L	50	22	80
Chloride	Cl^-	mg/L	8500	221	386
Sulphate	SO_4^{2-}	mg/L	360	2.8	264
Sodium	Na^+	mg/L	5700	110	266
Potassium	K^+	mg/L	950	112	285
Magnesium	Mg^{2+}	mg/L	150	31.6	0.18
Calcium	Ca^{2+}	mg/L	180	51.5	1.40

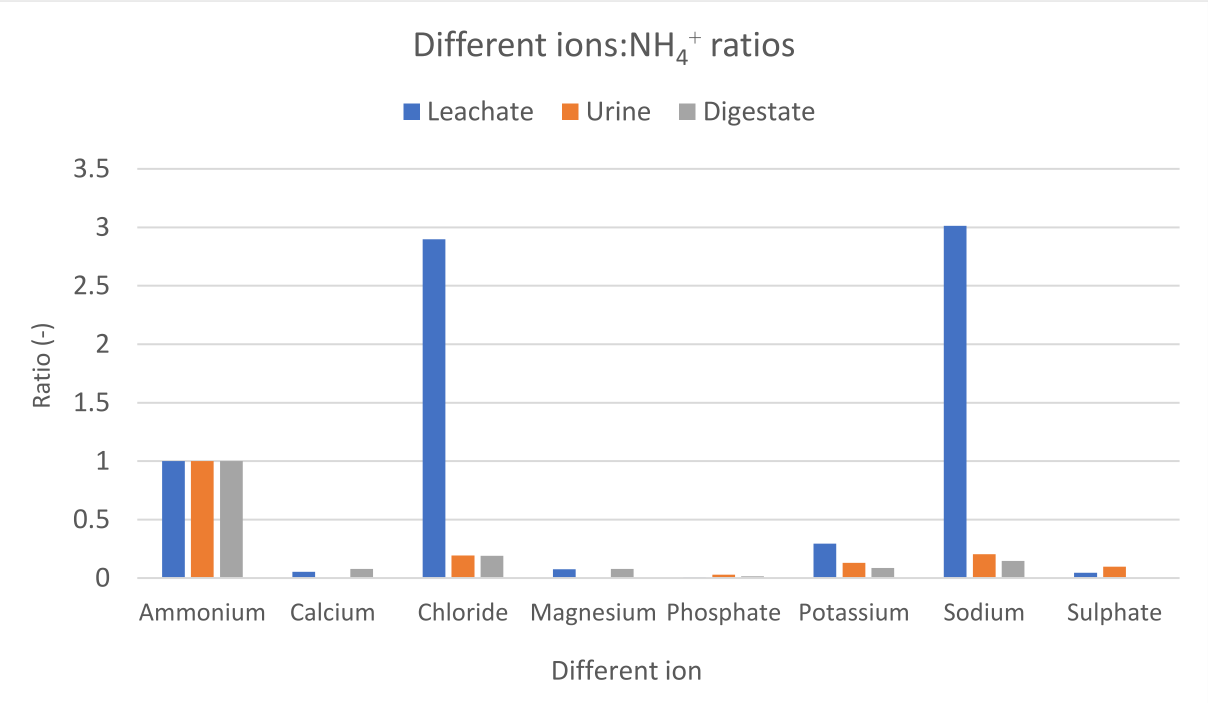

Figure 2: Ratio of the different ion over NH_4^+ concentration in the three streams tested with the N.E.W.B.I.E.S pilot

3. Materials and Methods

Newbies technology

The operational procedure of N.E.W.B.I.E.S. process is depicted in Figure 3 and is described in this paragraph. A waste stream containing high concentrations of N in the form of NH_4^+, landfill leachate in the third operational phase, is introduced into an Electro Dialysis (ED) stack in which the NH_4^+ is transported through the Cation Exchange Membranes (CEM) to a so-called concentrate stream ("ammonia-rich"). It must be noted that Bipolar Membranes (BPM) are also part of the ED stack. The BPM breaks water molecules (H_2O) and thus hydroxyl (OH^-) ions end up in the concentrate stream leading to pH increase. At high pH, the NH_4^+ is converted into volatile NH_3. This step is required for the subsequent step to function properly. Specifically, the concentrate is then introduced into a gas membrane stripper (Trans Membrane ChemiSorption, TMCS), where the gaseous ammonia (NH_3) diffuses across the membrane. In this way, NH_4 is constantly being extracted from the concentrate stream. Therefore, the concentrate coming out of the TMCS is an "ammonia-depleted" stream , which is re-circulated in the ED stack. The NH_3 diffused in the product liquid is turned into NH_4^+ and subsequently recovered as ammonium sulfate ($(NH_4)_2SO_4$) with sulfuric acid (H_2SO_4) dosing. The final product of the process, being the $(NH_4)_2SO_4$, can be used as a fertilizer.

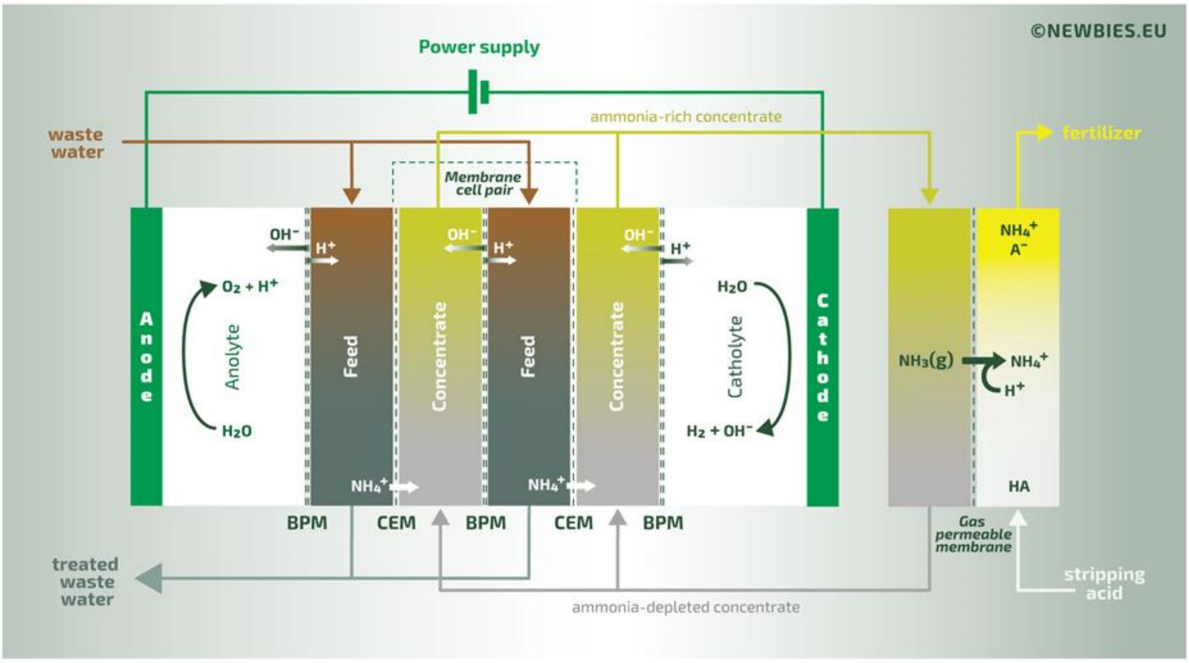

Figure 3: N.E.W.B.I.E.S. process

Terminology and Key Performance Indicators

Before the experimental plan is presented an introduction to some terminology and the Key Performance Indicators (KPI's) is required.

