



## A novel proton transfer model of the closed equilibrium system $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3-\text{NH}_x$

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**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 ( $\Delta[\text{H}^+]_{\text{CO}_3^{2-}}$ ), which originate from two sources: the reversible dissociation of water ( $\Delta[\text{H}^+]_{\text{H}_2\text{O}}$ ) or  $\text{H}_2\text{CO}_3$  ( $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ ), which is the product of the reaction between  $\text{H}_2\text{O}$  and  $(\text{CO}_2)_{w0}$ . 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 ( $\Delta[\text{H}^+]_{\text{NH}_4^+}$ ) comes from the dissociation of  $\text{NH}_4^+$ , or if there are higher concentrations of  $[\text{CO}_2]_{w0}$ , the source of protons is  $\text{H}_2\text{CO}_3$  ( $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ ). The developed models were experimentally validated.

**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].

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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  $\text{NH}_x\text{-N}$  ( $\text{NH}_4^+\text{-N}$  together with  $\text{NH}_3\text{-N}$ ) is a pollutant present in high concentrations in the reject water from the anaerobic digestion of organic substrates and landfill leachate. The concentration of  $[\text{NH}_x\text{-N}]$  is up to  $2200 \text{ mg L}^{-1}$  in the case of landfill leachate [10–12] and up to  $1500 \text{ mg L}^{-1}$  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  $\text{CaCO}_3$ . On the other hand, the liquid phase is exposed to the gas phase of which about a third is  $\text{CO}_2$  [17]. The liquid phase in the anaerobic digester of the Tallinn Municipal Wastewater Treatment Plant has a pH value of  $7.2 (\pm 0.2)$  [18]. During dewatering the digested sludge, the reject water comes into contact with ambient air and the degassing of  $\text{CO}_2$  from the liquid phase takes place, which causes the pH value of the reject water to increase to  $8.1 (\pm 0.2)$  [18,19], shifting the equilibrium of the reaction  $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$  towards the dissociation of  $\text{NH}_4^+$  and the formation of free ammonia ( $\text{NH}_3$ ) [20–22].

In the case of anaerobic ammonium-oxidizing (anammox) bacteria, an elevated concentration of  $\text{NH}_3\text{-N}$  ( $\geq 8 \text{ mg L}^{-1}$ ) acts as an inhibitor on biological wastewater treatment processes, including the activity of bacteria performing autotrophic nitrogen removal [20–24]. The lowest  $\text{NH}_3$  toxicity threshold concentration, provided by Jung et al. (2007) [25], is  $1.7 \text{ mg N L}^{-1}$  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  $\text{NH}_3\text{-N}$  concentrations of  $38 \text{ mg L}^{-1}$ , and long-term tests in sequencing batch reactors showed performance instability when the  $\text{NH}_3\text{-N}$  concentration exceeded  $20\text{--}25 \text{ mg L}^{-1}$  [23]. Thus, the adjustment of the pH is required in waste- and reject-water treatment systems in streams with a high content of  $[\text{NH}_x\text{-N}]$  in cases when there is contact with limestone [15,18]. The concentration of  $\text{NH}_3$  has so far been calculated from the empirical formula published by Anthonisen et al. in 1976, which is a function of the concentration of  $\text{NH}_4^+$ , pH, and temperature [20]:

$$[\text{NH}_3] = \frac{[\text{NH}_4^+] \cdot 10^{\text{pH}}}{\frac{K_b}{K_w} + 10^{\text{pH}}}, \quad (1)$$

where

$$\frac{K_b}{K_w} = e^{\frac{6344}{273+t}}. \quad (2)$$

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  $^\circ\text{C}$ .

