Toomas Tenno*, Ergo Rikmann, Kalev Uiga, Ivar Zekker, Alexey Mashirin, and Taavo Tenno
Institute of Chemistry, University of Tartu, Ravila 14A, 50411 Tartu, Estonia
Received 7 December 2017, accepted 12 January 2018, available online 15 June 2018
© 2018 Authors. This is an Open Access article distributed under the terms and conditions of the Creative Commons Attribution-NonCommercial 4.0 International License (http://creativecommons.org/licenses/by-nc/4.0/).

Abstract. Variation in the concentration of dissolved carbon dioxide \([\text{CO}_2]_W\) causes changes in the solubility of limestone and in the pH of an equilibrium system. An elevation of the pH will shift the equilibrium of the reversible reaction \(\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+\) towards the formation of free ammonia (\(\text{NH}_3\)). This results in the inhibition of the activity of microorganisms that perform the biological waste- and reject-water treatment. The model of the system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3\) was upgraded on the basis of proton transfer principles and taken as the basis for modelling the closed system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3-\text{NH}_4\text{Cl}\). The distribution of ions and molecules in the closed system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3-\text{NH}_X\) is described in terms of a structural scheme. A novel proton transfer model was developed to calculate the pH, concentrations of the formed ions and molecules, and proton transfer parameters of the closed equilibrium system using an iteration method. In the formation of the equilibrium system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3\), as a result of the dissolution of \(\text{CaCO}_3\), the \(\text{CO}_3^{2-}\) ions are released and these will accept a certain quantity of protons \((\Delta[H^+]_{\text{H}_2\text{CO}_3})\) which originate from two sources: the reversible dissociation of water \((\Delta[H^+]_{\text{H}_2\text{O}})\) or \(\text{H}_2\text{CO}_3\). In case the final closed system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3-\text{NH}_4\text{Cl}\) includes small initial concentrations of \([\text{CO}_2]_{W0}\) the main amount of protons \((\Delta[H^+]_{\text{H}_2\text{CO}_3})\) comes from the dissociation of \(\text{NH}_4^+\), or if there are higher concentrations of \([\text{CO}_2]_{W0}\) the source of protons is \(\text{H}_2\text{CO}_3\).

Key words: proton transfer model, equilibrium system \(\text{H}_2\text{O}-(\text{CO}_2)-\text{CaCO}_3-\text{NH}_X\), bicarbonate, free ammonia.

1. INTRODUCTION

Limestone bedrock, which consists mainly of \(\text{CaCO}_3\), affects the treatment of wastewater including reject water generated in biogas plants. The variation in the concentration of dissolved carbon dioxide \([\text{CO}_2]_W\) changes \(\text{CaCO}_3\) solubility in and the pH of equilibrium systems. The equilibrium system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3\) (where \((\text{CO}_2)_W\) stands for dissolved carbon dioxide) has been extensively studied \([1–6]\), but no systemic interpretation of equilibrium reactions has been proposed. We have previously published the models of the equilibrium system \(\text{H}_2\text{O}-(\text{CO}_2)_W-\text{CaCO}_3\) based on proton-centred acid–base equilibria for both open \([7]\) and closed systems \([8]\).

* Corresponding author, toomas.tenno@ut.ee
The aqueous systems with prevailing carbonaceous and ammoniacal species are present in many wastewaters of various types and origin. However, there are relatively few studies modelling interconnected equilibrium processes that affect wastewater treatment [9]. No proton-centred models have been proposed for interconnected equilibria in wastewaters. Ammonia nitrogen NH$_X$-N (NH$^+_4$-N together with NH$_3$-N) is a pollutant present in high concentrations in the reject water from the anaerobic digestion of organic substrates and landfill leachate. The concentration of [NH$_X$-N] is up to 2200 mg·L$^{-1}$ in the case of landfill leachate [10–12] and up to 1500 mg·L$^{-1}$ in the reject water [13,14] that comes from the dewatering of anaerobically digested wastewater sludge [15,16].

In an anaerobic digester, the pH of the liquid phase is affected by carbonaceous equilibria. In case of limestone bedrocks, the water has been in contact with CaCO$_3$. On the other hand, the liquid phase is exposed to the gas phase of which about a third is CO$_2$ [17]. The liquid phase in the anaerobic digester of the Tallinn Municipal Wastewater Treatment Plant has a pH value of 7.2 (±0.2) [18]. During dewatering the digested sludge, the reject water comes into contact with ambient air and the degassing of CO$_2$ from the liquid phase takes place, which causes the pH value of the reject water to increase to 8.1 (±0.2) [18,19], shifting the equilibrium of the reaction NH$^+_4$ $\rightleftharpoons$ NH$_3$ + H$^+$ towards the dissociation of NH$^+_4$ and the formation of free ammonia (NH$_3$) [20–22].

In the case of anaerobic ammonium-oxidizing (anammox) bacteria, an elevated concentration of NH$_3$-N (≥8 mg·L$^{-1}$) acts as an inhibitor on biological wastewater treatment processes, including the activity of bacteria performing autotrophic nitrogen removal [20–24]. The lowest NH$_3$ toxicity threshold concentration, provided by Jung et al. (2007) [25], is 1.7 mgN·L$^{-1}$ during the startup period, which is significantly smaller than the values typically observed in pilot and full-scale anammox reactors [23,26]. Zekker et al. (2012) [27] investigated short- and long-term effects of various bicarbonate and free ammonia concentrations on wastewater treatment in the biofilm process showing a decrease in the bacterial activity at very low and high bicarbonate concentrations. A similar inhibition effect was determined in batch tests, with a decrease of 50% in the specific anammox microorganisms’ activity at NH$_3$-N concentrations of 38 mg·L$^{-1}$, and long-term tests in sequencing batch reactors showed performance instability when the NH$_3$-N concentration exceeded 20–25 mg·L$^{-1}$ [23]. Thus, the adjustment of the pH is required in waste- and reject-water treatment systems in streams with a high content of [NH$_X$-N] in cases when there is contact with limestone [15,18]. The concentration of NH$_3$ has so far been calculated from the empirical formula published by Anthonisen et al. in 1976, which is a function of the concentration of NH$^+_4$, pH, and temperature [20]:

$$[\text{NH}_3] = \frac{[\text{NH}_4^+]}{K_b + 10^{\Delta pH}} \cdot 10^{\Delta pH},$$

(1)

where

$$\frac{K_b}{K_W} = e^{6344/273 + t}.$$  

(2)

In equations (1) and (2), $K_b$ is the basicity constant of ammonia, $K_W$ is the ion-product constant of water, $e$ is the base of the natural logarithm, and $t$ the temperature in °C.