Terms Relevant to ED:

- **Operational Current density (OCD)** with units A/m² is the amount of current applied over the membrane surface.

- **Load ratio (LR)** is the ratio between the applied current and the NH_4-N loading rate and it can be calculated with the formula 1:

$$LR = \frac{Current\ Denisty\ (\frac{A}{m^2}) * Total\ surface\ area\ (m^2)}{NH_4^+\ Concentartion\ (\frac{mol}{L}) * \ Influent\ flow\ (\frac{L}{s}) * \ Faraday\ Constant\ (\frac{C}{mol})} \quad (1)$$

- **Power Supply Unit (PSU) duty cycle (%)** shows the percentage of time when current is applied in the system.

- The **Operation Mode** can be either:
  i. **Continuous,** where the PSU duty cycle (%) is equal to 100. Current is applied throughout all operational time.
  ii. **Donnan,** where the PSU duty cycle (%) is below 100. Current is applied in part of operational time following specific intervals.

KPIs:

- **NH_4^+ Removal (%)** is calculated with formula 2 below based on NH_4 removal from the wastewater:

$$Removal\ (\%) = \frac{NH_4^+ influent\ - \ NH_4^+ effluent}{NH_4^+ influent} \quad (2)$$

- **NH_4^+ Recovery (%)** is calculated with formula 3 below based on the amount of acid used to produce $(NH_4)_2SO_4$:

$$Recovery\ (\%) = \frac{mass\ NH_4^+ produced}{mass\ NH_4^+ influent} \quad (3)$$

- **Ion transport (%)** is calculated with formula 4 and expresses the part of the total charge that is used for the transport of a certain ion (x) over the CEM:

$$Ion\ Transport\ \ (\%) = \frac{Transport\ of\ ion\ x\ over\ the\ CEM}{total\ charge\ applied} \quad (4)$$

  This parameter is interchangeable for the coulombic efficiency (CE) of the process.

- **Product Concentration (g/L)** expresses the $(NH_4)_2SO_4$ concentration in the product stream.

- **Mass recovered (kg N/d)** expresses the N mass recovered in a day.

- **Energy consumption (Wh/g N)** is calculated based on NH_4^+ amount removed.

ED-stack design: Spider-stack versus Third Generation Stack

In the third phase of the N.E.W.B.I.E.S. pilot research (leachate case) two ED-stacks with different designs were tested (Figure 4). The first ED-stack used was the spider-stack, which was also used during the second part of the N.E.W.B.I.E.S. pilot research with urine in Arnhem. The spider-stack consisted of 65 cell pairs and the membrane dimensions were 22x22 cm resulting in a surface of 484 mm^2. The second ED-stack used was the “third generation stack”, which consisted of only 7 cell pairs. It was considered that a design of an ED-stack with lower number of cell pairs can reduce the phenomenon of ionic shortcuts, since ions face less resistance when crossing the membranes than going through the liquid. In order to maintain the treatment capacity of the system despite the lower cell pair number, the surface area of the “third generation stack” was increased to 1936 mm^2 (membrane dimensions

44x44 cm). In both stacks the same CEM and BPM membrane types were used. These were the fumasep® FBM-PK and the fumasep® FKB-PK-130 for the CEM and BPM, respectively.

Figure 4: Spider-stack (left) and third generation stack (right)

Experimental plan

The experimental period during the N.E.W.B.I.E.S. pilot research with leachate was divided in two parts since two ED-stacks were used as it was mentioned in the previous sub-chapter. In Table 4 the experimental plan for the first part of the pilot research with leachate is given. Due to the leachate complexity it was decided to create a matrix of short-term experiments with large steps for the load ratio and the OCD values tested. The loads ratios chosen to be tested were 1, 3 and 9. The chosen OCDs to be tested were 25, 75, 150 and 300 A/m^2. These values result in 12 short-term experiments (characterization runs). However, three experiments (2.3, 2.4 and 3.4 in Table 4) were not possible to be performed, due to hardware limitations (feed flows required could not be reached with the pilot pumps). From them, experiment 2.3 was performed by adjusting the OCD to 120 A/m^2. Also, it should be mentioned that some experiments were performed in duplicate.

An outcome from N.E.W.B.I.E.S. pilot research with digestate was that the Donnan mode of operation is not the optimal choice in presence of divalent ions. Leachate contains in high concentrations Ca^{2+} and Mg^{2+} as mentioned in the previous chapter. Therefore, in the first experimental plan the operation mode for all experiments was chosen to be continuous. Then, depending on the results evaluation of this first experimental plan it was decided whether experiments in Donnan mode will be interesting to be performed. It was found that experiments in Donnan mode did not have to offer added value to the research.

After each short-term experiment, the ED-stack and the TMCS were manually CIP. This was done by removing all liquids from the feed, concentrate, and TMCS sections, followed by a 15-30mins caustic wash of the feed section with a 0.5M NaOH solution, and a 15-30min acid wash of the concentrate and TMCS sections with a 2% HCl solution. Then, the compartments were thoroughly emptied by air sparging. The concentrate and TMCS sections were refilled with fresh tap water. Between the experiments, the recirculated liquids for the acid stripper (product) and electrode rinse solutions (anolyte and catholyte) were kept the same. The reasons for not replacing these two process flows were that (1) for the anolyte and catholyte, the impact of its composition on the system performance is deemed negligible, while (2) for the stripper liquid, its concentration builds up slowly over multiple

CIP liquids (as it becomes a very concentrated stream, eventually limited by osmotic water transport) and replacing it each time would result in unrealistically low water fluxes directed towards the product.

Table 4: Experimental plan first part – Spider-stack

Experiments	LR	OCD (A/m^2)	Operation mode
1.1	3	25	Continuous
1.2	3	75	Continuous
1.3	3	150	Continuous
1.4	3	300	Continuous
2.1	1	25	Continuous
2.2	1	75	Continuous
2.3	1	120	Continuous
2.4	1	300	Continuous
3.1	9	25	Continuous
3.2	9	75	Continuous
3.3	9	150	Continuous
3.4	9	300	Continuous

During the second part of the pilot research with leachate, the three experiments presented in Table 5 took place with the third generation stack. In these experiments, the control of the feed flow treated by the pilot was based on a set pH in the re-circulated feed/pilot's effluent (Feed ED) instead of being based on a specific load ratio. Experiment 1 was a short-term one at a pH control of 4. Experiment 2 was a long-term that lasted for 4 days and the automated CIP was not activated. In contrast, experiment 3 was a long-term that lasted for 3 days and the automated CIP was activated.

