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Electrochemically Induced Precipitation Enables Fresh Urine Stabilization and Facilitates Source Separation

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ABSTRACT: Source separation of urine can enable nutrient recycling, facilitate wastewater management, and conserve water. Without stabilization of the urine, urea is quickly hydrolyzed into ammonia and (bi)carbonate, causing nutrient loss, clogging of collection systems, ammonia volatilization, and odor nuisance. In this study, electrochemically induced precipitation and stabilization of fresh urine was successfully demonstrated. By recirculating the urine over the cathodic compartment of an electrochemical cell, the pH was increased due to the production of hydroxyl ions at the cathode. The pH increased to 11−12, decreasing calcium and magnesium concentrations by >80%, and minimizing scaling and clogging during downstream processing. At pH 11, urine could be stabilized for one week, while an increase to pH 12 allowed urine storage without urea hydrolysis for >18 months. By a smart selection of membranes [anion exchange membrane (AEM) with a cation exchange membrane (CEM) or a bipolar membrane (BPM)], no chemical input was required in the electrochemical cell and an acidic stream was produced that can be used to periodically rinse the electrochemical cell and toilet. On-site electrochemical treatment, close to the toilet, is a promising new concept to minimize clogging in collection systems by forcing controlled precipitation and to inhibit urea hydrolysis during storage until further treatment in more centralized nutrient recovery plants.
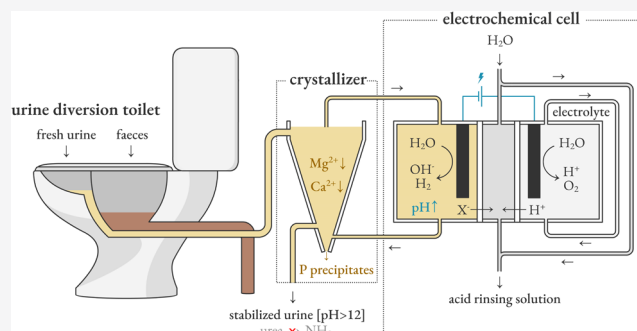
1. INTRODUCTION

Urged by the depletion of nonrenewable phosphorus reserves and the currently energy-intensive nitrogen fertilizer production using Haber−Bosch, more sustainable fertilizers are being explored to meet the rapidly increasing food demand.[1,2] In the past decade, many technologies to recover nutrients (mainly N and P) from source-separated urine have been developed and evaluated.[2,3] The instability of urine, caused by the enzymatic hydrolysis of urea into ammonia/ammonium and bicarbonate (eq 1), however, presents a challenge for an efficient urine collection and recovery.

$$CO(NH_2)_2 + 2H_2O \rightarrow NH_3 + NH_4^+ + HCO_3^- \qquad (1)$$
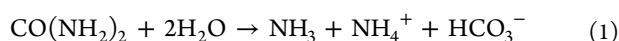
Part of the ammonia can volatilize during collection, storage, treatment, and/or application, resulting in a loss of nitrogen, odor nuisance, and environmental pollution.[4,5] Moreover, spontaneous, uncontrolled precipitation of calcium and magnesium salts, resulting from the increase in pH to ∼9.2 and release of ammonia and bicarbonate upon hydrolysis, leads to clogging of pipes in collection systems and a loss of phosphorus (and to a limited extent also nitrogen).[6−8] Clogging of pipes by the precipitating salts is a common problem in nonwater urinals and urine-separating toilets, creating odor nuisance, blockages, and leakages and requiring extensive cleaning and maintenance.[2,5,6,8−10] It is believed that

this is currently one of the major barriers for the widespread implementation of source separation.[6] The presence of calcium and magnesium can also cause problems during further downstream urine treatment, e.g., through scaling on membranes (used in reverse osmosis, forward osmosis, electrodialysis, (bio)electrochemical systems, etc.), which reduces the efficiency and requires thorough cleaning.[5,11−14]

Urea hydrolysis is initiated by urease-positive bacteria growing in the pipes of urine collection systems and is usually completed within a few days.[15] Urea hydrolysis can be prevented by inhibiting the microbial activity and hence the production of urea-degrading enzymes.[16] This can be achieved by (i) the addition of acids to decrease the pH,[17−19] (ii) the addition of caustics, wood ash, or biochar to increase the pH,[20,21] (iii) the addition of hydrogen peroxide[22] or urease inhibitors,[18] (iv) filtration, (v) evaporation,[23] (vi) electrochemical chlorine production,[24] and (vii) thermal treatment.[25] Interestingly, increasing the pH not only prevents urea
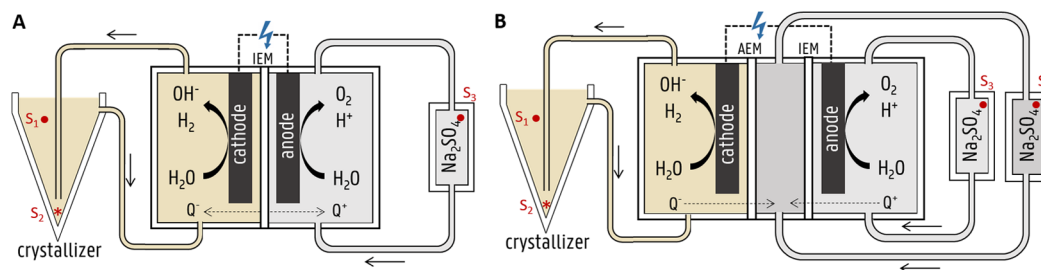
Figure 1. Schematic overview of the experimental setup. (A) Two-chamber electrochemical cell with AEM or CEM, (B) three-chamber electrochemical cell with AEM−CEM or AEM−BPM. A picture of the setup is shown in Figure S1 (SI). $S_{1,2,3,4}$ = sampling point for catholyte (1), precipitate (2), anolyte (3), and middle compartment (4).