Equation (1) does not take into account the effect of interactions between the carbonaceous and ammoniacal equilibrium processes, which alter the concentration of  $[\text{NH}_3]$ . Therefore, the actual concentration of  $[\text{NH}_3]$  may be significantly different from that calculated using equation (1). To calculate  $[\text{NH}_3]$  in a system having a high concentration of dissolved  $[\text{NH}_x]$  and carbonaceous species, a mathematical model needs to be developed. In the present study 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 to model the closed system  $\text{H}_2\text{O}-(\text{CO}_2)_w\text{-CaCO}_3\text{-NH}_4\text{Cl}$ . 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

### $\text{H}_2\text{O}-(\text{CO}_2)_\text{W}-\text{CaCO}_3-\text{NH}_4\text{Cl}$

#### 2.1. The development of the proton transfer based model of the initial system $\text{H}_2\text{O}-(\text{CO}_2)_\text{W}-\text{CaCO}_3$

When solid  $\text{CaCO}_3$  is added to the equilibrium system  $\text{H}_2\text{O}-(\text{CO}_2)_\text{W}$  with a summarized concentration of all inorganic carbon containing particles  $\sum[\text{CO}_x]_{\text{W}_0}$ , including  $(\text{CO}_2)_\text{W}$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$ , supplementary amounts of  $[\text{Ca}^{2+}]$  and  $[\text{CO}_3^{2-}]$  ions are released by the reversible dissolution of  $\text{CaCO}_3$  [8]. The reversible dissociation reaction is as follows:



It is always present in the water phase, which acts as a host solvent for other chemical reactions. If reactions involve  $\text{H}^+$  or  $\text{OH}^-$  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  $\text{H}^+$  and  $\text{OH}^-$  ions, and if the dissociation products of the solute can bind or release either  $\text{H}^+$  and  $\text{OH}^-$  ions, these reactions will always take place, changing the chemical equilibrium of the system.

In the formation of the equilibrium system  $\text{H}_2\text{O}-(\text{CO}_2)_\text{W}-\text{CaCO}_3$ , as a result of the dissolution of  $\text{CaCO}_3$ , the  $\text{CO}_3^{2-}$  ions are released and they will accept a certain amount of protons ( $\Delta[\text{H}^+]_{\text{CO}_3^{2-}}$ ) originating from two sources, either the reversible dissociation of water ( $\Delta[\text{H}^+]_{\text{H}_2\text{O}}$ ) or  $\text{H}_2\text{CO}_3$  ( $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ ) formed in the reaction between  $(\text{CO}_2)_\text{W}_0$  and  $\text{H}_2\text{O}$ . Thus, the  $\text{H}^+$  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  $\text{NH}_4\text{Cl}$  are presented in Table 1.

The data in Table 1 show that at the range of concentrations from  $[\text{CO}_2]_{\text{W}_0} \cong 3.39 \times 10^{-7}$  to  $[\text{CO}_2]_{\text{W}_0} \cong 33.9 \text{ mmol} \cdot \text{L}^{-1}$  in the closed equilibrium system  $\text{H}_2\text{O}-(\text{CO}_2)_\text{W}-\text{CaCO}_3$ , the pH will increase up to a maximum value of 9.88 at the decreasing concentration of  $[\text{CO}_2]_{\text{W}_0}$  [8]. The smaller the initial concentration of  $[\text{CO}_2]_{\text{W}_0}$ , the fewer protons are produced due to the dissociation of  $\text{H}_2\text{CO}_3$ . Thus, the dissociation of water at lower concentrations of  $[\text{CO}_2]_{\text{W}_0}$  produces the main amount of protons to form an equilibrium of the system. As a result of equilibrium reactions, the protons bind to  $\text{CO}_3^{2-}$  ions, the concentration of  $[\text{OH}^-]$  ions increases, and the pH rises, whereas the value of the ion product of water ( $K_\text{W}$ )

**Table 1.** Calculated proton transfer values between different species, pH, and concentrations of  $[\text{CO}_2]_{\text{W}_0}$ ,  $[\text{Ca}^{2+}]$ , and  $[\text{HCO}_3^-]$  in the closed equilibrium system  $\text{H}_2\text{O}-(\text{CO}_2)_\text{W}-\text{CaCO}_3$  at 25 °C before  $\text{NH}_4\text{Cl}$  was added. The parameters in bold represent an equilibrium state between  $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ ,  $\Delta[\text{H}^+]_{\text{CO}_3^{2-}}$ , and  $[\text{Ca}^{2+}]$