An important piece of information is how the CIP was triggered. The automatic CIP once activated was triggered when the voltage would exceed a given high voltage value, but only after the minimum operational time value given was also reached. During the long-term experiment with the activated automatic CIP, the high voltage value was set to a low value of 6V. Then, the desired time interval for the CIP was filled in the min operational time in the pilot's software settings. This setting was adjusted a few times during the long-term experiment as will be explained in chapter 4 Results.

Table 5: Experimental plan second part – third generation stack

Experiments	OCD (A/m^2)	Operation mode	pH control at	Auto-CIP	Duration
1	75	Continuous	4	No	3.5h
2	75	Continuous	6	No	4 days
3	75	Continuous	6	Yes	3 days

Finally, it must be mentioned that during the pilot research with the third generation stack at Nieuwdorp three experiments with digestate transported from the WWTP of Venlo took place. These experiments are not directly related to the N.E.W.B.I.E.S. pilot research with leachate and therefore their results are presented in Appendix B.

Pilot's installation, Sample Handling and Analyses

The Newbies pilot was placed nearby the PWZI of EIW as depicted in Figure 5. It was connected to receive 1 m^3/d of PWZI influent, which was first settled in two influent IBCs. The pilot's effluent, product and waste streams were collected in a waste pit close by the pilot and from there it was sent back to the influent pit of the PWZI.

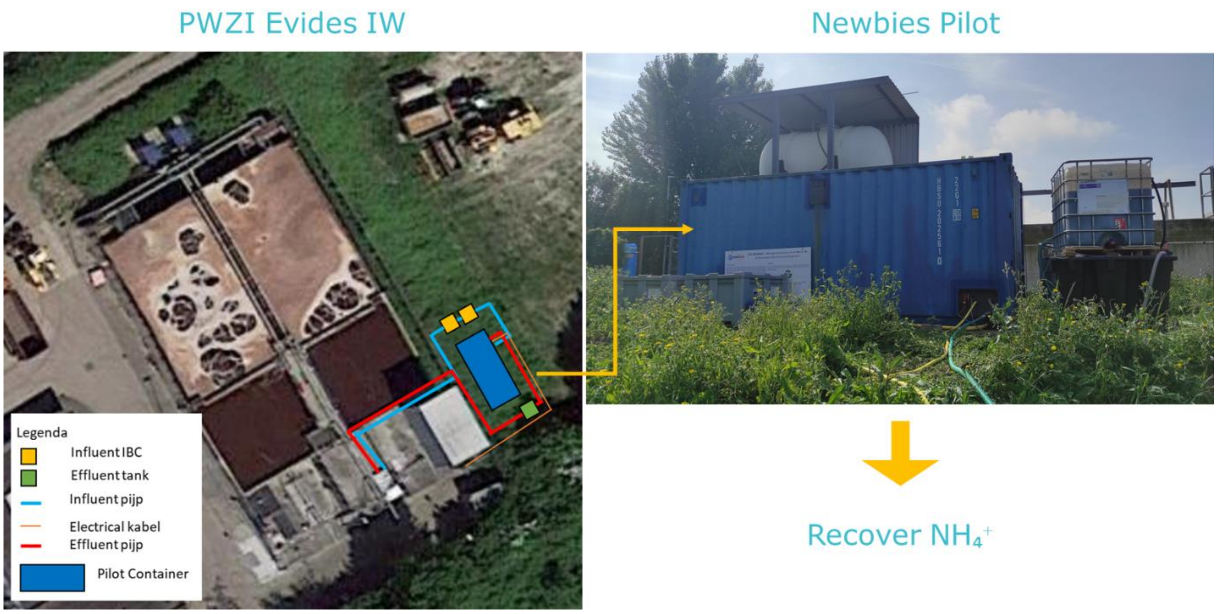

Figure 5: Pilot's installation at PWZI of EIW in Nieuwdorp

The type of samples (names) that were collected during the experiments are listed below:

1. Feed was used for the pilot's influent samples.
2. Feed ED was used for the samples of the "feed" stream that comes out of the ED stack, thus the treated waste water.
3. Cation Concentrate was used for the samples of the mixed "ammonia-depleted concentrate" and "ammonia-rich concentrate" streams.
4. Anolyte/Catholyte stream was used for the sample of the stream that recirculates in the anolyte and the catholyte parts of the ED stack.
5. STR was used for the product samples and is an acronym of the word "Stripper".

During the short-term experiments, liquid samples were taken from all process flows mentioned above (Figure 6) as soon as the in-line measured variables such as electrical conductivity (EC), pH and most notably, H_2SO_4 pumping rate had stabilized/flattened out. Depending on the condition tested this took place between 2-6 hours after the system was started. The samples were filtered (0.22 µm) and stored in a refrigerator at the location to be later transported in batches to Wetsus European centre of excellence for sustainable water technology (Leeuwarden) for detailed water analyses. The samples were analyzed for:

- Total Inorganic / Organic Carbon (TIC/TOC)
- Ion Chromatography for cations: Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_3^+
- Ion Chromatography for anions: Cl^-, NO_2^-, NO_3^-, HPO_4^{2-}, SO_4^{2-}
- ICP-MS for elemental analysis of: Ca, Fe, K, Mg, Na, P, S, Si

Figure 6: Sampling of the N.E.W.B.I.E.S. pilot

The in-line process data, consisting of real-time measurements for all process flows of (a) pH, (b) EC, (c) net resulting water flux (using recirculated volume level control), (d) measured voltage and current as applied by the power supply, and (e) – specifically for the stripper section – acid dosing was monitored using the Labview-based integrated software package from Pro Control, The Netherlands. The measurement interval for data logging was set to 1 second. In addition to these key variables, other relevant operational data like recirculation water fluxes (L/h) were monitored to check for mechanical blocking or pump malfunctioning.

The inline measured data was processed with open-source mathematical software package R (www.r-project.org). The same script with urine case (second pilot phase) was used for the calculation/determination of the relevant fluxes and KPIs. In short, the script plotted all in-line measured data for the operational period, and asks the user to select a time window within which averages are obtained for all recorded process variables, plus calculated averages for (a) effective feed pump rate, (b) applied voltage, (c) applied current, (d) apparent recovery efficiency by means of acid dosing, (e) apparent product concentration, (f) apparent recovery energy efficiency, (g) water fluxes for cation concentrate, catholyte, stripper and acid sections.