hydrolysis but also can reduce the scaling potential of urine by inducing controlled precipitation of calcium and magnesium salts in a designated precipitation tank. Randall et al.[21] proposed dosing $Ca(OH)_2$ powder to increase the pH to stabilize urine. The authors recommended a dosage of 10 g of $Ca(OH)_2$ L^{-1} of fresh urine to ensure sufficiently high pH values and oversaturation, obviating the need for pH control. The same approach is used in the Autarky toilet, the on-site resource recovery toilet is currently under development in the Blue Diversion Autarky project,[26] to stabilize the urine before evaporation. Senecal and Vinneras[20] used a bed of wood ash to alkalinize urine (20 L of urine kg^{-1} ash) before drying. The high pH (13−14) inhibited enzymatic urea hydrolysis but promoted nonenzymatic urea hydrolysis, resulting in some nitrogen loss (5−35%) during drying. Due to the addition of calcium or ash, these stabilization methods do not address the scaling issue besides requiring the addition of external chemicals to the urine. In this study, the pH of fresh urine is increased by means of an electrochemical cell, which can be integrated into the source separation toilet to stabilize the urine immediately after collection. The setup is inspired by a concept developed for water softening by Clauwaert et al.[27] and consists of a crystallizer coupled to an electrochemical cell, in which the electrode compartments are separated by an ion-exchange membrane to create a pH gradient between the anode and cathode. In this research, urine is fed to the system and continuously recirculated between the crystallizer and the cathodic compartment of the electrochemical cell. By applying electrical energy, oxygen or water is reduced at the cathode, releasing hydroxyl ions that increase the pH of the urine (eq 2), while water is oxidized at the anode (eq 3), creating an acidic stream. The pH of fresh urine was increased above 11, which was reported as the upper limit for enzymatic urea hydrolysis.[21] The high pH also results in supersaturation and thus triggers precipitation. As a result, most of the calcium and magnesium ions are removed from the urine, reducing the scaling potential in downstream processing.

Cathode reactions: 1) $H_2O + e^- \rightarrow 1/2\ H_2 + OH^-$
$E^0(SHE) = -0.8277$ V

2) $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ $E^0(SHE) = 0.401$ V

$$(2)$$

Anode reaction: $H_2O \rightarrow O_2 + 2H^+ + 2e^-$

$E^0(SHE) = 1.229$ V

$$(3)$$
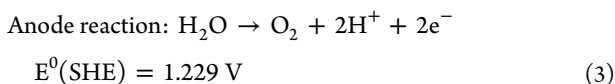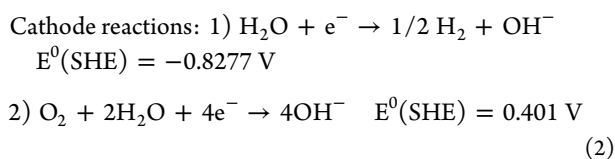
Electrochemically induced precipitation has already been applied for water softening, i.e., to remove hardness ions in tap water, brackish water, and/or seawater.[28−30] This study aims to increase the pH of fresh urine with an electrochemical cell to stabilize the urine and to precipitate bivalent ions to reduce the scaling potential downstream of the unit. Four different configurations of the electrochemical cell (two- or three-chamber cell with an anion exchange membrane (AEM), a cation exchange membrane (CEM), and/or a bipolar membrane (BPM)) were compared in terms of pH increase, energy requirement, bivalent cation and phosphate removal, and ion migration to identify the best performing configuration. Stabilization was assessed by storing the effluent (at pH 11 and 12) and measuring the pH, electrical conductivity (EC), and ammonium concentration over time.

2. MATERIALS AND METHODS

2.1. Urine Collection. Fresh urine from healthy male donors, not taking any medication, was collected using a nonwater urinal and stored for a maximum of one day at 4 °C to prevent urea hydrolysis prior to the tests. Urine collection was approved by the Ethical Committee of Ghent University Hospital (registration number B670201731862). The urine was diluted 1:1 with demineralized water at the start of each experiment to simulate flushing with water (urine composition is given in Table S1).