Equation (1) does not take into account the effect of interactions between the carbonaceous and ammoniacal equilibrium processes, which alter the concentration of [NH$_3$]. Therefore, the actual concentration of [NH$_3$] may be significantly different from that calculated using equation (1). To calculate [NH$_3$] in a system having a high concentration of dissolved [NH$_X$] and carbonaceous species, a mathematical model needs to be developed. In the present study the model of the system H$_2$O–(CO$_2$)$_W$–CaCO$_3$ was upgraded on the basis of proton transfer principles and taken as the basis to model the closed system H$_2$O–(CO$_2$)$_W$–CaCO$_3$–NH$_4$Cl. Proton transfer parameters, pH, and equilibrium concentrations of ions and molecules in the liquid phase were calculated using the developed model, which was also experimentally validated.
2. DERIVATION OF THE THEORETICAL MODEL OF THE SYSTEM
H₂O–(CO₂)₇w–CaCO₃–NH₄Cl

2.1. The development of the proton transfer based model of the initial system H₂O–(CO₂)₇w–CaCO₃

When solid CaCO₃ is added to the equilibrium system H₂O–(CO₂)₇w with a summarized concentration of all inorganic carbon containing particles \( \sum [COX]_w \), including (CO₂)₇w, H₂CO₃, HCO₃⁻ and CO₃²⁻, supplementary amounts of [Ca²⁺] and [CO₃²⁻] ions are released by the reversible dissolution of CaCO₃ [8]. The reversible dissociation reaction is as follows:

\[
H₂O ⇌ H⁺ + OH⁻. \quad (3)
\]

It is always present in the water phase, which acts as a host solvent for other chemical reactions. If reactions involve H⁺ or OH⁻ ions, a strong coupling will arise between the solvent and solute reactions. The reversible dissociation reactions in aqueous media involve intermolecular proton transfer. Water dissociates into H⁺ and OH⁻ ions, and if the dissociation products of the solute can bind or release either H⁺ and OH⁻ ions, these reactions will always take place, changing the chemical equilibrium of the system.

In the formation of the equilibrium system H₂O–(CO₂)₇w–CaCO₃, as a result of the dissolution of CaCO₃, the CO₃²⁻ ions are released and they will accept a certain amount of protons (\( \Delta[H⁺]_{CO₃²⁻} \)) originating from two sources, either the reversible dissociation of water (\( \Delta[H⁺]_{H₂O} \)) or H₂CO₃ (\( \Delta[H⁺]_{H₂CO₃} \)) formed in the reaction between (CO₂)₇w and H₂O. Thus, the H⁺ ions have a central role in the evolution of the equilibrium system and form a link between acid–base equilibrium processes. The results of the calculations before adding NH₄Cl are presented in Table 1.

The data in Table 1 show that at the range of concentrations from [CO₂]₇w ≈ 3.39×10⁻⁷ to [CO₂]₇w ≈ 33.9 mmol·L⁻¹ in the closed equilibrium system H₂O–(CO₂)₇w–CaCO₃, the pH will increase up to a maximum value of 9.88 at the decreasing concentration of [CO₂]₇w [8]. The smaller the initial concentration of [CO₂]₇w, the fewer protons are produced due to the dissociation of H₂CO₃. Thus, the dissociation of water at lower concentrations of [CO₂]₇w produces the main amount of protons to form an equilibrium of the system. As a result of equilibrium reactions, the protons bind to CO₃²⁻ ions, the concentration of [OH⁻] ions increases, and the pH rises, whereas the value of the ion product of water (Kw) decreases.

Table 1. Calculated proton transfer values between different species, pH, and concentrations of [CO₂]₇w, [Ca²⁺], and [HCO₃⁻] in the closed equilibrium system H₂O–(CO₂)₇w–CaCO₃ at 25 °C before NH₄Cl was added. The parameters in bold represent an equilibrium state between \( \Delta[H⁺]_{H₂CO₃} \) and \( \Delta[H⁺]_{CO₃²⁻} \) for [Ca²⁺] and [HCO₃⁻].