The averages obtained using the R-script for the different water fluxes as they occurred, were used in conjunction with the chemical composition data to calculate the direct removals, recoveries, and energy efficiencies. The product concentration was directly obtained from the IC analysis of the product.

4. Results

First Experimental Part – Spider-stack

In Table 6 the results from the 10 short-term experiments (characterization runs) performed are given. Moreover, the results of two runs performed in duplicate (1.1 and R1.1, 1.2 and R1.2) are also included and were found to be similar. From a first glance on the experimental results with leachate, it is obvious that really small removal and recoveries were overall achieved (below 45 and 33 % respectively). Subsequently, the energy consumptions were high and of course much higher than the aimed value of 8.9 Wh/g N.

In Table 6 the results are grouped based on the intended LRs (1, 3 and 9), while the actual LRs achieved are given per experiment. Comparing the runs with approximately the same LR, it can be seen that the best performing OCD as far as removal/recovery is concerned for the leachate case was 75 A/m^2. Moreover, only in the case of LR 3 (actual 2.6) the OCD of 75 A/m^2 resulted in lower energy consumption also compared to the experiments with OCD of 25 A/m^2.

When comparing the experiments of Table 6 based on the same OCD and different LRs, it is obvious that the higher the LR the higher removal and recovery values of NH_4^+ were. Specifically, the highest removals/recoveries were found at the LR of 9 (actual 7.6, 7.7 and 8.4). However, the LR of 9 means that 9 times more charge is supplied compared to how much is needed for the transport of the NH_4^+ present in the wastewater. Also, from an operational point of view higher LR would mean that the same current is used to treat much smaller flows of wastewater, which results in higher energy consumption.

Table 6: Experimental plan first part – Spider-stack – All Results

Exp.	Actual LR	OCD (A/m^2)	Removal (%)	Recovery (%)	NH_4^+ Transport (%)	Product Concentration (g$(NH_4)_2SO_4$/ L)	Energy consumption (Wh/g N Removed)
Intended Load Ratio → 3							
1.1	2.6	25	8	18	2.7	93	36
R1.1	2.6	25	10	13	2.6	68	37
1.2	2.6	75	19	11	7	108	32
R1.2	2.6	75	24	16	8	108	33
1.3	2.6	150	11	7	4.1	110	67
1.4	2.6	300	6	1	2.1	84	185
Intended Load Ratio → 1							
2.1	0.9	25	6	7	37.3	86	2.6
2.2	0.85	75	11	2	12.4	72	17
2.3	0.9	120	5	3	5.4	101	49
Intended Load Ratio → 9							
3.1	7.7	25	36	33	4.5	56	26
3.2	7.6	75	45	28	5.6	76	41
3.3	8.4	150	30	18	3.5	91	85

Another KPI that is important to take into account when assessing the results from the experiments with leachate is ionic transport. In Table 6 the ion transport for NH_4^+ over the cation membrane is given for all experiments. We note this value was quite low ranging from 2.7 to 12.4% with an exception of run 2.1 which reached 37.3%. This observation suggests that there were high charge losses in all experiments. The question that needed to be answered is “where does this charge go?”.

As was mentioned in chapter 2, leachate water quality is complex and contains in high concentrations competitive cations such as Na^+, K^+, Ca^{2+}, and Mg^{2+}. Thus, it was considered valuable to calculate the ion transport number for other ions and the overall transport number. These results are presented in Table 7 for all experiments. The charge that was used for the transport of other ions and not for NH_4^+ ranged from 34 to 72%. Na^+ transport numbers were close to NH_4^+ transport numbers for most of the experiments even though the N.E.W.B.I.E.S. process is designed to favor NH_4^+ transport, indicating that high content of Na^+ and specifically the higher than the unit Na^+/NH_4^+ ratio (equal to 2.9 based on Figure 2) was the main limiting factor of the process.

The loss of charge due to the presence of other ions is a consequence related to the water composition of leachate and not to the N.E.W.B.I.E.S process. However, it was a valuable outcome that offers knowledge on the applicability of the N.E.W.B.I.E.S process in different wastewaters that might have a similar composition to leachate (high content of competitive cations).

Table 7: Ion Transport (%) for the leachate experiments - the first part

Exp.	Actual LR	OCD (A/m^2)	X ion Transport (%)						Charge for other ions/ Total (%)
			NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sum	
Intended Load Ratio → 3									
1.1	2.6	25	2.7	2.7	0.2	0.5	0.3	6.4	58
R1.1	2.6	25	2.6	2.0	0.4	0.8	0.4	6.2	58
1.2	2.6	75	7	4	0.8	0.5	0.4	12.7	45
R1.2	2.6	75	8	2.6	0.9	0.6	0.6	12.7	37
1.3[1]	2.6	150	4.1	0.0	0.0	0.0	0.0	4.1	0
1.4	2.6	300	2.1	4.3	0.7	0.2	0.1	7.4	72
Intended Load Ratio → 1									
2.1	0.9	25	37.3	0.0	6.7	8.8	3.8	56.6	34
2.2	0.85	75	12.4	7.9	2.3	0.8	1.0	24.4	49
2.3	0.9	120	5.4	4.2	1.0	0.4	0.4	11.4	53
Intended Load Ratio → 9									
3.1	7.7	25	4.5	3.5	1.0	0.0	0.0	9	50
3.2	7.6	75	5.6	7.2	1.1	0.4	0.4	14.7	62
3.3	8.4	150	3.5	6.0	0.8	0.3	0.2	10.8	68

However, the sum of total charge used for the transport of NH_4^+ and other ions (column “sum” in Table 7) was overall low with values between 7.4 to 24.4 % (run 1.3 and 2.1 are considered not representative extremes). The spider stack was also used in the experiments with urine, where NH_4^+ ionic transport numbers between 13 to 27% were noted. Urine mostly contains NH_4^+, thus the sum of total charge

[1] In run 1.3 issues with sampling or analyses are to be considered.

used for the transport of NH_4^+ and other ions is expected to be more or less equal to that of just for NH_4^+. Taking into account the experiments with the spider stack with both urine and leachate, it was considered that there were high charge losses also in the spider stack due to ionic shortcuts.

To evaluate the spider-stack performance two extra experiments took place; (1) a membrane integrity test and (2) an ionic shortcut test. A detailed explanation about those two test methodology and specific results can be found in Appendix C – Membranes Integrity Test & Ionic Short-cut Test. The main conclusions of these tests were the following:

- No damage was found on the ion exchange membranes of the ED stack
- There were leakages due to stack design (ionic shortcuts).

It was then decided to continue the experimentation using a new stack with a design that could potentially limit the ionic shortcut issue, which was the third generation stack. Having performed the characterization experiments with the spider-stack for leachate case, presented in the previous sub-chapter, it was clear that an OCD of about 75 A/m^2 was the most promising. Therefore, 75 A/m^2 was chosen as the OCD value for all experiments with the third generation stack.