2.2. Electrochemical Cell and Crystallizer. The setup was tested with a two-chamber and three-chamber electrochemical cell, separated by an AEM, a CEM, and/or a BPM [Figures 1 and S2, Supporting Information (SI)]. A crystallizer with an active volume of 4 L was used as a precipitation vessel. The content of the crystallizer was continuously recirculated over the cathodic compartment of the electrochemical cell by means of a peristaltic pump (Watson Marlow 323E/D, MA). A recirculation rate of 15 L h^{-1} was applied to efficiently distribute the alkalinity generated in the vicinity of the electrode over the content of the whole cathodic compartment and crystallizer to minimize scaling on the electrode. The inlet of the recirculation loop was located at the top of the crystallizer. The outlet was located at the bottom of the crystallizer to obtain a good mixing in the crystallizer and to promote precipitation by contact with the crystal seeds at the bottom of the crystallizer. The anolyte was recirculated over a glass bottle and the anodic compartment of the electrochemical cell with a peristaltic pump (DULCOflex DF2a, ProMinent GmbH, Germany) at a flow rate of 1.2 L h^{-1}. For the tests with the three-chamber cell, a sodium sulfate solution was recirculated over a glass bottle and the middle compartment with a peristaltic pump (DULCOflex DF2a, ProMinent GmbH, Germany) at a flow rate of 1.7 L h^{-1}.
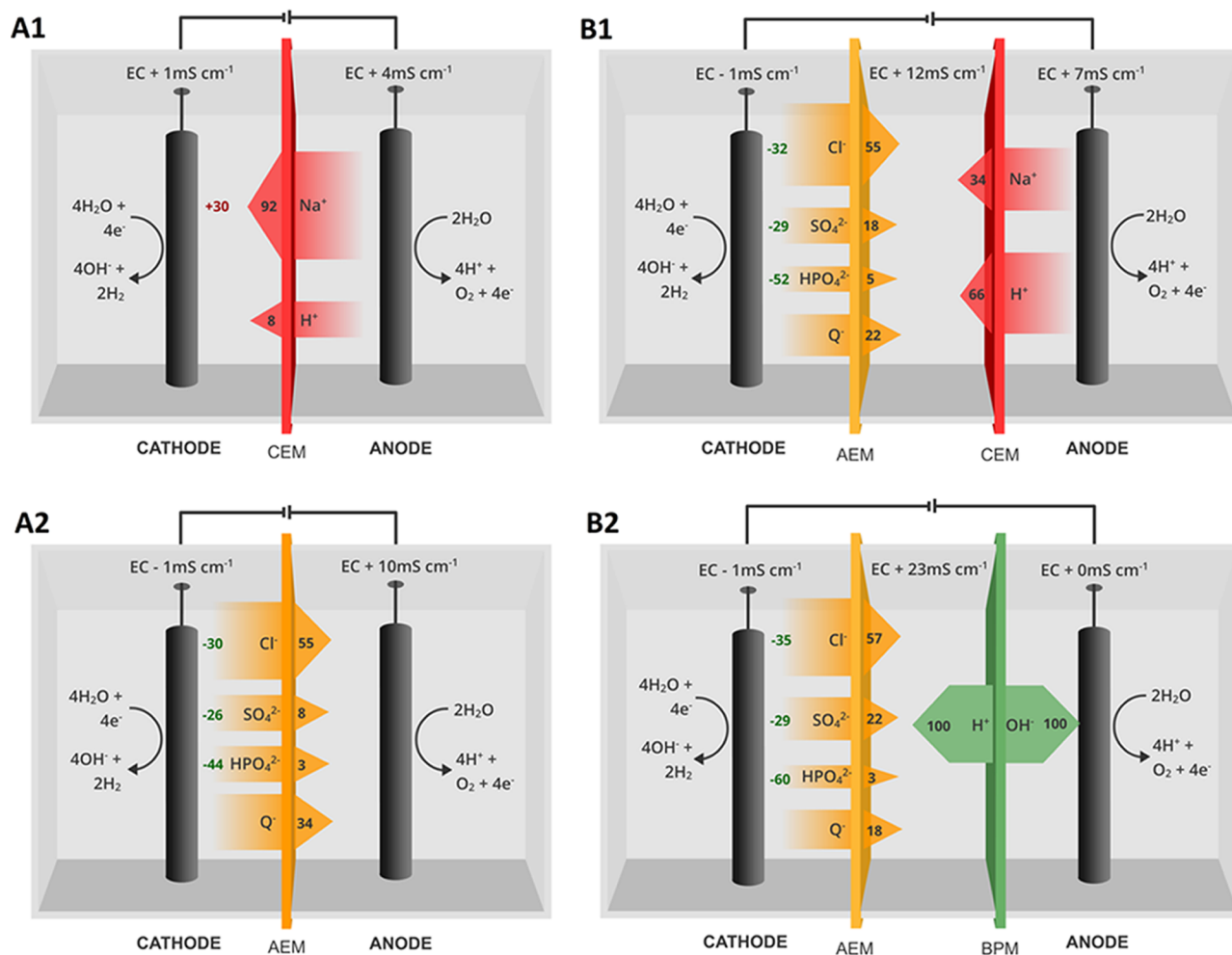
Figure 2. Schematic overview of the ion migration in the four configurations: CEM (A1), AEM + CEM (B1), AEM (A2), and AEM + BPM (B2). The difference in electrical conductivity (EC) between the start and the end (at pH 11) of the experiment is mentioned at the top of each compartment. The arrows illustrate the direction of the migration through the membranes. The numbers displayed on the arrows represent the relative contribution (%) of each ion to the total migration (calculation in Section D, SI). Q^- represents the residual anions that were not quantified (including hydroxyl ions, carbonate ions, and negatively charged organics). The percentages mentioned in the cathodic compartment (in green or red) indicate the increase (+, red) or decrease (−, green) in concentration in the urine, caused by the migration and/or precipitation (in the case of phosphate and sulfate). All values are averages ($n = 3$). Standard deviations can be found in Table S3 (SI).

The electrochemical cell consisted of two Perspex plates and frames with an internal volume of 200 mL (dimension of $20 \times 5 \times 2$ cm^3), a stainless steel wire mesh (564 μm mesh width, 20×5 cm^2, Solana, Belgium) as a cathode, and a dimensionally stable titanium anode coated with iridium oxide (Magneto Special Anodes, The Netherlands). The compartments were separated by an ion-exchange membrane with a surface area of 100 cm^2 to create a pH gradient between the electrode compartments. The middle compartment in the three-chamber electrochemical cell was made from a rubber frame ($\sim$5 mm thick). The cell was galvanostatically controlled at a current density of 60 A m^{-2} (membrane projected surface) using a digital-control DC power supply (LABPS3005, Velleman, Belgium).

2.3. Experimental Protocol. Four different membrane configurations were tested (Figure S2, SI). In configuration A1 (CEM), the anodic and cathodic compartments were separated by a CEM (Ultrex CMI-7000s, Membranes International Inc., NJ). In configuration A2 (AEM), the CEM was replaced by an AEM (Ultrex AMI-7001, Membranes International Inc., NJ). In the CEM configuration, a higher anolyte concentration (1.5

L of 0.2 M Na$_2$SO$_4$) was used to compensate for ion migration out of the anodic compartment, in contrast to the AEM configuration (1.5 L of 0.05 M Na$_2$SO$_4$) where ions migrate toward the anolyte. Configurations B1 (AEM + CEM) and B2 (AEM + BPM) consisted of a three-chamber electrochemical cell with an AEM separating the cathodic from the middle compartment. The middle compartment was separated from the anodic compartment by a CEM or a BPM (Fumasep FBM, Fumatech, Germany), respectively. Initially, all experiments with the three-chamber cell were conducted with 1 L of 0.05 M Na$_2$SO$_4$ as the anolyte and 1 L of 0.05 M Na$_2$SO$_4$ as the middle compartment solution.