$[\text{CO}_2]_{\text{W}_0}$ , $\text{mmol} \cdot \text{L}^{-1}$	$\Delta[\text{H}^+]_{\text{H}_2\text{O}}$ $\text{mmol} \cdot \text{L}^{-1}$	$\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ $\text{mmol} \cdot \text{L}^{-1}$	$\Delta[\text{H}^+]_{\text{CO}_3^{2-}}$ , $\text{mmol} \cdot \text{L}^{-1}$	pH	$[\text{Ca}^{2+}]$ , $\text{mmol} \cdot \text{L}^{-1}$	$[\text{HCO}_3^-]$ , $\text{mmol} \cdot \text{L}^{-1}$
$3.39 \times 10^{-7}$	$7.63 \times 10^{-2}$	$-2.03 \times 10^{-5}$	$-7.63 \times 10^{-2}$	9.88	$1.03 \times 10^{-1}$	$7.63 \times 10^{-2}$
$1.00 \times 10^{-6}$	$7.63 \times 10^{-2}$	$-1.68 \times 10^{-5}$	$-7.63 \times 10^{-2}$	9.88	$1.03 \times 10^{-1}$	$7.63 \times 10^{-2}$
$1.02 \times 10^{-5}$	$7.63 \times 10^{-2}$	$2.65 \times 10^{-5}$	$-7.63 \times 10^{-2}$	9.88	$1.03 \times 10^{-1}$	$7.63 \times 10^{-2}$
$2.37 \times 10^{-5}$	$7.62 \times 10^{-2}$	$7.67 \times 10^{-5}$	$-7.63 \times 10^{-2}$	9.88	$1.03 \times 10^{-1}$	$7.64 \times 10^{-2}$
$3.39 \times 10^{-5}$	$7.62 \times 10^{-2}$	$1.09 \times 10^{-4}$	$-7.63 \times 10^{-2}$	9.88	$1.03 \times 10^{-1}$	$7.64 \times 10^{-2}$
$3.39 \times 10^{-4}$	$7.56 \times 10^{-2}$	$7.00 \times 10^{-4}$	$-7.63 \times 10^{-2}$	9.87	$1.03 \times 10^{-1}$	$7.70 \times 10^{-2}$
$3.05 \times 10^{-3}$	$7.22 \times 10^{-2}$	$4.21 \times 10^{-3}$	$-7.64 \times 10^{-2}$	9.85	$1.03 \times 10^{-1}$	$8.06 \times 10^{-2}$
$1.32 \times 10^{-2}$	$6.19 \times 10^{-2}$	$1.57 \times 10^{-2}$	$-7.75 \times 10^{-2}$	9.79	$1.04 \times 10^{-1}$	$9.32 \times 10^{-2}$
$3.39 \times 10^{-2}$	$4.55 \times 10^{-2}$	$3.79 \times 10^{-2}$	$-8.34 \times 10^{-2}$	9.65	$1.09 \times 10^{-1}$	$1.21 \times 10^{-1}$
$3.39 \times 10^{-1}$	$2.43 \times 10^{-3}$	$3.46 \times 10^{-1}$	$-3.49 \times 10^{-1}$	8.38	$3.56 \times 10^{-1}$	$6.95 \times 10^{-1}$
2.01	$5.07 \times 10^{-5}$	1.53	-1.53	7.11	1.53	3.05
2.15	$3.27 \times 10^{-5}$	1.59	-1.59	7.07	1.60	3.19
<b>2.45</b>	<b><math>-1.55 \times 10^{-7}</math></b>	<b>1.73</b>	<b>-1.73</b>	<b>7.00</b>	<b>1.73</b>	<b>3.46</b>
3.39	$-7.86 \times 10^{-5}$	2.09	-2.09	6.83	2.10	4.19
$1.02 \times 10^1$	$-4.30 \times 10^{-4}$	3.58	-3.58	6.37	3.58	7.16
$3.39 \times 10^1$	$-1.11 \times 10^{-3}$	5.78	-5.78	5.95	5.78	$1.16 \times 10^1$