Moreover, based on the results achieved with the spider-stack, it was considered that experiments in Donnan mode did not have to offer a beneficial effect to the NH_4^+ transport and therefore to its removal/recovery due to the presence of divalent ions in high concentrations as well as the high $Na^+/NH4^+$ ratio found in leachate.

In parallel, by plotting the effluent pH (Feed ED) in the different experiments with the spider-stack and the subsequent NH_4^+ removal achieved (Figure 7), it was possible to observe that higher removals were obtained when the pH of the effluent (Feed ED) was around 4. Therefore, for the experiments with the third generation stack, the control of the feed flow treated by the pilot was decided to be based on a requested pH in the effluent (Feed ED). Specifically, a pH of 4 was aimed.

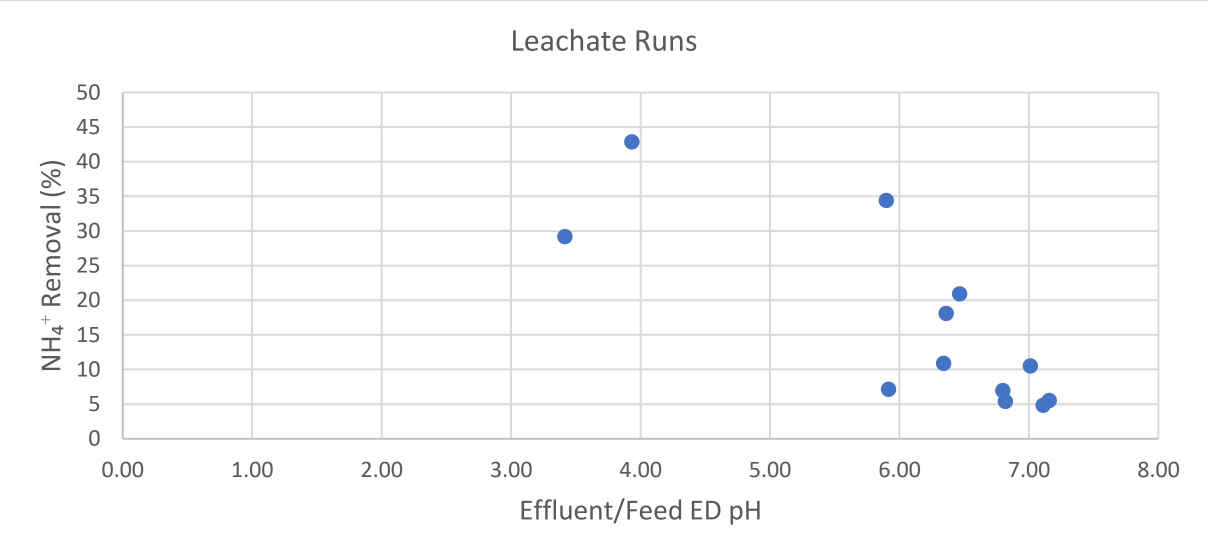

Figure 7: Feed pH effect to NH_4^+removal based on results with spider-stack

Second Experimental Part – Third Generation Stack

The results of all experiments performed with leachate in the third generation stack are given in Table 8. The first experiment was a short-term experiment at a Feed ED pH control of 4. The highest recovery and removal values (41% and 30%, respectively) were achieved at this pH. However, pH control at 4 was not possible to be performed in long-term experiments, because foaming was noted in the feed re-circulation tank (Feed ED returns in it) which was so intensive that reached the venting holes and excited the pilot container from that point as it can be seen in Figure 8. A possible explanation for the foaming could be (1) HCO_3^- present in the Feed ED (effluent stream) that becomes gaseous CO_2 at a pH of 4 and/or (2) organic compounds that are contained in leachate that tend to foam in low pH such as 4. As a result of the continuation of the research with the third generation stack, a pH value of 6 was chosen for the pH control of the Feed ED.

Table 8: Experimental plan second part – Third generation stack – Results

Exp.	OC	pH control at	Actual LR	Removal (%)	Recovery (%)	NH_4^+ Transport (%)	Product Concentration (g$(NH_4)_2SO_4$/ L)	Energy consumption (Wh/g N Removed)
1	75 A/m^2	4	2.95	41	30	12.5	168	27
2		6	2.65	24	13	6.4	105	103
3.1		6	1.6	28	16	13.6	198	29
3.2		6	1.7	30	17	13.6	198	29

Figure 8: Foaming during Experiment 1 with the third generation stack – pH control at 4

The second and the third experiments were both long-term with the same conditions (pH control at 6 and OCD at 75 A/m^2). However, there was a crucial difference between the two experiments; the automatic CIP was active in experiment 3, while not in experiment 2. The long run of the pilot without any cleaning in certain intervals resulted in lower removal and recovery numbers as well as higher energy consumption. As a result, experiment 2 is not considered representative.

Experiment 3 was considered to be the most representative long run on leachate with a possible pH control at 6 for the Feed ED. After some trials during this experiment, it was found out that a frequency of 5 hours for the CIP of both the ED-stack and TMCS section was needed. It must be also mentioned that experiment 3 was separated into two sets of results (see Table 8, exp 3.1 and 3.2) due to the two sampling campaigns performed.

Comparing the results of experiment 3 achieved with the third generation stack and the results with the similar LRs (either 0.85 or 2.6) achieved with the spider-stack it is obvious that higher removals/ recoveries were achieved with the new stack while maintaining a similar or lower energy consumption.

Furthermore, as mentioned before the new stack was designed in a way to reduce the ionic shortcuts. The NH_4^+ transport over the CEM was similar or higher than those noted in the experiments with similar LRs (either 0.85 or 2.6) with the spider-stack. However, the ionic transport for all ions was significantly increased to a range of 47 to 60% as can be seen in Table 9. In addition, 71 to 74% of the charge applied was used for the transport of competitive ions (mostly for Na^+). This was expected since it is related to the leachate's water composition and not the design of the stack.

Table 9: Ion Transport (%) for the leachate experiments – Third generation stack

Exp.	Actual LR	OCD (A/m^2)	X ion Transport (%)						Charge for other ions/ Total (%)
			NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sum	
1	2.95	75	12.5	28.1	3.9	0.2	0.3	48.3	74
3.1	1.6	75	13.6	38.8	5.9	0.8	0.8	60	77
3.2	1.6	75	13.6	27.5	5.2	0.4	0.3	47	71

Leachate compared to Digestate and Urine

For the leachate case the most promising and practically possible to be achieved results were found to be those of Experiment 3 with third generation stack, where an OCD of 75 A/m^2 and the LD of 1.6 (pH control at 6) were the main settings. Considering all the operations conditions tested for the different wastewaters, the most relevant KPIs where the system was stable and the high performance can be further reproduced are gathered in **Error! Reference source not found.**Table 10. From this overview, it is straightforward that treating this leachate from all perspectives was the most challenging stream; the lowest removals, highest energy consumptions, and lower mass recovered values were obtained. An important observation is that for leachate (as already mentioned) the Na^+/NH_4^+ ratio was high above the unit (specifically 2.9), while for the rest of the tested streams it was below the unit. This seems to have a major effect on the NH_4^+ transport numbers achieved.