| [CO₂]₇w, mmol·L⁻¹ | \( \Delta[H⁺]_{H₂O} \), mmol·L⁻¹ | \( \Delta[H⁺]_{H₂CO₃} \), mmol·L⁻¹ | \( \Delta[H⁺]_{CO₃²⁻} \), mmol·L⁻¹ | pH | [Ca²⁺], mmol·L⁻¹ | [HCO₃⁻], mmol·L⁻¹ |
|-----------------|----------------------|----------------------|----------------------|-----|----------------|------------------|
| 3.39×10⁻⁷       | 7.63×10⁻²            | -2.03×10⁻⁵           | -7.63×10⁻²           | 9.88| 1.03×10⁻¹      | 7.63×10⁻²         |
| 1.00×10⁻⁴       | 7.63×10⁻²            | -1.68×10⁻⁵           | -7.63×10⁻²           | 9.88| 1.03×10⁻¹      | 7.63×10⁻²         |
| 1.02×10⁻⁵       | 7.63×10⁻²            | 2.65×10⁻⁵            | -7.63×10⁻²           | 9.88| 1.03×10⁻¹      | 7.63×10⁻²         |
| 2.37×10⁻⁵       | 7.62×10⁻²            | 7.67×10⁻⁵            | -7.63×10⁻²           | 9.88| 1.03×10⁻¹      | 7.64×10⁻²         |
| 3.39×10⁻⁵       | 7.62×10⁻²            | 1.09×10⁻⁴            | -7.63×10⁻²           | 9.88| 1.03×10⁻¹      | 7.64×10⁻²         |
| 3.39×10⁻⁴       | 7.56×10⁻²            | 7.00×10⁻⁴            | -7.63×10⁻²           | 9.87| 1.03×10⁻¹      | 7.70×10⁻²         |
| 3.05×10⁻⁴       | 7.22×10⁻²            | 4.21×10⁻³            | -7.64×10⁻²           | 9.85| 1.03×10⁻¹      | 8.06×10⁻²         |
| 1.32×10⁻²       | 6.19×10⁻²            | 1.57×10⁻²            | -7.75×10⁻²           | 9.79| 1.04×10⁻¹      | 9.32×10⁻²         |
| 3.39×10⁻²       | 4.55×10⁻²            | 3.79×10⁻²            | -8.34×10⁻²           | 9.65| 1.09×10⁻¹      | 1.21×10⁻¹         |
| 3.39×10⁻¹       | 2.43×10⁻³            | 3.46×10⁻¹            | -3.49×10⁻¹           | 8.38| 3.56×10⁻¹      | 6.95×10⁻³         |
| 2.01            | 5.07×10⁻⁵            | 1.53                 | -1.53                | 7.11| 1.53           | 3.05             |
| 2.15            | 3.27×10⁻⁵            | 1.59                 | -1.59                | 7.07| 1.60           | 3.19             |
| **2.45**        | **-1.55×10⁻⁷**       | **1.73**             | **-4.73**            | **7.00**| **1.73** | **3.46** |
| 3.39×10⁻¹       | -7.86×10⁻⁵           | 2.09                 | -2.09                | 6.83| 2.10           | 4.19             |
| 1.02×10⁻¹       | -4.30×10⁻⁴           | 3.58                 | -3.58                | 6.37| 3.58           | 7.16             |
| 3.39×10⁻¹       | -1.11×10⁻³           | 5.78                 | -5.78                | 5.95| 5.78           | 1.16×10⁻¹         |
remains constant. The maximum value of pH = 9.88 is related to the solubility product of CaCO₃ ($K_{SP}$) and the ion product of water ($K_W$) as it is not necessary to take into account the dissociation of H₂CO₃ at small concentrations of [CO₂]₀.

As seen in Table 1, at small values of [CO₂]₀ the concentration of the formed $[\text{HCO}_3^-]$ ions is nearly equal to the concentration of the $[\text{H}^+]$ ions released by the dissociation of water. In this case, the dissociation of water and the solubility of CaCO₃ determine the equilibrium of the system. At a concentration of [CO₂]₀ = 2.45 mmol·L⁻¹, the pH is equal to 7.0. When the concentration of [CO₂]₀ exceeds 2.45 mmol·L⁻¹, the pH will fall below 7. The reaction between (CO₂)₀ and H₂O produces H⁺ ions, which partly participate in the reaction between CO₃²⁻ and H⁺, which forms HCO₃⁻ ions, and the other part of the dissociation products of H₂CO₃ stays in the equilibrium system in the form of HCO₃⁻ and H⁺ ions.

The positive values of $\Delta[H^+][\text{H}_2 \text{O}]$ are an outcome of the dissociation reaction of water, which acts as a proton donor, and (Δ[H⁺][H₂CO₃]) has a negative value because CO₃²⁻ ion is an acceptor of protons. At higher [CO₂]₀ values, the concentration of the formed protons is elevated due to the dissociation of H₂CO₃. As a result, the reversible dissociation of water is suppressed, because the ion product of water ($K_W$) remains constant. The protons will be bound to OH⁻ ions and $\Delta[H^+][\text{H}_2 \text{O}]$ will acquire a negative value. In this region the source of protons, which will react with CO₃²⁻, is formed by the dissociation of H₂CO₃. In the region of [CO₂]₀ ≤ 1.00×10⁻⁶, $\Delta[H^+][\text{H}_2 \text{O}]$ has a negative value as a reversible dehydration of H₂CO₃ is taking place.

2.2. Model of the final equilibrium system after adding NH₄Cl to H₂O–(CO₂)₇–CaCO₃

To the equilibrium system H₂O–(CO₂)₇–CaCO₃, with the initial concentrations of [CO₂]₀ (shown in Table 1), NH₄Cl was added. As a result, a final equilibrium system H₂O–(CO₂)₇–CaCO₃–NH₄Cl was formed. The ions and molecules in the system were quantitatively distributed in accordance with the equilibrium constants as shown in Fig. 1. The values of the initial concentrations of dissolved [CO₂]₀ in the water phase were taken as constants to model the final closed system H₂O–(CO₂)₇–CaCO₃–NH₄Cl.

![Fig. 1. Structural scheme of the equilibrium distribution of ions and molecules in the final closed equilibrium system H₂O–(CO₂)₇–CaCO₃–NH₄Cl, where $K_h$ is the hydration constant of CO₂, $K'_a$ is the true acid dissociation constant of H₂CO₃, $K_{a1}$ is the acid dissociation constant of HCO₃⁻, $K_{SP}$ is the solubility product constant of CaCO₃, $K_W$ is the ion product constant of water, and $K_a$ is the dissociation constant of NH₄⁺ ions.](image-url)
The values of the equilibrium constants of the system under investigation are given as equations (4–9):

\[
K_h = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]_W} = 2.58 \times 10^{-3} [28],
\]

\[
K_{al} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 1.72 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} [29],
\]

\[
K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1} [30],
\]

\[
K_W = [\text{H}^+][\text{OH}^-] = 1.01 \times 10^{-14} (\text{mol} \cdot \text{L}^{-1})^2 [31],
\]

\[
K_{SP} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] = 2.8 \times 10^{-9} (\text{mol} \cdot \text{L}^{-1})^2 [32],
\]

\[
K_a = \frac{[\text{NH}_3]_W[H^+]}{[\text{NH}_4^+]} = 5.6 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1} [33].
\]

In the closed system H$_2$O–(CO$_2$)$_W$–CaCO$_3$–NH$_4$Cl, the charge balance equation is

\[
2[\text{Ca}^{2+}][\text{H}^+] + [\text{NH}_4^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] + [\text{Cl}^-],
\]

and the molar balance equation of carbon containing particles is

\[
\sum [\text{CO}_X]_W = \sum [\text{CO}_X]_{W0} + [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_2]_W,
\]

where $\sum [\text{CO}_X]_W$ is the total amount of carbon containing particles. The molar balance equation of carbon containing particles is the same as in the closed equilibrium system H$_2$O–(CO$_2$)$_W$–solid CaCO$_3$ [8] and does not change at adding NH$_4$Cl.