The setup was operated as a fed-batch reactor. The crystallizer was filled with 4 L of fresh, diluted urine (2 L of urine and 2 L of demineralized water) at the start of each test. Subsequently, the recirculation pumps and power supply were switched on. Samples were taken every hour, filtered (0.20 μm Chromafil Xtra filter, Macherey-Nagel, PA), and stored in a fridge prior to analysis. Once the pH set point was reached, the power supply was switched off and the crystallizer and anode vessel were emptied. A pH of 11 was targeted in the tests with

the two-chamber setup, whereas the tests with a three-chamber cell were ceased at a pH of 12 to investigate the urine stabilization at pH 11 and pH 12 (Section 2.4). All tests were performed in triplicate with different batches of urine to account for the variability in urine composition. Samples were analyzed for pH, EC, anions, and cations.

2.4. Assessment of Urine Stabilization. A pH higher than 11 was targeted in the crystallizer to stabilize the urine. Fresh (nontreated, 1:1 (50%) diluted) urine and stabilized urine (effluent at pH 11 from the tests with a CEM ($n = 3$) and at pH 12 from the tests with the AEM−CEM ($n = 3$) setup) was stored in falcon tubes at room temperature to follow the urea hydrolysis over time. Samples were taken regularly to measure the pH, electrical conductivity (EC), and ammonium concentration. The stabilization experiment with fresh urine and the effluent from the tests with the CEM setup (pH 11) was conducted for 25 days, whereas the effluent of the tests with the AEM−CEM setup (pH 12) was stored for 568 days. After 561 days, Jack bean urease (0.53 g L^{-1} after Ray et al.,[18] Sigma Aldrich) was added to the falcon tubes to initiate urea hydrolysis and samples were taken after two and seven days. Urea hydrolysis was evaluated by measuring the total ammoniacal nitrogen (TAN)/total nitrogen (TN) ratio over time.

2.5. Analytical Methods. Anions (chloride, nitrite, nitrate, sulfate, and phosphate) were analyzed on a Metrohm 930 compact ion chromatograph, equipped with a conductivity detector and a Metrosep A supp 5-150/4.0 column (Metrohm, Switzerland). Sodium, total ammonium nitrogen (TAN), and potassium were quantified using a Metrohm 761 compact ion chromatograph, equipped with a conductivity detector and a Metrosep C6-250/4.0 column (Metrohm, Switzerland). Calcium and magnesium concentrations were measured by flame atomic absorption spectrometry (Shimadzu AA-6300, Shimadzu, Japan). Prior to analysis, samples were diluted with Milli-Q water and acidified with 1% nitric acid and 2% of lanthanum solution. Nanocolor tube test kits (Nanocolor TN220, Macherey-Nagel, PA) were used to determine the total nitrogen (TN) concentration. The electrical conductivity (EC) was measured with a conductivity meter (Consort C6010 with a Metrohm 6.0912.110 conductivity probe), calibrated with 0.01, 0.1, and 1 M KCl solutions before use. pH measurements were performed with a portable pH meter (744 pH meter, Metrohm, with a 6.0228.000 electrode).

3. RESULTS AND DISCUSSION

3.1. Configuration-Specific Electromigration. The electrode compartments were separated by an ion-exchange membrane to create a pH gradient between the anode and cathode. At the cathode, hydroxyl ions were generated, increasing the pH of the urine, while at the anode, protons were generated, acidifying the anolyte. To restore the electroneutrality in the electrode compartments, ions migrated between the anodic and cathodic compartments. In the CEM configuration, only cations are expected to migrate (when assuming perfect permselectivity of the membrane) due to the negatively charged functional groups (i.e., sulfonic acid) on the CEM. Mainly, sodium, originating from the sodium sulfate solution that was used as anolyte, migrated from the anodic to the cathodic compartment (Figure 2). As a result, the sodium concentration in the urine increased by 30%. Because of the high anolyte Na_2SO_4 concentration (0.2 M), protons accounted for only ∼8% of the migration, although evidently

over a longer time duration the impact of protons would be more substantial due to sodium depletion. The disadvantage of this configuration is thus that the anolyte solution needs to be replaced during long-term operation since the sodium sulfate solution is gradually replaced by sulfuric acid (due to the migration of sodium to the cathodic compartment and the proton production at the anode). Once the sodium gets depleted in the anodic compartment, the migration of protons to the cathodic compartment will increase and compensate the hydroxyl produced at the cathode. In cases where an AEM is used, the anolyte does not need to be replaced as ions move from the catholyte (urine) to the anolyte to maintain the charge balance. Chloride, sulfate, and phosphate accounted for 55, 8, and 3%, respectively, of the migration of charges through the AEM. Due to the migration and some precipitation of phosphate and sulfate, the concentrations of chloride, sulfate, and phosphate in urine decreased by 30, 26, and 44%, respectively. Due to the chloride migration to the anodic compartment and the limited selectivity of the anode, some chlorine can be formed at the anode (eq 4), besides the intended water oxidation. The chlorine can diffuse to the atmosphere or react with water to form hydrochloric and hypochlorous acid (eq 5), which can oxidize materials such as the membrane.[28] When chlorine gas diffuses to the cathode compartment, it could react with the organics or ammonia present in urine.