For Girona digestate, urine and Venlo digestate the KPIs values achieved might not be at the proposed project values, but they were quite close. Especially, for Venlo digestate the highest mass was recovered in a day while the lowest energy consumption was recorded (below the proposed). Therefore, it is considered that the proposed KPI's could be achieved with some extra "fine-tuning" of the N.E.W.B.I.E.S. process for these streams. On the contrary, for Indaver's leachate or other streams with similar composition (high content of competitive ions), any further research is considered not recommended from an economical perspective.

Table 10: Comparison of KPIs from the 3 different streams tested with N.E.W.B.I.E.S. pilot[2]

Tested Stream	**Digestate Girona**	**Urine**	**Leachate**	**Digestate Venlo**
Stack	First	Spider	Third generation	Third generation
Mode of Operation	Donnan	Continuous	Continuous	Continuous
OCD (A/m^2)	75	100	75	75
LR	1.34	3	1.6	0.55
Removal (%)	40-60	83	≈ 30	30
NH_4^+ Transport (%)	20-40	30	≈ 13	≈ 50
Product Concentration ($g(NH_4)_2SO_4$/ L)	≈ 150	≈ 200	≈ 200	≈ 200
Energy consumption (Wh/g N Removed)	10-20	8.8	≈ 28	≈ 5
Mass recovered (kg N/d)	0.35	0.7	0.17	≈ 0.8

[2] Girona Digestate and urine results are sourced from the respective deliverables. Venlo Digestate results are based on Appendix B.

5. Conclusions

It was possible to treat the landfill leachate water from the solid waste landfill of Indaver with the N.E.W.B.I.E.S. technology, however, the proposed KPI's were not met. In general with the spider stack, low removal and recoveries of NH_4^+ were reached during the characterization runs while energy consumption was very high. Part of the supplied charge was used to transport competitive cations being mainly Na^+, while another part of the added charge was lost due to ionic shortcuts, which is a characteristic of the stack design.

Designing a new stack with less cell pairs decreased the ionic shortcuts. This step was crucial to make the process more energy-efficient. A higher coulombic efficiency was reached with the new stack, but still, 71-76% of the applied energy was lost due to the transport of competitive cations. The most promising and practically possible results were found to be an OCD of 75 A/m^2 and the LR of 1.6 (pH control at 6). The pilot system removed up to 30% of the NH_4^+ in the influent or 0.17kg N/day while consuming on average 28 Wh/gN removed reaching product concentrations of 200 g$(NH_4)_2SO_4$/ L.

Valuable information was gained while testing the N.E.W.B.I.E.S. technology for this type of water. However, the proposed KPI values of 1kg N removal/day while consuming less than 8.9 Wh/gN were not achieved, and NH_4^+ recovery in the leachate from the solid waste landfill of Indaver was found to be challenging. This is mainly due to the presence of other competitive ions in this leachate and the high Na^+/ NH_4^+ ratio of 2.9.

Streams with a lower amount of competitive ions need to be looked at to limit the energy use and make the process economically viable. As mentioned above, it was found in the literature that the leachate from the solid waste landfill of Indaver has a high amount of Na and Cl. Therefore other leachates might be suitable. To assess the suitability of another (leachate) stream for this technology, it is important to check the all ions/ NH_4^+ ratio and especially the Na^+/ NH_4^+ ratio to estimate the influence of other competitive ions.

Appendix A – Water Quality of Landfills Throughout the Word

Table 11: Average water quality concentrations of different landfills throughout Europe (Ehrig & Stegmann, 2018)

Parameter	Symbol	Unit	German	UK	French	Italian	Greek	Greek
pH	-	-	6.1	6.7	8.2	8.2	6.2	7.9
Biological Oxygen Demand	BOD_5	mg/L	13000	18632	200	2300	70900	1050
Chemical Oxygen Demand	COD	mg/L	22000	36817	4100	10540	26800	5350
Total Organic Carbon	TOC	mg/L	n/a	12217	1430	3900	n/a	n/a
Ammonium	NH_4^+	mg/L	1286	1185	1337	6699	3986	1209
Nitrate	NO_3^-	mg/L	13.3	8	550	n/a	664	244
Nitrite	NO_2^-	mg/L	1.6	0.66	n/a	n/a	n/a	5.75
Phosphate	HPO_4^{2-}	mg/L	n/a	15.5	26	99	517	27
Alkalinity	as $CaCO_3$	mg/L	6700	7251	n.a	21470	12880	4950
Chloride	Cl^-	mg/L	2100	1805	5420	4900	3260	4120
Sulphate	SO_4^{2-}	mg/L	500	676	550	n/a	n/a	210
Sodium	Na^+	mg/L	1350	1371	3000	3970	n/a	n/a
Potassium	K^+	mg/L	1100	1143	880	3460	n/a	n/a
Magnesium	Mg^{2+}	mg/L	470	384	110	24.1	85.2	140
Calcium	Ca^{2+}	mg/L	1200	2241	68	15.7	n/a	n/a
Zinc	Zn^{2+}	mg/L	5	17.4	0.73	0.16	n/a	n/a
Manganese	Mn^{2+}	mg/L	25	32.9	n/a	0.04	n/a	n/a
Iron	Fe^{3+}	mg/L	780	654	0.91	2.7	5	16.2
Arsenic	As^{5+}	µg/L	160	24	n/a	n/a	n/a	n/a
Cadmium	Cd^{2+}	µg/L	6	20	100	<20	<100	<100
Chromium	Cr^{2+}	µg/L	300	130	n/a	2210	90	1910
Copper	Cu^+	µg/L	80	130	390	n/a	90	280
Nickel	Ni^+	µg/L	200	420	810	310	670	1350
Lead	Pb^{2+}	µg/L	90	280	460	<30	<100	<100

Table 12: Average water quality concentrations of different landfills outside Europe (Robinson, 2005; Salem, Hamouri, Djemnaa, & Allia, 2008)