The molar balance equation of nitrogen containing particles is

\[
s[\text{NH}_4\text{Cl}] = [\text{NH}_4^+] + [\text{NH}_3]_W = [\text{Cl}^-] = \text{constant},
\]

where $s[\text{NH}_4\text{Cl}]$ is the amount of NH$_4$Cl added to the equilibrium system H$_2$O–(CO$_2$)$_W$–CaCO$_3$.

To calculate the concentrations of [CO$_2$]$_W$, [CO$_3^{2-}$], [H$_2$CO$_3$], [HCO$_3^-$], [H$^+$], [OH$^-$], [Ca$^{2+}$], [NH$_4^+$], and [NH$_3$] in the final equilibrium system, it is necessary to solve nine equations: (4)–(12).

To decrease the number of unknowns, the composite constant $K_{al}$ was used. The first pseudo-acid ionization constant $K_{al}$ [7,34] is expressed as a product of the constants $K_h$ and $K'_{al}$:

\[
K_{al} = K_h \times K'_{al} = 4.44 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}.
\]
On the basis of equations (9) and (12) the next equation was developed:

$$[	ext{NH}_4^+] = [\text{Cl}^-] \times \frac{[\text{H}^+]}{[\text{H}^+] + K_a}.$$  \hfill (14)

The concentrations of variables in charge and molar balance equations were eliminated by replacing them by equilibrium constant equations. As a result of replacing the variables, the system is characterized by two equations with two unknown concentrations ([HCO$_3^-$] and [H$^+$]). The charge and molar balance equations were converted to the following forms:

$$[\text{HCO}_3^-] = -\left(\frac{K_w}{[\text{H}^+]} - [\text{H}^+] + \frac{[\text{Cl}^-] 	imes K_a}{[\text{H}^+] + K_a} + \frac{K_w}{[\text{H}^+]} - [\text{H}^+] + \frac{[\text{Cl}^-] 	imes K_a}{[\text{H}^+] + K_a} \right)^2 + 8 \left(\frac{K_{a2}}{[\text{H}^+] + 1} \right) \left(\frac{K_{sp} \times [\text{H}^+]}{K_{a2}} \right),$$  \hfill (15)

$$[\text{HCO}_3^-] = \frac{\sum[\text{CO}_x]_{w0} + \left(\sum[\text{CO}_x]_{w0}\right)^2 + 4 \left(\frac{K_{a2}}{[\text{H}^+] + 1} \right) + \left(\frac{[[\text{H}^+]]}{K_{a1}} \right) \times \frac{K_{sp} \times [\text{H}^+]}{K_{a2}}}{2 \left(\frac{K_{a2}}{[\text{H}^+] + 1} \right) + \left(\frac{[[\text{H}^+]]}{K_{a1}} \right)}.$$  \hfill (16)

Equations (15) and (16) contain only one unknown: the concentration of [H$^+$]. The equilibrium concentrations of the [HCO$_3^-$] and [H$^+$] ions are calculated by an iterative method, using different values of the concentration of [H$^+$] \cite{8}.

The calculation of the final equilibrium concentrations of [Ca$^{2+}$], [NH$_3$], $\sum$[CO$X$]$_w$, and pH was performed on the basis of the calculated equilibrium concentrations of [HCO$_3^-$] and [H$^+$] ions. The amount of H$^+$ ions taken up by CO$_3^{2-}$ ions ($\Delta$[H$^+$]$_{\text{CO}_3^{2-}}$) and the quantity of H$^+$ ions released from the dissociation of water ($\Delta$[H$^+$]$_{\text{H}_2\text{O}}$), H$_2$CO$_3$ ($\Delta$[H$^+$]$_{\text{H}_2\text{CO}_3}$), and NH$_4^+$ ions ($\Delta$[H$^+$]$_{\text{NH}_4^+}$) at a concentration of NH$_4$Cl = 71 mmol·L$^{-1}$ together with the concentrations of [CO$_2$]$_{w0}$, [NH$_3$], [Ca$^{2+}$], [HCO$_3^-$], and pH are presented in Table 2. The concentration of NH$_4$Cl = 71 mmol·L$^{-1}$ equalled the average measured concentration in the reject water of the pilot study by Rikmann et al. \cite{18}.

At the given range of concentrations ([CO$_2$]$_{w0} \approx 33.9$ mmol·L$^{-1}$ to [CO$_2$]$_{w0} \approx 3.39 \times 10^{-7}$ mmol·L$^{-1}$), adding NH$_4$Cl to the initial closed system H$_2$O–[CO$_2$]$_{w0}$–CaCO$_3$ resulted in a reduction in the pH value of the formed equilibrium system H$_2$O–[CO$_2$]$_{w0}$–CaCO$_3$–NH$_4$Cl presented in Tables 1 and 2. The smaller the initial concentration of (CO$_2$)$_{w0}$, the fewer protons were released from the dissociation of H$_2$CO$_3$, while the bulk of the protons that would react with CO$_3^{2-}$ came from the dissociation of NH$_4^+$. In the range of concentrations of [CO$_2$]$_{w0}$ from $3.39 \times 10^{-7}$ to $3.39 \times 10^{-2}$ mmol·L$^{-1}$, the concentration of [HCO$_3^-$] ions is less than the concentration of H$^+$ ions released from the dissociation of NH$_4^+$ (Table 2). The difference between the $\Delta$[H$^+$]$_{\text{NH}_4^+}$ and $\Delta$[H$^+$]$_{\text{CO}_3^{2-}}$ is equal to the negative proton transfer value of $\Delta$[H$^+$]$_{\text{H}_2\text{CO}_3}$, which is related to the reversible dehydration of H$_2$CO$_3$ that is taking place in the given range of [CO$_2$]$_{w0}$. In this case, the dissociation of NH$_4^+$, dehydration of H$_2$CO$_3$, and dissolution of CaCO$_3$ will determine the equilibrium processes in the system.