$$2Cl^- \rightarrow Cl_2 + 2e \quad E^0(SHE) = 1.36 \text{ V} \tag{4}$$

$$Cl_2 + H_2O \rightarrow HCl + HOCl \tag{5}$$
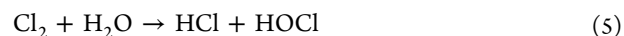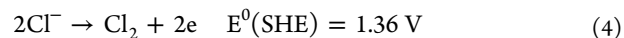
Chlorine production can be prevented by a more selective electrode designed to suppress chlorine generation[28] or by a three-chamber cell. In the AEM + CEM and AEM + BPM configuration, migration of chloride from the urine to the anodic compartment is prevented by the CEM or BPM membrane between the middle compartment and the anodic compartment. Similar to the AEM configuration, chloride was the predominant migrating ion through the AEM (accounting for 55−57%), followed by sulfate (18−22%). Also, the reduction in chloride, sulfate, and phosphate concentrations and EC in the crystallizer was comparable in all configurations with an AEM. In the AEM + CEM configuration, sodium and protons migrated from the anodic compartment to the middle compartment. Relatively more protons migrated through the CEM in the AEM + CEM compared to those in the CEM configuration due to the lower sodium concentration in the anolyte (0.05 M Na_2SO_4 instead of 0.2 M). Similar to the CEM configuration, the proton migration will increase over time as the sodium in the anolyte becomes depleted. In conjunction with the AEM, however, the protons cannot reach the catholyte, by which the pH gradient can be maintained. Hence, unlike the CEM configuration, the anolyte does not need to be replaced during long-term operation with the AEM + CEM configuration. In the AEM + BPM configuration, sodium migration from the anodic compartment to the middle compartment is prevented by the BPM. A BPM consists of an AEM and a CEM layer joined together.[28] Due to the electric field across the membranes, water molecules split in the transition region between the layers. The protons migrate through the CEM layer to the middle compartment, whereas hydroxyl ions migrate through the AEM layer to the anodic compartment. Hence, the anolyte composition does at least theoretically not change.
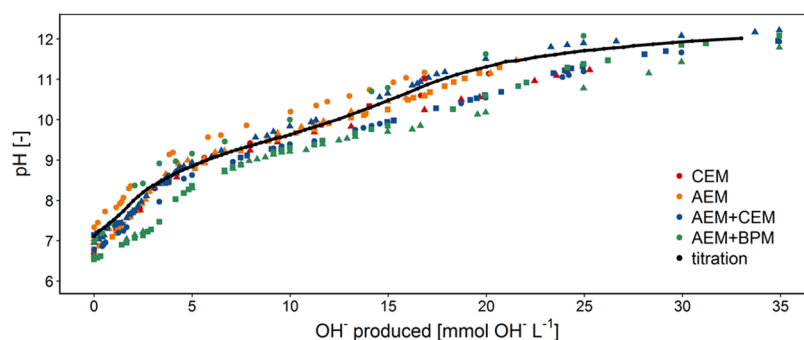
Figure 3. pH increase in the crystallizer as a function of the OH^- produced by the electrochemical cell. The amount of hydroxyl [mmol OH^- L^{-1}] produced by the electrochemical cell was calculated by dividing the cumulative electric charge by the Faraday constant and crystallizer volume, assuming a Faradaic (current) efficiency of 100% (i.e., one mole of electrons corresponds to one mole of hydroxyl ions). Each configuration was tested in triplicate (shown with different shapes) with 1:1 diluted urine. The black line represents a titration curve of fresh urine with 1 M NaOH (90 data points).
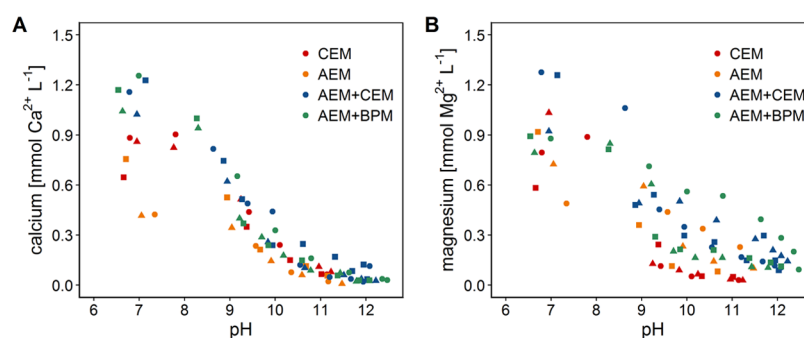

Figure 4. Calcium (A) and magnesium (B) concentrations as a function of the pH in the crystallizer. Each configuration was tested in triplicate (shown with different shapes). The concentration for each individual test is displayed in Figures S3 and S4 (Section C, SI).

3.2. pH Profile in the Crystallizer. A high pH was induced in a crystallizer by recirculating the urine over the cathodic compartment of the electrochemical cell, in which hydroxyl ions were produced through the reduction of water or oxygen. The pH increased as a function of the amount of hydroxyl ions produced by the electrochemical cell (Figure 3), calculated by dividing the cumulative electric charge by the Faraday constant and crystallizer volume, assuming a Faradaic (current) efficiency of 100%. All curves display a characteristic pH increase in three stages: the slope decreases at a pH above 8.5 due to the buffering activity of the NH_4^+/NH_3 equilibrium, followed by the HCO_3^-/CO_3^{2-} equilibrium and the curve flattens out as the pH approaches to pH 12 due to the buffering activity of the HPO_4^{2-}/PO_4^{3-} equilibrium. The differences between the tests can be explained by the use of different batches of urine (with different ammonium, carbonate, and/or phosphate concentrations and initial pH). There were no profound differences between the four configurations. The pH increase in the crystallizer coincides with a titration curve of fresh urine with NaOH (black line in Figure 3), indicating a high Faradaic efficiency and a limited migration and diffusion of hydroxyl ions or protons from and to the cathodic compartment. About 20 mmol OH^- L^{-1} was needed to raise the pH to 11. An additional 10−15 mmol OH^- L^{-1} was required to reach a pH of 12 in the tests with the three-chamber cell. This corresponds to applied total electric charges of about 2000 and 3500 C L^{-1} to obtain pH values of 11 and 12, respectively (Section B, SI). In theory (without overpotentials and Ohmic drop), an applied cell voltage between 1.3 and 1.7 V is necessary to drive the water reduction

and water oxidation reactions at the cathode and anode (Section B, SI), which would require ~1.5 ± 0.3 Wh L^{-1} urine or 2.9 ± 0.3 Wh L^{-1} urine to increase the pH of fresh urine to 11 or 12, respectively. The real electrochemical energy consumption in the tests was between 4.9 and 8.8 Wh L^{-1} urine (pH 11) and 14.3 Wh L^{-1} urine (pH 12) (Section B, SI). The lower voltage and, hence, the lower energy consumption in the tests with a CEM (Table S2, SI) can be attributed to the lower electrical resistance of the CEM (<30 Ω·cm², according to the supplier) compared to that of the AEM (<40 Ω·m²) and to the higher electrical conductivity of the anolyte (~35 ms cm^{-1} compared to only ~10−20 mS cm^{-1} in all other configurations). The voltage and electrode energy consumptions of the three-chamber cells (AEM + CEM and AEM + BPM) were not substantially higher than those of the two-chamber cell with the AEM, despite the additional membrane and increased distance between the electrodes (~0.5 cm, corresponding to a theoretical Ohmic drop of ~0.1−0.3V, which is low compared to the total voltage of ~7.5V).