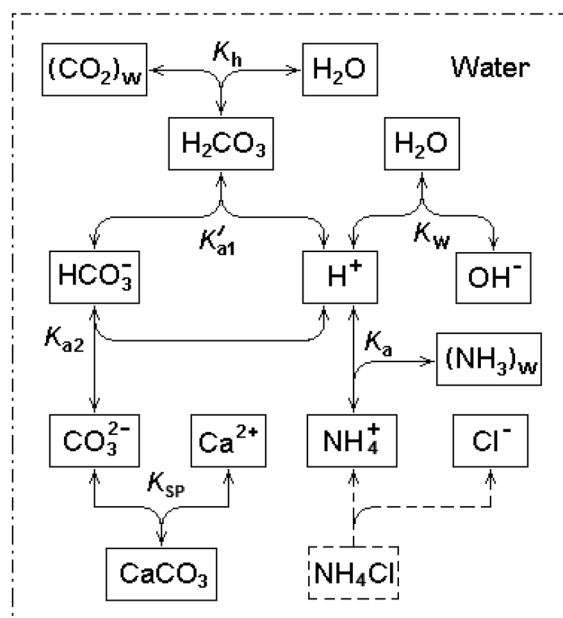
remains constant. The maximum value of  $\text{pH} = 9.88$  is related to the solubility product of  $\text{CaCO}_3$  ( $K_{\text{SP}}$ ) and the ion product of water ( $K_{\text{W}}$ ) as it is not necessary to take into account the dissociation of  $\text{H}_2\text{CO}_3$  at small concentrations of  $[\text{CO}_2]_{\text{w0}}$ .

As seen in Table 1, at small values of  $[\text{CO}_2]_{\text{w0}}$  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  $\text{CaCO}_3$  determine the equilibrium of the system. At a concentration of  $[\text{CO}_2]_{\text{w0}} = 2.45 \text{ mmol}\cdot\text{L}^{-1}$ , the pH is equal to 7.0. When the concentration of  $[\text{CO}_2]_{\text{w0}}$  exceeds  $2.45 \text{ mmol}\cdot\text{L}^{-1}$ , the pH will fall below 7. The reaction between  $(\text{CO}_2)_{\text{w0}}$  and  $\text{H}_2\text{O}$  produces  $\text{H}^+$  ions, which partly participate in the reaction between  $\text{CO}_3^{2-}$  and  $\text{H}^+$ , which forms  $\text{HCO}_3^-$  ions, and the other part of the dissociation products of  $\text{H}_2\text{CO}_3$  stays in the equilibrium system in the form of  $\text{HCO}_3^-$  and  $\text{H}^+$  ions.

The positive values of  $\Delta[\text{H}^+]_{\text{H}_2\text{O}}$  are an outcome of the dissociation reaction of water, which acts as a proton donor, and  $(\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3})$  has a negative value because  $\text{CO}_3^{2-}$  ion is an acceptor of protons. At higher  $[\text{CO}_2]_{\text{w0}}$  values, the concentration of the formed protons is elevated due to the dissociation of  $\text{H}_2\text{CO}_3$ . As a result, the reversible dissociation of water is suppressed, because the ion product of water ( $K_{\text{W}}$ ) remains constant. The protons will be bound to  $\text{OH}^-$  ions and  $\Delta[\text{H}^+]_{\text{H}_2\text{O}}$  will acquire a negative value. In this region the source of protons, which will react with  $\text{CO}_3^{2-}$ , is formed by the dissociation of  $\text{H}_2\text{CO}_3$ . In the region of  $[\text{CO}_2]_{\text{w0}} \leq 1.00 \times 10^{-6}$ ,  $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$  has a negative value as a reversible dehydration of  $\text{H}_2\text{CO}_3$  is taking place.

## 2.2. Model of the final equilibrium system after adding $\text{NH}_4\text{Cl}$ to $\text{H}_2\text{O}-(\text{CO}_2)_{\text{w}}-\text{CaCO}_3$

To the equilibrium system  $\text{H}_2\text{O}-(\text{CO}_2)_{\text{w}}-\text{CaCO}_3$ , with the initial concentrations of  $[\text{CO}_2]_{\text{w0}}$  (shown in Table 1),  $\text{NH}_4\text{Cl}$  was added. As a result, a final equilibrium system  $\text{H}_2\text{O}-(\text{CO}_2)_{\text{w}}-\text{CaCO}_3-\text{NH}_4\text{Cl}$  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  $[\text{CO}_2]_{\text{w0}}$  in the water phase were taken as constants to model the final closed system  $\text{H}_2\text{O}-(\text{CO}_2)_{\text{w}}-\text{CaCO}_3-\text{NH}_4\text{Cl}$ .