Parameter	Symbol	Unit	South Africa		Hong Kong		Thailand			Indonesia	New Zeeland		Algerian
pH	-	-	7.5	8.2	8.6	7.8	7.6	7.2	7.0	8.4	7.2	7	8.27
Biological Oxygen Demand	BOD5	mg/L	170	550	167	117	n/a	n/a	n/a	TOC = 968	76	737	980
Chemical Oxygen Demand	COD	mg/L	760	4560	2580	873	2700	1560	1980		1181	1969	3792
Ammonium	NH_4^+	mg/L	559	1998	3295	1486	3898	1831	1736	2571	n/a	n/a	110
Nitrate	NO_3^-	mg/L	<0.5	40.7	11	<0.5	<5	<5	<5	<5	n/a	n/a	65
Nitrite	NO_2^-	mg/L	n/a	1.3	<0.3	<0.3	2.3	<1.5	1	<3	n/a	n/a	n/a
Phosphate	HPO_4^{2-}	mg/L	4.3	40	85	68	5	46	43	37	n/a	n/a	180
Alkalinity	as $CaCO_3$	mg/L	2422	9652	11500	4940	23910	12505	15970	7840	n/a	n/a	n/a
Chloride	Cl^-	mg/L	1690	4626	2740	821	3802	2498	3650	2330	859	978	4569
Sulphate	SO_4^{2-}	mg/L	n/a	n/a	n/a	n/a	15	6.4	1.6	159	1	1	3056
Sodium	Na^+	mg/L	590	2825	2100	217	2453	1460	2179	1130	669	429	n/a
Potassium	K^+	mg/L	n/a	1615	1000	375	1932	1010	1819	1600	471	649	n/a
Magnesium	Mg^{2+}	mg/L	80	195	31	18	121	132	182	56	95	160	n/a
Calcium	Ca^{2+}	mg/L	105	198	19	22	55	126	199	86			n/a
Zinc	Zn^{2+}	mg/L	0.15	n/a	n/a	n/a	0.15	0.61	0.24	0.46	1.24	1.65	1.43
Manganese	Mn^{2+}	mg/L	0.86	n/a	5.5	7.8	0.24	0.6	1.65	0.47	0.4	6.56	0.41
Iron	Fe^{3+}	mg/L	15	9.35	2	0.9	2.77	1.57	3.08	6.23	0.2	0.89	8.23
Arsenic	As^{5+}	µg/L	62	n/a	n/a	n/a	n/a	n/a	n/a	n/a	32	12	n/a
Cadmium	Cd^{2+}	µg/L	<1	n/a	n/a	n/a	<50	<50	<50	<20	10	20	<30
Chromium	Cr^{2+}	µg/L	80	n/a	n/a	n/a	780	<500	160	250	60	70	200
Copper	Cu^+	µg/L	<10	64	n/a	n/a	<50	<50	<50	386	50	50	390
Nickel	Ni^+	µg/L	120	n/a	n/a	n/a	<1000			380	110	100	370
Lead	Pb^{2+}	µg/L	<4	20	n/a	n/a	<1000			<300	70	150	3490

References of Appendix A

Ehrig, H. J., & Stegmann, R. (2018). Chapter 10.2 - Leachate Quality. In R. Cossu, & R. Stegmann, Solid Waste Landfilling: Concepts, Processes, Technologies (pp. 511-539).

Robinson, H. (2005, Sardinia). The Composition of Leachates from Very Large Landfills: An International Review. Tenth International Waste Management and Landfill Symposium. Sardinia: CISA, Environmental Sanitary Engineering Centre, Italy.

Salem, Z., Hamouri, K., Djemnaa, R., & Allia, K. (2008). Evaluation of landfill leachate pollution and treatment. Desalination 220.

Appendix B – Digestate Runs with the Third Generation Stack

Some extra experiments were performed with the third generation stack treating digestate from the WWTP of Venlo and containing 1.5-2.5 g N/L. This water is considered to be 'less challenging' than the leachate water. The loss of charge due to the presence of other ions is expected to be less than in the leachate case. The ratio of all ions versus NH_4^+ is visualized in Figure 9 and compared to the other streams tested in the Newbies pilot. It is indeed clear that the Venlo digestate contains proportionally less competitive ions than the leachate. Furthermore, ratios are more or less comparable than the digestate of Girona. Only chloride is present in a somewhat higher ratio. Further, there were some scaling issues in the Girona case due to higher amounts of Ca^{2+} and Mg^{2+}. For the Venlo digestate, Ca and Mg^{2+} ratios are lower, so scaling is expected to be less of an issue.

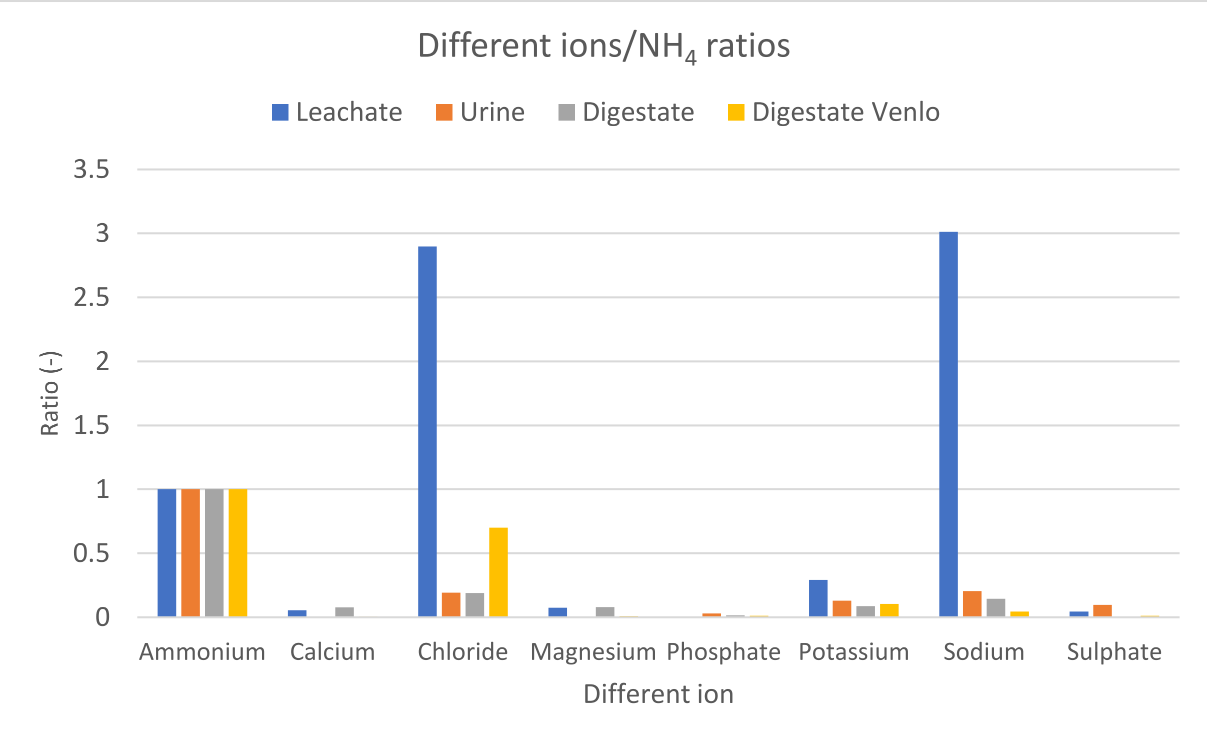

Figure 9 - Ratio of the different ions over NH_4^+ content in the streams tested with the N.E.W.B.I.E.S pilot