The concentration of H$^+$ ions released from the dissociation of NH$_4^+$ ions ($\Delta$[H$^+$]$_{\text{NH}_4^+}$) is equal to the concentration of NH$_3$. In the closed system under investigation, at higher concentrations of [CO$_2$]$_{w0}$ in the range from 2.45 to 33.9 mmol·L$^{-1}$, the dissociation of H$_2$CO$_3$ will predominate and produce more protons.
Table 2. Results of the calculations of the equilibrium parameters after adding 71 mmol·L⁻¹ NH₄Cl to the closed initial system H₂O–(CO₂)W₀–CaCO₃ containing [CO₂]W₀ ≈ 3.39 × 10⁻⁷ to 33.9 mmol·L⁻¹ at a t = 25 °C

| [CO₂]W₀ mmol·L⁻¹ | Δ[H⁺]H₂O mmol·L⁻¹ | Δ[H⁺]H⁺CO₃ mmol·L⁻¹ | Δ[H⁺]H⁺CO₂ mmol·L⁻¹ | Δ[H⁺]Ca²⁺ mmol·L⁻¹ | pH | [NH₃] mmol·L⁻¹ | [Ca²⁺] mmol·L⁻¹ | [HCO₃⁻] mmol·L⁻¹ |
|------------------|------------------|------------------|------------------|------------------|-----|----------------|----------------|-----------------|
| 3.39×10⁻⁷       | 3.63×10⁻⁴        | -6.85×10⁻²       | -1.28            | 1.35             | 7.59| 1.35          | 1.28           | 1.21            |
| 1.00×10⁻⁶       | 3.63×10⁻⁴        | -6.85×10⁻²       | -1.28            | 1.35             | 7.59| 1.35          | 1.28           | 1.21            |
| 1.02×10⁻⁵       | 3.63×10⁻⁴        | -6.84×10⁻²       | -1.28            | 1.35             | 7.59| 1.35          | 1.28           | 1.21            |
| 2.37×10⁻⁵       | 3.63×10⁻⁴        | -6.84×10⁻²       | -1.28            | 1.35             | 7.59| 1.35          | 1.28           | 1.21            |
| 3.39×10⁻⁵       | 3.63×10⁻⁴        | -6.83×10⁻²       | -1.28            | 1.35             | 7.59| 1.35          | 1.28           | 1.21            |
| 3.39×10⁻⁴       | 3.63×10⁻⁴        | -6.78×10⁻²       | -1.28            | 1.35             | 7.59| 1.35          | 1.28           | 1.21            |
| 3.05×10⁻⁴       | 3.62×10⁻⁴        | -6.47×10⁻²       | -1.28            | 1.34             | 7.58| 1.34          | 1.28           | 1.21            |
| 1.32×10⁻³       | 3.59×10⁻⁴        | -5.43×10⁻²       | -1.28            | 1.33             | 7.58| 1.33          | 1.28           | 1.22            |
| 3.39×10⁻³       | 3.52×10⁻⁴        | -4.44×10⁻²       | -1.28            | 1.31             | 7.57| 1.31          | 1.28           | 1.24            |
| 2.37×10⁻³       | 2.70×10⁻⁵        | -2.41×10⁻²       | -1.30            | 1.05             | 7.48| 1.05          | 1.29           | 1.53            |
| 2.01            | 1.29×10⁻⁵        | 1.40             | 3.78×10⁻¹        | 7.03             | 3.78×10⁻¹| 1.77          | 3.18            |
| 2.15            | 3.29×10⁻⁴        | 1.47             | -1.82            | 3.52×10⁻¹        | 7.00| 3.52×10⁻¹| 1.82           | 3.29            |
| 2.45            | -2.54×10⁻⁷       | 1.61             | -1.92            | 3.11×10⁻¹        | 6.94| 3.11×10⁻¹| 1.92           | 3.53            |
| 3.39            | -9.27×10⁻⁵       | 1.99             | -2.22            | 2.26×10⁻¹        | 6.80| 2.26×10⁻¹| 2.22           | 4.21            |
| 1.02×10¹        | -4.12×10⁻⁴       | 3.51             | -3.63            | 1.21×10⁻¹        | 6.36| 1.21×10⁻¹| 3.63           | 7.14            |
| 3.39×10¹        | -1.12×10⁻³       | 5.76             | -5.79            | 3.17×10⁻²        | 5.95| 3.17×10⁻²| 5.79           | 11.56           |

than are released by the dissociation of NH₄⁺, with a corresponding decrease in the pH below 7. The range where Δ[H⁺]H⁺CO₃ have negative values is widened towards the higher values of [CO₂]W₀ in the range from 3.39×10⁻⁷ to 3.39×10⁻² mmol·L⁻¹ after NH₄Cl is added. At [CO₂]W₀ ≈ 2.15 mmol·L⁻¹ and [NH₄Cl] ≈ 71 mmol·L⁻¹, the corresponding pH value is 7.00. At the range from [CO₂]W₀ ≈ 2.45 to 33.9 mmol·L⁻¹, Δ[H⁺]H₂O have negative values as the dissociation of water is suppressed.