**Fig. 1.** Structural scheme of the equilibrium distribution of ions and molecules in the final closed equilibrium system  $\text{H}_2\text{O}-[\text{CO}_2]_{\text{w}}-\text{CaCO}_3-\text{NH}_4\text{Cl}$ , where  $K_{\text{h}}$  is the hydration constant of  $\text{CO}_2$ ,  $K'_{\text{a1}}$  is the true acid dissociation constant of  $\text{H}_2\text{CO}_3$ ,  $K_{\text{a2}}$  is the acid dissociation constant of  $\text{HCO}_3^-$ ,  $K_{\text{SP}}$  is the solubility product constant of  $\text{CaCO}_3$ ,  $K_{\text{W}}$  is the ion product constant of water, and  $K_{\text{a}}$  is the dissociation constant of  $\text{NH}_4^+$  ions.

The values of the equilibrium constants of the system under investigation are given as equations (4–9):

$$K_h = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]_w} = 2.58 \times 10^{-3} \text{ [28]}, \quad (4)$$

$$K'_{a1} = \frac{[\text{H}^+] \times [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 1.72 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \text{ [29]}, \quad (5)$$

$$K_{a2} = \frac{[\text{H}^+] \times [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 4.7 \times 10^{-11} \text{ mol} \cdot \text{L}^{-1} \text{ [30]}, \quad (6)$$

$$K_w = [\text{H}^+] \times [\text{OH}^-] = 1.01 \times 10^{-14} (\text{mol} \cdot \text{L}^{-1})^2 \text{ [31]}, \quad (7)$$

$$K_{\text{SP}} = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] \cong 2.8 \times 10^{-9} (\text{mol} \cdot \text{L}^{-1})^2 \text{ [32]}, \quad (8)$$

$$K_a = \frac{[\text{NH}_3]_w \times [\text{H}^+]}{[\text{NH}_4^+]} \cong 5.6 \times 10^{-10} \text{ mol} \cdot \text{L}^{-1} \text{ [33]}. \quad (9)$$

In the closed system  $\text{H}_2\text{O}-(\text{CO}_2)_w-\text{CaCO}_3-\text{NH}_4\text{Cl}$ , the charge balance equation is

$$2[\text{Ca}^{2+}] + [\text{H}^+] + [\text{NH}_4^+] = 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-] + [\text{Cl}^-], \quad (10)$$

and the molar balance equation of carbon containing particles is

$$\sum[\text{CO}_x]_w = \sum[\text{CO}_x]_{w0} + [\text{Ca}^{2+}] = [\text{CO}_3^{2-}] + [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_2]_w, \quad (11)$$

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  $\text{H}_2\text{O}-(\text{CO}_2)_w$ –solid  $\text{CaCO}_3$  [8] and does not change at adding  $\text{NH}_4\text{Cl}$ .

The molar balance equation of nitrogen containing particles is

$$s[\text{NH}_4\text{Cl}] = [\text{NH}_4^+] + [\text{NH}_3]_w = [\text{Cl}^-] = \text{constant}, \quad (12)$$

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

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

To decrease the number of unknowns, the composite constant  $K_{a1}$  was used. The first pseudo-acid ionization constant  $K_{a1}$  [7,34] is expressed as a product of the constants  $K_h$  and  $K'_{a1}$ :

$$K_{a1} = K_h \times K'_{a1} = 4.44 \times 10^{-7} \text{ mol} \cdot \text{L}^{-1}. \quad (13)$$

On the basis of equations (9) and (12) the next equation was developed:

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

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 ( $[\text{HCO}_3^-]$  and  $[\text{H}^+]$ ). The charge and molar balance equations were converted to the following forms:

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

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

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

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

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

The concentration of  $\text{H}^+$  ions released from the dissociation of  $\text{NH}_4^+$  ions ( $\Delta[\text{H}^+]_{\text{NH}_4^+}$ ) is equal to the concentration of  $\text{NH}_3$ . In the closed system under investigation, at higher concentrations of  $[\text{CO}_2]_{w0}$  in the range from 2.45 to 33.9  $\text{mmol} \cdot \text{L}^{-1}$ , the dissociation of  $\text{H}_2\text{CO}_3$  will predominate and produce more protons