3.3. Precipitation of Bivalent Cations at High pH. The pH increase shifts the speciation of phosphate and carbonate ions, creating supersaturation of calcium and magnesium phosphate and carbonate salts (e.g., hydroxyapatite and calcite) and thus precipitation in the crystallizer. As a result, calcium and magnesium are removed from the urine, reducing the scaling potential in downstream processing. The higher the pH, the higher the supersaturation and thus the lower the final remaining calcium and magnesium concentrations (Figure 4). At a pH of ~9.25, which is the pH of urine after urea hydrolysis, only about 53 ± 16% of the calcium and 52 ± 29%
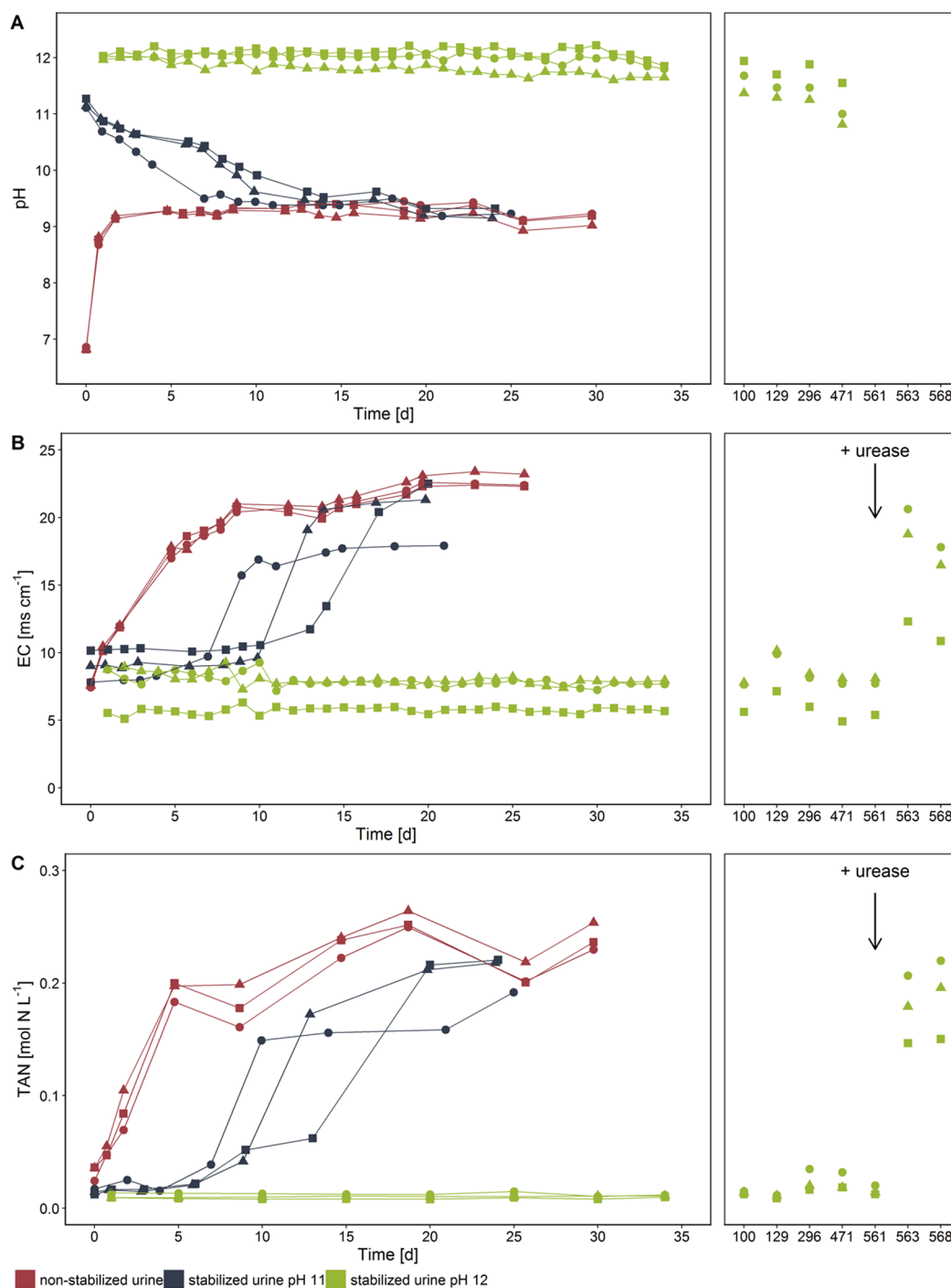
Figure 5. pH, electrical conductivity (EC), and total ammoniacal nitrogen (TAN) concentration in nonstabilized urine and stabilized urine at pH values of 11 and 12 over time. The triplicates are represented with different symbols. After 561 days, Jack bean urease (0.53 g L^{-1}) was added to the stabilized urine (pH 12) to initiate urea hydrolysis (indicated with the arrow).

of the magnesium were removed, whereas at a pH of 11, 93 $\pm$ 3% of the calcium and 79 $\pm$ 16% of the magnesium were precipitated. The removal efficiencies increased to 96 $\pm$ 3% (calcium) and 85 $\pm$ 9% (magnesium) at a pH of 12. The final calcium and magnesium concentrations were 0.065 $\pm$ 0.039 mmol Ca^{2+} L^{-1} and 0.15 $\pm$ 0.11 mmol Mg^{2+} L^{-1} (pH 11) and 0.042 $\pm$ 0.035 mmol Ca^{2+} L^{-1} and 0.14 $\pm$ 0.07 mmol Mg^{2+} L^{-1} (pH 12). Overall, there was a similar pH increase and calcium and magnesium removal in all configurations.