3. MATERIALS AND METHODS

In the initial phase of the experiment, MilliQ water was purged with argon (99.999% pure) to remove any residual (CO₂)w. To guarantee an equilibrium distribution of CO₂ between the gas and liquid phases, the aqueous phase was saturated by purging it with a gas mixture with a selected constant concentration of CO₂ until a stable pH value was achieved. The measured pH values were registered using a Jenway type 3520 pH meter and Dataway software. A one-litre closed reaction cell was kept at 25.0 ± 0.1 °C using a thermostat equipped with a pH and temperature measuring system (Mettler Toledo InLab® Routine and Jenway model 027500 sensors, respectively). The gas mixtures were ordered from AGA Eesti Ltd. (stored as compressed gas in cylinders containing 1010 ± 2 ppm and 395 ± 2 ppm CO₂) or prepared using a Bronkhorst EL-FLOW® controller-equipped digital thermal mass flow meter (stored in 25 L gas collection bags). The prepared mixture might have a higher degree of variation of CO₂ concentration; also, the gas flow from gas collection bags might be less uniform. The experiments were conducted in a closed system H₂O–(CO₂)W₀–CaCO₃–NH₄Cl with 1000 mg of solid CaCO₃ (CAS # 471-34-1, 99.95% Sigma-Aldrich) and 3821 mg (~71 mmol·L⁻¹) of NH₄Cl (CAS # 12125-02-9, 99.5% Acros Organics, US), which corresponds to 1000 mg·L⁻¹ NH₄-N. The salts were added to the liquid in the reaction cell (volume 1 L, after purged with certain concentrations of [CO₂]W₀ using gas bags from AGA). At the end of the experiment, samples were taken and filtered through a 0.45 μm membrane filter. From the filtered samples, [Ca²⁺] concentrations were determined by titration using a 0.001 M EDTA solution (other ions that might react with EDTA were not present). Dissolved CO₂ was measured using a Hach-Lange DR2800 spectrophotometer and LCK388 cuvettes. Nessler’s reagent, which forms a complex with ammonia, was used to determine NH₃-N. The experiments were performed in triplicate for each initial concentration of [CO₂]W₀ in a closed reaction cell, where CaCO₃ was added to the equilibrium system H₂O–(CO₂)W₀, and a supplementary amount of CO₃⁻ and Ca²⁺ ions was released by the dissolution of CaCO₃.
4. RESULTS AND DISCUSSION

As shown in Fig. 2, at the range of concentrations from \([\text{CO}_2]_{W0} \approx 3.39 \times 10^{-5} \text{ mmol·L}^{-1}\) to \([\text{CO}_2]_{W0} \approx 33.9 \text{ mmol·L}^{-1}\), adding CaCO3 to the equilibrium system caused the pH value to rise about 2–4 units depending on the initial concentration of \([\text{CO}_2]_{W0}\). The \(\text{CO}_3^{2-}\) ions released by the dissolution of CaCO3 will accept a certain amount of protons (\(\Delta[H^+]_{\text{CO}_3}\)) originating from two sources: the reversible dissociation of water (\(\Delta[H^+]_{\text{H}_2\text{O}}\)) or \(\text{H}_2\text{CO}_3\) (\(\Delta[H^+]_{\text{H}_2\text{CO}_3}\)). The smaller the initial concentration of \([\text{CO}_2]_{W0}\), the fewer protons are produced on the basis of the dissociation of \(\text{H}_2\text{CO}_3\). Thus, the dissociation of water at lower concentrations of \([\text{CO}_2]_{W0}\) gives the main amount of protons to form the equilibrium of the system. As a result, the protons bind to \(\text{CO}_3^{2-}\) ions, the concentration of \(\text{OH}^-\) ions increases, and the pH will rise up to a maximum theoretical value of 9.88. The experimentally measured maximum pH value of 9.89 ± 0.03 (with a standard deviation) occurred at \([\text{CO}_2]_{W0} \approx 3.39 \times 10^{-5} \text{ mmol·L}^{-1}\), which coincides well with the theoretically calculated pH value. On the other hand, in the range of \([\text{CO}_2]_{W0} \approx 3.39 \text{ mmol·L}^{-1}\) to \([\text{CO}_2]_{W0} \approx 33.9 \text{ mmol·L}^{-1}\), adding solid CaCO3 to the equilibrium system \(\text{H}_2\text{O}–\text{[CO}_2]_{W0}\) resulted in the final experimentally measured pH value lower than 7. The main source of protons in this range of \([\text{CO}_2]_{W0}\) is \(\text{H}_2\text{CO}_3\).

After the pH of the equilibrium system \(\text{H}_2\text{O}–\text{[CO}_2]_{W0}\) had stabilized following CaCO3 addition, 71 mmol of \(\text{NH}_4\text{Cl}\) was added to 1 L of the liquid phase, which approximately corresponds to the concentration of \(\text{NH}_3\)-N in the reject water \([15,18,19]\). Consistently, as shown in Fig. 2, at the initial concentration of \([\text{CO}_2]_{W0} \approx 3.39 \times 10^{-5} \text{ mmol·L}^{-1}\), the pH value decreased after \(\text{NH}_4\text{Cl}\) was added to the initial system \(\text{H}_2\text{O}–\text{[CO}_2]_{W0}–\text{CaCO}_3\) from 9.89 ± 0.03 to 7.65 ± 0.02. The change in the pH value was 2.24 ± 0.02 units. In the system \(\text{H}_2\text{O}–\text{[CO}_2]_{W0}–\text{CaCO}_3–\text{NH}_3\)-N, at lower initial concentrations of \([\text{CO}_2]_{W0}\), the main source of protons is \(\text{NH}_4^+\) ions. However, at higher initial concentrations of \([\text{CO}_2]_{W0}\) in the range

![Fig. 2. Experimentally measured pH values of the closed equilibrium system \(\text{H}_2\text{O}–\text{[CO}_2]_{W0}–\text{CaCO}_3–\text{NH}_3\)-N at a concentration range from \([\text{CO}_2]_{W0} \approx 3.39 \times 10^{-5}\) to 33.9 mmol·L\(^{-1}\) at \(t = 25 \, ^\circ\text{C}\).](image-url)
Table 3. Experimental and model-predicted concentrations of \([Ca^{2+}]\) and the corresponding final pH values in the closed H\(_2\)O–[CO\(_2\)]\(_w\)–CaCO\(_3\)–NH\(_x\)–N equilibrium system

| [CO\(_2\)]\(_w\) (mmol·L\(^{-1}\)) | [Ca\(^{2+}\)] measured (mmol·L\(^{-1}\)) | [Ca\(^{2+}\)] theoretically predicted (mmol·L\(^{-1}\)) | pH value measured after addition of NH\(_4\)Cl | pH value theoretically predicted |
|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 3.39×10\(^{-5}\)              | 0.11 ± 0.01                     | 0.10                            | 7.65 ± 0.06                      | 7.59                            |
| 1.32×10\(^{-2}\)              | 0.12 ± 0.01                     | 0.11                            | 7.60 ± 0.03                      | 7.58                            |
| 3.39×10\(^{-1}\)              | 0.37 ± 0.01                     | 0.36                            | 7.52 ± 0.04                      | 7.48                            |
| 3.39                            | 2.07 ± 0.02                     | 2.09                            | 7.18 ± 0.06                      | 6.80                            |
| 1.02×10\(^1\)                 | 3.62 ± 0.04                     | 3.57                            | 6.52 ± 0.05                      | 6.36                            |
| 3.39×10\(^1\)                 | 5.82 ± 0.04                     | 5.78                            | 6.08 ± 0.04                      | 5.95                            |