**Table 2.** Results of the calculations of the equilibrium parameters after adding 71 mmol·L<sup>-1</sup> NH<sub>4</sub>Cl to the closed initial system H<sub>2</sub>O–(CO<sub>2</sub>)<sub>w0</sub>–CaCO<sub>3</sub> containing [CO<sub>2</sub>]<sub>w0</sub> ≅ 3.39 × 10<sup>-7</sup> to 33.9 mmol·L<sup>-1</sup> at a *t* = 25 °C

[CO <sub>2</sub> ] <sub>w0</sub> mmol·L <sup>-1</sup>	Δ[H <sup>+</sup> ] <sub>H<sub>2</sub>O</sub> mmol·L <sup>-1</sup>	Δ[H <sup>+</sup> ] <sub>H<sub>2</sub>CO<sub>3</sub></sub> mmol·L <sup>-1</sup>	Δ[H <sup>+</sup> ] <sub>CO<sub>3</sub><sup>2-</sup></sub> mmol·L <sup>-1</sup>	Δ[H <sup>+</sup> ] <sub>NH<sub>4</sub></sub> mmol·L <sup>-1</sup>	pH	[NH <sub>3</sub> ] mmol·L <sup>-1</sup>	[Ca <sup>2+</sup> ] mmol·L <sup>-1</sup>	[HCO <sub>3</sub> <sup>-</sup> ] mmol·L <sup>-1</sup>
3.39×10 <sup>-7</sup>	3.63×10 <sup>-4</sup>	-6.85×10 <sup>-2</sup>	-1.28	1.35	7.59	1.35	1.28	1.21
1.00×10 <sup>-6</sup>	3.63×10 <sup>-4</sup>	-6.85×10 <sup>-2</sup>	-1.28	1.35	7.59	1.35	1.28	1.21
1.02×10 <sup>-5</sup>	3.63×10 <sup>-4</sup>	-6.84×10 <sup>-2</sup>	-1.28	1.35	7.59	1.35	1.28	1.21
2.37×10 <sup>-5</sup>	3.63×10 <sup>-4</sup>	-6.84×10 <sup>-2</sup>	-1.28	1.35	7.59	1.35	1.28	1.21
3.39×10 <sup>-5</sup>	3.63×10 <sup>-4</sup>	-6.83×10 <sup>-2</sup>	-1.28	1.35	7.59	1.35	1.28	1.21
3.39×10 <sup>-4</sup>	3.63×10 <sup>-4</sup>	-6.78×10 <sup>-2</sup>	-1.28	1.35	7.59	1.35	1.28	1.21
3.05×10 <sup>-3</sup>	3.62×10 <sup>-4</sup>	-6.47×10 <sup>-2</sup>	-1.28	1.34	7.58	1.34	1.28	1.21
1.32×10 <sup>-2</sup>	3.59×10 <sup>-4</sup>	-5.43×10 <sup>-2</sup>	-1.28	1.331	7.58	1.33	1.28	1.22
3.39×10 <sup>-2</sup>	3.52×10 <sup>-4</sup>	-3.44×10 <sup>-2</sup>	-1.28	1.310	7.57	1.31	1.28	1.24
3.39×10 <sup>-1</sup>	2.70×10 <sup>-4</sup>	2.41×10 <sup>-2</sup>	-1.30	1.052	7.48	1.052	1.29	1.53
2.01	1.29×10 <sup>-5</sup>	1.40	-1.77	3.78×10 <sup>-1</sup>	7.03	3.78×10 <sup>-1</sup>	1.77	3.18
<b>2.15</b>	<b>3.29×10<sup>-8</sup></b>	<b>1.47</b>	<b>-1.82</b>	<b>3.52×10<sup>-1</sup></b>	<b>7.00</b>	<b>3.52×10<sup>-1</sup></b>	<b>1.82</b>	<b>3.29</b>
2.45	-2.54×10 <sup>-7</sup>	1.61	-1.92	3.11×10 <sup>-1</sup>	6.94	3.11×10 <sup>-1</sup>	1.92	3.53
3.39	-9.27×10 <sup>-5</sup>	1.99	-2.22	2.26×10 <sup>-1</sup>	6.80	2.26×10 <sup>-1</sup>	2.22	4.21
1.02×10 <sup>1</sup>	-4.12×10 <sup>-4</sup>	3.51	-3.63	1.21×10 <sup>-1</sup>	6.36	1.21×10 <sup>-1</sup>	3.63	7.14
3.39×10 <sup>1</sup>	-1.12×10 <sup>-3</sup>	5.76	-5.79	3.17×10 <sup>-2</sup>	5.95	3.17×10 <sup>-2</sup>	5.79	11.56