3.4. Urine Long-Term Stabilization. The aim of this study was to stabilize fresh urine by increasing the pH. Ideally,

it should be possible to preserve the treated urine for a long time without urea hydrolysis to avoid malodor and ammonia volatilization during storage. pH 11 was identified as the upper limit for enzymatic urea hydrolysis by Randall et al.[21] Urine could be stored for one month without urea hydrolysis by increasing the pH to 11 with NaOH.[21] To follow up the urea hydrolysis in the electrochemically stabilized urine produced in this study over time, the effluent from the three tests with the CEM configuration with a pH around 11 was stored at room temperature and the pH, EC, and TAN concentration were measured regularly (Figure 5). Urea hydrolysis is characterized

by a sharp increase in pH to ~9.25 due to the release of TAN and bicarbonate, whereas the EC gradually increases during hydrolysis because of the conversion of uncharged urea into charged molecules (ammonium and bicarbonate). Hence, the pH is a good indicator of the onset of hydrolysis, while the EC can be used as a measure of the urea hydrolysis progression.[18,31] Fresh, nontreated urine (in red) was included as a control and started to hydrolyze immediately, resulting in a sharp increase in pH, EC, and TAN concentration. After two days, the pH reached a plateau at ~9.25, while it took 10−15 days to reach the maximum EC and TAN concentration. No significant increase in EC or TAN concentration occurred in the stabilized urine at pH 11 (in blue) during the first ~7 days, indicating that urea hydrolysis was inhibited. However, the pH gradually decreased and reached a pH of ~9.25 after 7−10 days. Due to the lower pH, urea hydrolysis was no longer inhibited, resulting in an increase in EC and TAN concentration. It is not known what caused the pH decrease, possibly alkaline hydrolysis of urine constituents (e.g., organics) or some CO_2 absorption from the headspace or during sampling. In the study by Randall et al.,[21] the pH was daily adjusted with NaOH to keep the pH at 11, which might explain the different outcomes of the study. Overall, the increase in EC corresponds well to the increase in TAN concentration, confirming the results obtained by Zhang et al.[31] and Ray et al.[18] Since increasing the pH to 11 did not suppress the enzymatic urea hydrolysis for longer than one week, a pH of 12 was targeted in the tests with the AEM + CEM configuration. To reach this set point, almost double the amount of hydroxyl ions was added compared to a pH of 11 due to the buffering effect of the HPO_4^{2-}/PO_4^{3-} equilibrium. As a result, the pH decreased much slower during storage and was still sufficiently high (>11) to inhibit urea hydrolysis for up to 18 months (Figure 5, green). Over a period of 18 months, the TAN/TN ratio only increased from ~5 to ~8% (Table S4, SI). The urine also did not have the typical dark color and smell of hydrolyzed urine (Figure S7, SI). The presence of organics in urine (~10 g chemical oxygen demand (COD) L^{-1}) fuels biological growth, resulting in the production of volatile fatty acids, which contribute to the strong smell of urine.[4,31] The high pH probably inhibits the biological growth and, hence, prevents malodor.

Some nitrogen recovery technologies (e.g., NH_3 stripping, NH_3 extraction with BES and EC systems) require ammonium or ammonia as nitrogen input instead of urea.[32] After 561 days, Jack bean urease was added to initiate urea hydrolysis in the stabilized urine. Two days after addition, 80−100% of the total nitrogen was converted into TAN (Figure 5 and Table S4). Mixing with stale (hydrolyzed) urine[31] or treatment in an anaerobic ureolysis reactor[32] can probably also induce urea hydrolysis in stabilized urine after long-term storage.

3.5. Phosphorus Recovery from Precipitates. The phosphate concentration in the crystallizer decreased by 48 ± 14%. This is mainly due to the precipitation of phosphates with calcium and magnesium, accounting for a 38 ± 11% (1.12 ± 0.31 mmol PO_4^{3-} L^{-1}) removal. In addition, migration through the membrane accounted for 13 ± 3% in the three configurations with an AEM (Figure S8, SI). Measurements[8] and simulations[7] with undiluted urine by Udert et al. showed that about 30% of the phosphate was precipitated by urea hydrolysis. The amount of phosphate that can be precipitated in urine is limited by the calcium and magnesium

concentrations in urine and by competition with other anions such as carbonate.[7,8]

Precipitation reduces the phosphate content of the urine and thus limits the P recovery potential in later treatment.[7] On the other hand, if the precipitates can be harvested, they can be valorized as inorganic fertilizers in agriculture or resources for the phosphate industry.[2,4] Randall and Naidoo[2] proposed to install a replaceable conical cartridge at the bottom of the toilet to allow user-friendly precipitate harvesting.

Udert et al.[8] identified struvite, calcite, and calcium phosphate minerals (e.g., hydroxyapatite) as the main precipitates in urine after urea hydrolysis. Hydroxyapatite and struvite are believed to be good slow-release fertilizers on acid soils.[8] The precipitates formed by electrochemical precipitation are probably more enriched in calcium phosphate minerals since fresh urine contains less ammonium and carbonate, which are necessary for struvite and calcite precipitation, respectively. Moreover, computer simulation by Randall et al.[21] pointed out that magnesium mainly precipitates as $Mg(OH)_2$ at high pH values. The precipitate produced in this study could not be identified by X-ray diffraction (XRD) (no clear diffraction peaks). X-ray fluorescence (XRF) identified calcium and phosphate as the predominant ions in the precipitate. More research is necessary to characterize the composition of the precipitates to assess their fertilizer potential.