From [CO\(_2\)]\(_w\) ≈ 3.39 mmol·L\(^{-1}\) to ≈ 33.9 mmol·L\(^{-1}\), the pH values of the system rose up to the value of 7.18 ± 0.03 after 71 mmol·L\(^{-1}\) NH\(_4\)Cl was added to the initial system H\(_2\)O–(CO\(_2\))\(_w\)–CaCO\(_3\), with the maximum change in the pH being 0.54 ± 0.03 at [CO\(_2\)]\(_w\) ≈ 3.39 mmol·L\(^{-1}\). This indicates that the final pH values of the system were affected by higher [CO\(_2\)]\(_w\) concentrations in the solution.

As shown in Table 3, experimentally measured final stabilized pH values of the closed equilibrium system H\(_2\)O–[CO\(_2\)]\(_w\)–CaCO\(_3\)–NH\(_x\)–N were generally close to the theoretical ones and the small differences in the obtained values might be due to the gas prepared-flow control system’s accuracy.

The experimentally determined values of the concentration of Ca\(^{2+}\) ions in the range of 0.11–5.82 mmol·L\(^{-1}\) were in accordance with the developed theoretical model (Table 3). As seen in Fig. 2 and Tables 1 and 2, the experimental results corresponded to the theoretical model, which supported the validity of the developed novel proton transfer model linking different acid–base equilibria. The same approach can be applied to complex systems involving more acid–base equilibria (e.g. phosphoric acid equilibrium). Thus, the present experimental study confirmed the validity of the theoretical model we developed.

The developed model of equilibrium in the closed system H\(_2\)O–(CO\(_2\))\(_w\)–CaCO\(_3\)–NH\(_4\)Cl can be used to determine concentrations of all components in the water phase over a wide range of natural and industrial conditions, based on the known concentrations of [CO\(_2\)]\(_w\) in the water phase. The model allows one to assess the impact of anthropogenic processes in the environment and could be applied in environmental technology.

5. CONCLUSIONS

In this study of modelling the closed system H\(_2\)O–(CO\(_2\))\(_w\)–CaCO\(_3\)–NH\(_4\)Cl, the system H\(_2\)O–(CO\(_2\))\(_w\)–CaCO\(_3\) was taken as the basis and upgraded using proton transfer principles. In the developed model, proton transfer parameters, pH, and the equilibrium concentrations of ions and molecules in the liquid phase were calculated.

In the formation of the equilibrium system H\(_2\)O–(CO\(_2\))\(_w\)–CaCO\(_3\) by the dissociation of CaCO\(_3\), CO\(_3^{2-}\) ions will release and accept protons (\(\Delta[H^+]_{CO_3^{2-}}\)) originating from two sources: the dissociation of water (\(\Delta[H^+]_{H_2O}\)) or H\(_2\)CO\(_3\) (\(\Delta[H^+]_{H_2CO_3}\)). The smaller the initial concentration of [CO\(_2\)]\(_w\), the fewer protons are produced on the basis of the dissociation of H\(_2\)CO\(_3\). Thus, the dissociation of water at lower concentrations of [CO\(_2\)]\(_w\) gives the main amount of protons to form the equilibrium of the system. As a result, protons will be bound to CO\(_3^{2-}\) ions and the pH of the formed equilibrium system will increase.

In the system H\(_2\)O–[CO\(_2\)]\(_w\)–CaCO\(_3\)–NH\(_x\)–N, at lower initial concentrations of [CO\(_2\)]\(_w\) the main source of protons is NH\(_4\)\(^+\) ions. Experimentally measured data coincided well with the theoretically calculated values.

At higher initial concentrations of [CO\(_2\)]\(_w\) the main source of protons is H\(_2\)CO\(_3\). The concentration of toxic [NH\(_3\)] in the system is affected by the interaction between carbonaceous and ammoniacal equilibrium processes. The developed model of the equilibrium closed system H\(_2\)O–(CO\(_2\))\(_w\)–CaCO\(_3\)–NH\(_4\)Cl
can be used to determine concentrations of all components in the water phase over a wide range of natural and industrial conditions, based on the known concentration of $[\text{CO}_2\text{]}_{\text{w}}$ in the water phase. The model allows one to assess the impact of anthropogenic processes on the environment and could be applied by environmental technologists in water and wastewater treatment. The model is useful in the development of innovative methods of measuring $[\text{CO}_2\text{]}_{\text{w}}$ and $[\text{NH}_3\text{]}_{\text{w}}$ concentrations in water.

ACKNOWLEDGEMENTS

The study was supported by the following projects: SLOKT12222T, SLOKT11027T, and IUT20-16, IWAMA. The publication costs of this article were covered by the University of Tartu and the Estonian Academy of Sciences.