than are released by the dissociation of NH<sub>4</sub><sup>+</sup>, with a corresponding decrease in the pH below 7. The range where Δ[H<sup>+</sup>]<sub>H<sub>2</sub>CO<sub>3</sub></sub> have negative values is widened towards the higher values of [CO<sub>2</sub>]<sub>w0</sub> in the range from 3.39×10<sup>-7</sup> to 3.39×10<sup>-2</sup> mmol·L<sup>-1</sup> after NH<sub>4</sub>Cl is added. At [CO<sub>2</sub>]<sub>w0</sub> ≅ 2.15 mmol·L<sup>-1</sup> and s[NH<sub>4</sub>Cl] ≅ 71 mmol·L<sup>-1</sup>, the corresponding pH value is 7.00. At the range from [CO<sub>2</sub>]<sub>w0</sub> ≅ 2.45 to 33.9 mmol·L<sup>-1</sup>, Δ[H<sup>+</sup>]<sub>H<sub>2</sub>O</sub> have negative values as the dissociation of water is suppressed.

### 3. MATERIALS AND METHODS

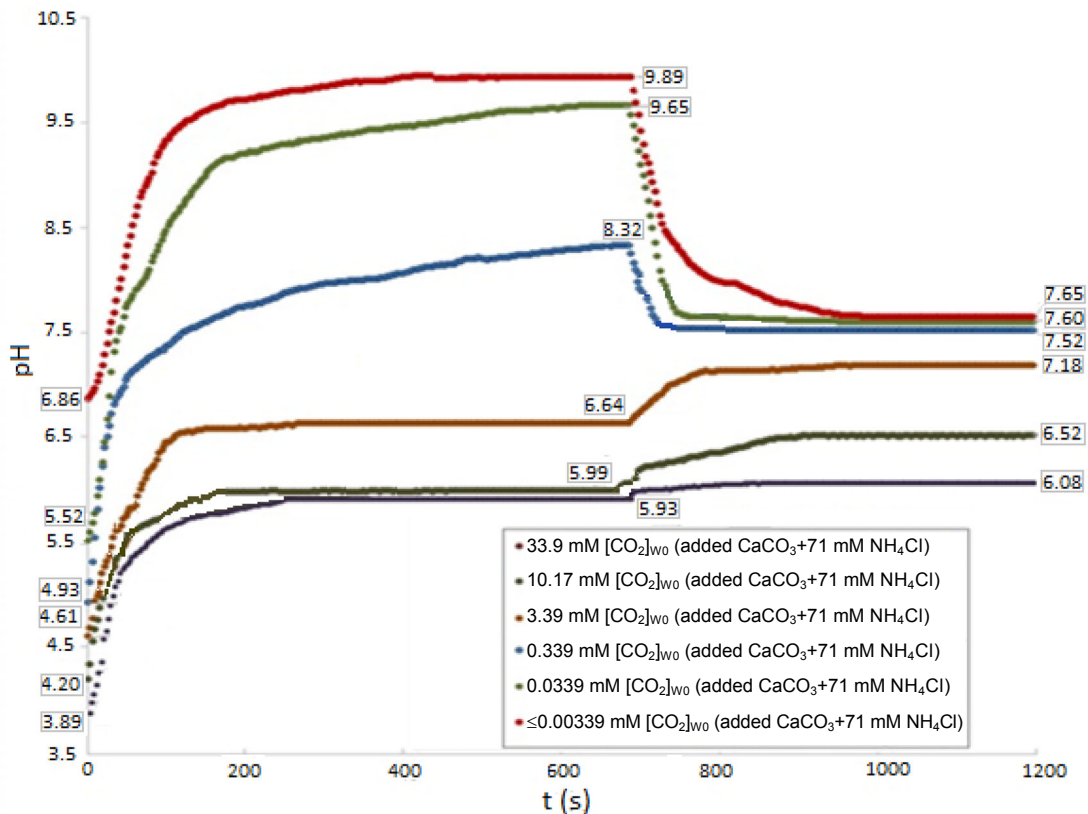
In the initial phase of the experiment, MilliQ water was purged with argon (99.999% pure) to remove any residual (CO<sub>2</sub>)<sub>w</sub>. To guarantee an equilibrium distribution of CO<sub>2</sub> between the gas and liquid phases, the aqueous phase was saturated by purging it with a gas mixture with a selected constant concentration of CO<sub>2</sub> 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<sup>®</sup> 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 CO<sub>2</sub>) or prepared using a Bronkhorst EL-FLOW<sup>®</sup> 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 CO<sub>2</sub> concentration; also, the gas flow from gas collection bags might be less uniform. The experiments were conducted in a closed system H<sub>2</sub>O–(CO<sub>2</sub>)<sub>w</sub>–CaCO<sub>3</sub>–NH<sub>4</sub>Cl with 1000 mg of solid CaCO<sub>3</sub> (CAS # 471-34-1, 99.95% Sigma-Aldrich) and 3821 mg (~71 mmol·L<sup>-1</sup>) of NH<sub>4</sub>Cl (CAS # 12125-02-9, 99.5% Acros Organics, US), which corresponds to 1000 mg·L<sup>-1</sup> NH<sub>x</sub>-N. The salts were added to the liquid in the reaction cell (volume 1 L, after purged with certain concentrations of [CO<sub>2</sub>]) 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, [Ca<sup>2+</sup>] ion concentrations were determined by titration using a 0.001 M EDTA solution (other ions that might react with EDTA were not present). Dissolved CO<sub>2</sub> was measured using a Hach-Lange DR2800 spectrophotometer and LCK388 cuvettes.