3.6. Implementation and Application of Electrochemical Urine Precipitation and Stabilization. In this study, the pH of fresh urine was increased using an electrochemical cell to prevent urea hydrolysis during storage and to facilitate downstream processing by the controlled precipitation of calcium and magnesium. Urea hydrolysis already starts in urine collection systems since urease-positive bacteria are widespread.[7,8,33] This can lead to odor nuisance, ammonia volatilization, and clogging of pipes. As it is more difficult to increase the pH of partially hydrolyzed urine due to the stronger ammonium and carbonate buffer, it is important that an electrochemical cell for urine stabilization is installed as close to the toilet as possible (or is integrated into the toilet) to minimize the time before stabilization. The setup can be operated as a fed-batch reactor, in which the pH of consecutive batches (donations) of urine is gradually increased from ~7 to 11−12. When the pH set point is reached, the crystallizer is emptied and the urine is sent to a storage tank until further treatment. If an efficient precipitate collection system is in place, phosphorus can be recovered by harvesting the precipitates. In this study, the urine was diluted 1:1 to simulate flushing with water. Treating undiluted urine instead would likely result in more precipitation (due to the higher bivalent cation concentration) and a lower energy consumption per volume of urine treated (due to the higher conductivity and thus lower Ohmic resistance of the catholyte).

The higher the pH in the crystallizer, the more the removal of calcium and magnesium and thus the lower the risk for scaling during further treatment. While precipitation is limited by the low calcium and magnesium concentrations, it can still occur since the ion product approximates the solubility product. To completely eliminate the risk for scaling, the pH should be lowered during or just before treatment. For stabilization, pH 11 was not sufficient to inhibit urea hydrolysis for longer than one week, whereas the urine at pH 12 could be preserved for ~18 months without hydrolysis. A pH ≫ 12 is unfavorable because a lot of energy needs to be invested to

increase the pH of fresh urine due to the strong HPO_4^{2-}/PO_4^{3-} buffer. Moreover, chemical urea hydrolysis can start to occur above pH 13,[21] which should be prevented. Hence, the optimal pH for electrochemical stabilization and precipitation is around 12. Interestingly, according to literature, most of the bacteria and viruses are inactivated or killed at this high pH.[21]

From the four electrochemical cell configurations that were tested, the three-chamber cells (AEM + CEM and AEM + BPM) are the most promising. Unlike the CEM configuration, no chemical input is required when an AEM is used, as ions migrate from the cathode (urine) to the anode. Due to this ion migration, the concentration of chloride is reduced with 30−35% in urine, which is beneficial as a high salinity (and in particular chloride) challenges biological processing (e.g., nitrification) and plant production. By incorporating a CEM or BPM in the cell, chlorine production at the anode can be prevented, protecting the membrane and electrode from highly oxidizing hypochlorous acid that can be formed.

During the experiments, the AEM in all configurations turned brown (Figure S6, SI), probably due to the adsorption of organics to the positively charged functional groups of the AEM.[34,35] It is not known whether this can affect the performance of the electrochemical cell during long-term operation. Using a monovalent AEM, through which only monovalent ions can pass, or an AEM with a modified surface might decrease the adsorption of organics to the AEM, but this has not been tested yet with urine.[36,37] Moreover, a monovalent AEM could prevent the migration and hence loss of phosphate to the middle compartment.

Due to the migration of anions from the cathode and protons from the anode, an acidic stream (mix of HCl, H_2SO_4, H_3PO_4, HNO_3, H_2CO_3, and organic acids) is produced in the middle compartment of the three-chamber cells. Likely, the best strategy to minimize salt accumulation (and the associated back diffusion to the catholyte or diffusion to the anolyte) is to regularly replenish a part of the middle compartment fluid with water. The acidic middle compartment fluid can be used to periodically rinse the cathodic compartment of the electrochemical cell to remove the precipitates accumulated on the electrode surface and/or membrane. It can also be used to periodically flush the toilet to remove scaling and to hygienize/suppress microbial activity in the toilet. Flushing urine diversion toilets with acids to remove precipitates is already a common practice.[9] After a flushing event, some acidified urine could enter the electrochemical cell, resulting in a temporary increase in hydroxyl requirement to reach a pH of 12. The anolyte solution of a three-compartment setup will also need to be replenished with water after some time because of osmotic and electro-osmotic water transport to the middle compartment, resulting from the high concentration gradient between the anolyte and middle compartment solution and the migration of cations (including hydration shell) to the middle compartment. The hydrogen gas produced at the anode would spontaneously degas; however, a small aeration could be installed to avoid any accumulation. On a large scale, it could be recovered and valorized as an energy source.

By a smart selection of membranes, no chemical input is required to increase the pH, which is not only interesting for terrestrial applications, where chemical storage and dosing are a nuisance, but could also prove useful in regenerative life support systems (RLSS) for space. Currently, on board of the International Space Station, water is recovered from urine using vapor compression distillation and filtration. Since ammonia volatilization can pose a hazard to the crew, the urine is pretreated with hazardous and toxic chemicals (sulfuric acid and chromium trioxide) to inhibit urea hydrolysis.[38] Furthermore, the distillation unit faces severe scaling problems due to uncontrolled calcium sulfate precipitation. The electrochemical pretreatment studied here allows the reduction of the scaling potential and the stabilization of urine, without consumables and the logistics related to the storage of chemicals. In Micro Ecological Life Support System Alternative (MELiSSA), urine is converted into a liquid fertilizer for plants and microalgae (cyanobacteria) by nitrification.[39,40] Apart from reducing the scaling potential and stabilizing the urine before nitrification, the electrochemical pretreatment would reduce the salinity of the urine due to the migration of anions (mainly chloride) to the middle compartment and the acid that is produced can be used to decrease the pH in the plant compartment. Moreover, nitrification lowers the pH, decreasing the ion product and thus eliminating the risk for scaling.

Further research should focus on the long-term (semi)-continuous functioning of the electrochemical cell, the design of a precipitate collection system, and the implementation/integration into a source separation toilet.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.est.9b06804.

> Experimental setup; schematic overview of the four configurations; urine composition after dilution with demineralized water; electric charge and electrode energy consumption; bivalent cation removal; electromigration; anion exchange membrane after two days of operation; long-term stabilization; and phosphate removal (PDF)

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■ ABBREVIATIONS USED

AEM anion exchange membrane
BPM bipolar membrane
CEM cation exchange membrane
EC electrical conductivity
TAN total ammoniacal nitrogen

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