REFERENCES

1. Plummer, L. N. and Busenberg, E. The solubilities of calcite, aragonite and vaterite in CO$_2$-H$_2$O solutions between 0 and 90°C, and an evaluation of the aqueous model for the system CaCO$_3$-CO$_2$-H$_2$O. Geochim. Cosmochim. Acta, 1982, 46, 1011–1040.
2. Butler, J. N. Carbon Dioxide Equilibria and Their Applications. Lewis Publishers, Inc., CRC Press, Michigan, 1991, p. 272.
3. Trikel, A., Zevenhoven, R., and Kussik, R. Modelling SO$_2$ capture by Estonian limestones and dolomites. Proc. Estonian Acad. Sci. Chem. 2000, 49, 53–70.
4. Moulin, P. and Roques, H. Zeta potential measurement of calcium carbonate. J. Colloid Interface Sci., 2003, 261, 115–126.
5. Panthi, S. R. Carbonate chemistry and calcium carbonate saturation state of rural water supply projects in Nepal. In Proceedings of the 7th IWTC, Cairo, Egypt, June 3–5, 2003, 545–560.
6. Eriksson, B. K., Rubach, A., and Hillebrand, H. Dominance by a canopy forming seaweed modifies resource and consumer control of bloom-forming macroalgae. Oikos, 2007, 116, 1211–1219.
7. Tenno, T., Rikmann, E., Zekker, I., Tenno, T., Daia, L., and Mashirin, A. Modelling equilibrium distribution of carbonaceous ions and molecules in a heterogeneous system of CaCO$_3$–water–gas. Proc. Estonian Acad. Sci., 2016, 65, 68–77.
8. Tenno, T., Uiga, K., Mashirin, A., Zekker, I., and Rikmann, E. Modelling closed equilibrium systems of H$_2$O–dissolved CO$_2$–solid CaCO$_3$. J. Phys. Chem. A., 2017, 121, 3094–3100.
9. Hafner, S. D. and Bisogni, J. J. Jr. Modeling of ammonia speciation in anaerobic digesters. Water Res., 2009, 43, 4105–4114.
10. Christensen, T. H., Kjeldsen, P., Bjerg, P. L., Jensen, D. L., Christensen, J. B., Baun, A., et al. Biogeochemistry of landfill leachate plumes. Appl. Geochem., 2001, 16(7–8), 659–718.
11. Kjeldsen, P., Barlaz, M. A., Rooker, A. P., Baun, A., Ledin, A., and Christensen, T. H. Present and long-term composition of MSW landfill leachate: a review. Crit. Rev. Environ. Sci. Technol., 2010, 32(4), 297–336.
12. Tatsi, A. A. and Zouboulis, A. I. A field investigation of the quantity and quality of leachate from a municipal solid waste landfill in a Mediterranean climate (Thessaloniki, Greece). Adv. Environ. Res., 2002, 6, 207–219.
13. Rajagopal, R., Massé, D. I., and Singh, G. A critical review on inhibition of anaerobic digestion process by excess ammonia. Bioresource Technol., 2013, 143, 632–641.
14. Zekker, I., Rikmann, E., Lootis, L., Tenno, T., Fritze, H., Tuomivirta, T., et al. Start-up of low temperature anammox in UASB systems in pilot scale. Int. J. Environ. Sci. Technol., 2013, 10, 87–98.
15. Zekker, I., Rikmann, E., Kroon, K., Mandel, A., Mihkelson, J., Tenno, T., and Tenno, T. Ameliorating nitrite inhibition in a low-temperature nitritation–anammox MBBR using bacterial intermediate nitric oxide. Int. J. Environ. Sci. Technol., 2017, 14, 2343–2356.
16. Zekker, I., Rikmann, E., Kroon, K., Mandel, A., Mihkelson, J., Tenno, T., and Tenno, T. Ameliorating nitrite inhibition in a low-temperature nitritation–anammox MBBR using bacterial intermediate nitric oxide. Int. J. Environ. Sci. Technol., 2017, 14, 2343–2356.
17. Anthonisen, A. C., Loehr, R. C., Prakasam, T. B. S., and Srithar, E. G. Inhibition of nitrification by ammonia and nitrous acid. J. Water Pollut. Control Fed., 1976, 48, 835–852.
18. Chung, J., Shim, H., Park S., Kim S. J., and Bae, W. Optimization of free ammonia concentration for nitrite accumulation in shortcut biological nitrogen removal process. Bioproc. Biosystems Eng., 2008, 28(4), 275–282.
19. Kim, D., Kim, T. S., and Ryu, H. D. Treatment of low carbon-to-nitrogen wastewater using two-stage sequencing batch reactor with independent nitrification. Process Biochem., 2008, 43(4), 406–413.
23. Jin, R-C., Yang, G-F., Yu, J-J., and Zheng, P. The inhibition of the Anammox process: a review. Chem. Eng. J., 2012, 197, 67–79.
24. Zheng, X., Sun, P., Lou, J., Cai, J., Song, Y., Yu, S., and Lu, X. Inhibition of free ammonia to the granule-based enhanced biological phosphorus removal system and the recoverability. Bioresource Technol., 2013, 148, 343–351.
25. Jung, J. Y., Kang, S. H., Chung, Y. C., and Ahn, D. H. Factors affecting the activity of Anammox bacteria during start up in the continuous culture reactor. Water Sci. Technol., 2007, 55(1), 459–468.
26. Jaroszynski, L. W., Cieck, N., Sparling, R., and Oleszkiewicz, J. A. Importance of the operating pH in maintaining the stability of anoxic ammonium oxidation (Anammox) activity in moving bed biofilm reactors. Bioresource Technol., 2011, 102, 7051–7056.
27. Zekker, I., Rikmann, E., Tenno, T., Vabamäe, P., Kroon, K., Loo rits, L., et al. Effect of HCO$_3^-$ concentration on anammox nitrogen removal rate in a moving bed biofilm reactor. Environ. Technol., 2012, 33, 2263–2271.
28. Chang, R. Physical Chemistry with Applications to Biological Systems 2nd ed. Williams College, Macmillan Publishing Co., Inc., New York, 1990, 320.
29. Pocker, Y. and Bjorkquist, D. W. Stopped-flow studies of carbon dioxide hydration and bicarbonate dehydration in water and water-$d_2$. Acid-base and metal ion catalysis. J. Am. Chem. Soc., 1977, 99, 6537–6543.
30. Segal, B. G. Chemistry, Experiment and Theory. John Wiley & Sons, Inc., New York, 1989, 363–365.
31. Skoog, D. A., West, D. M., and Holler, F. J. Fundamentals of Analytical Chemistry; Sixth ed. Saunders College Publishing, Philadelphia, 1992.
32. Dean, J. A. Lange’s Handbook of Chemistry. McGraw-Hill, Inc., New York, 1992.
33. Dickerson, R. E., Gray, H. B., and Haight, G. P. Chemical Principles. Third ed. The Benjamin/Cummings Publishing Company, Inc., Menlo Park, CA, 1979.
34. Rikmann, E., Zekker, I., Uiga, K., and Tenno, T. 2016. Modelling equilibrium distribution of ions and molecules in a heterogeneous system of CaCO$_3$–water–gas phase containing CO$_2$ under equilibrium condition. In Proceedings of the 10th Linnaeus Eco-Tech Conference, Kalmar, Sweden, November 21–23, 2016, 191–203.