Same as in the leachate tests, short term experiments with pH control and OCD of 75 A/m² were performed in continuous mode. The results of all digestate experiments performed in the third generation stack are given in Table 13. pH control of 8 was considered to be not favorable for the removal or recovery of NH_4^+ and the experiment is left out of consideration. For the other 2 experiments, the highest removal and recovery found were 31% and 24% respectively. This value is lower compared to the 40-60% removal that was reached with the digestate tests in Girona and the urine case but is comparable to the 30% that was reached with the same stack treating the leachate water. However, 6 times less energy was used for the removal compared to the leachate case, while similar values are found for the Girona digestate. While looking at the ionic transport for NH_4^+ and the sum of transport of all ions over the cation membrane, it is clear that NH_4^+ is the main ion being transported in the digestate and there is almost no transport of other ions taking place over the cation membrane, which was as expected.

Table 13 - Experimental plan Digestate runs – third generation stack – Results

Exp.	OCD	pH control at	Actual LR	Removal (%)	Recovery (%)	NH_4^+ Transport (%)	Transport of all ions (%)	Product Concentration ($g(NH_4)_2SO_4$/L)	Energy consumption (Wh/g NH_4^+ Removed)
1	75 A/m^2	4	0.6	28	24	42.7	44.0	191.18	5.6
2		6	0.5	31	24	56.2	56.2	191.55	3.7
3		8	0.2	0	0	0	0	178.7	0

For the Venlo digestate 0.7-0.92 kg, N/day could be removed in the N.E.W.B.I.E.S. pilot while using 3.7-5.6 Wh/g NH_4^+ removed. This is very close to the proposed KPI values set in the project.

Appendix C – Membranes Integrity Test & Ionic Short-cut Test

Two extra tests were performed in order to address the cause of the charge losses. To eliminate the presence of a broken membrane, a membrane integrity test was performed. To address the amount of charge being lost by ionic short-cutting, an IV test was performed. Results and conclusions of both tests are given in this appendix.

Membranes integrity test

In order to see if water was transported from the one side of the stack (concentrate compartment) to the other side of the stack (feed compartment) when no power was supplied, tap water was placed in the concentrate compartment, while the feed compartment was emptied with air. The liquid in the concentrate compartment was circulated for two hours. Transfer of tap water from the concentrate compartment to the feed compartment was occurring at a rate of 14mL/min. This was within the stack design range. It could be concluded that the observed water transport was not caused by a broken membrane, but was water leaking through the spacer gaskets which is caused by the current stacking method of the membranes.

Ionic short tests

Before the test, the feed and Concentrate/TMCS sections were chemically cleaned thoroughly to remove any form of existing scaling on the membranes. The TMCS section was closed off during the duration of the test. After chemical cleaning, the feed and concentrate section were flushed with demi water until a conductivity <0.1mS/cm was reached. The feed section was filled with demi water and the concentrate section was filled with a known concentration of Na_2SO_4 (0.250M). Anode and cathode were also filled with 0.250M Na_2SO_4. To control the Power Supply Unit manually, the Delta Elektronika software was used.

The voltage over the stack was linearly increased from 0 to 150V and back to 0V using Delta Elektronika sequencer software. The increase of current over the stack was measured while ramping up the voltage and logged with the Delta Elektronika logger app. Tests were performed in triplicates. The stack should theoretically be an insulator, because of the demi water in the feed compartment that acts as an insulator, while concentrate compartments allow the current to pass, unless ionic shortcuts are present. The demi water gives a really big resistance and the charge can only flow in minimal amounts of cross sectional area, therefore if ionic shortcutting is minimal it will not be possible to measure high shortcut current (Figure 10).

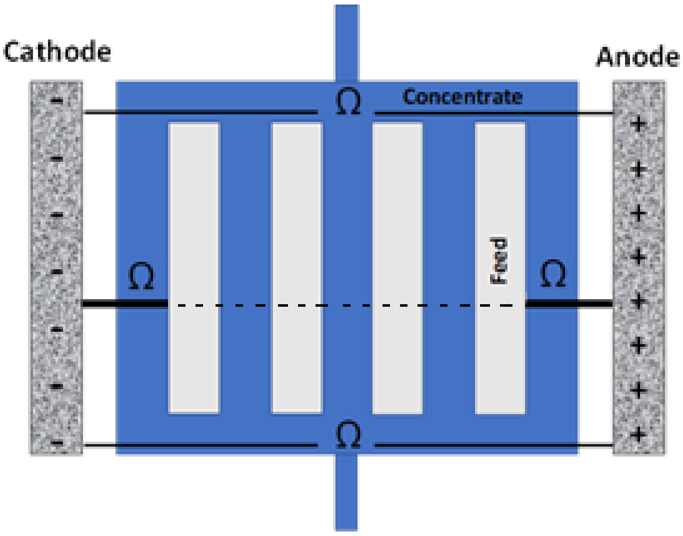

Figure 10 – Feed compartment filled with demi water acting as a good insulator, while concentrate compartment and cathode/anode filled with 0.250M Na_2SO_4 act as good conductors.

The moment after the start of recirculation, the conductivity in the feed compartment started rising because of the transfer of water between concentrate and feed compartment that was also found in the membrane integrity test above. Therefore it was not possible to make the stack an insulator and multiple tests were performed in order to limit the current transfer through the stack. Results and measured currents are shown in Table 14.

Table 14 - Measured current for the different IV tests performed.

Test	Feed	Concentrate	Anode/Cathode	Obtained current at 150V (A)
1	Demi 'contaminated' with Na_2SO_4	Na_2SO_4	Na_2SO_4	11.0
2	Empty	Na_2SO_4	Na_2SO_4	3.01
3	Demi water	Empty	Na_2SO_4	3.14
4	Empty	Empty	Na_2SO_4	1.00
5	Empty	Empty	Little Na_2SO_4[3]	0.65
6	Empty	Empty	Empty [4]	0.73
7	Empty	Empty	Demi water	0.58

In all tests, a gradually increasing current could be measured when the voltage was going up. The current reached a peak at 150V and started lowering again with decreasing voltage. The lowest high current was obtained when leaving the feed and concentrate side of the stack empty. However, this indicates ionic shortcuts to be present since the stack is not acting as an insulator. Therefore it was decided to rethink the stack design and eliminate the ionic shortcuts as much as possible.

[3] Little Na_2SO_4 obtained by applying extra drying with air.

[4] The emptying of the anode and cathode compartment in experiment 6 failed because it was not possible to completely drain both compartments with air.