Nessler's reagent, which forms a complex with ammonia, was used to determine NH<sub>x</sub>-N. The experiments were performed in triplicate for each initial concentration of [CO<sub>2</sub>]<sub>w0</sub> in a closed reaction cell, where CaCO<sub>3</sub> was added to the equilibrium system H<sub>2</sub>O–[CO<sub>2</sub>]<sub>w0</sub>, and a supplementary amount of CO<sub>3</sub><sup>2-</sup> and Ca<sup>2+</sup> ions was released by the dissolution of CaCO<sub>3</sub>.

#### 4. RESULTS AND DISCUSSION

As shown in Fig. 2, at the range of concentrations from  $[\text{CO}_2]_{\text{w}0} \cong 3.39 \times 10^{-5} \text{ mmol}\cdot\text{L}^{-1}$  to  $[\text{CO}_2]_{\text{w}0} \cong 33.9 \text{ mmol}\cdot\text{L}^{-1}$ , adding  $\text{CaCO}_3$  to the equilibrium system caused the pH value to rise about 2–4 units depending on the initial concentration of  $[\text{CO}_2]_{\text{w}0}$ . The  $\text{CO}_3^{2-}$  ions released by the dissolution of  $\text{CaCO}_3$  will accept a certain amount of protons ( $\Delta[\text{H}^+]_{\text{CO}_3^{2-}}$ ) originating from two sources: the reversible dissociation of water ( $\Delta[\text{H}^+]_{\text{H}_2\text{O}}$ ) or  $\text{H}_2\text{CO}_3$  ( $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ ). The smaller the initial concentration of  $[\text{CO}_2]_{\text{w}0}$ , 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  $[\text{CO}_2]_{\text{w}0}$  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  $9.89 \pm 0.03$  (with a standard deviation) occurred at  $[\text{CO}_2]_{\text{w}0} \cong 3.39 \times 10^{-5} \text{ mmol}\cdot\text{L}^{-1}$ , which coincides well with the theoretically calculated pH value. On the other hand, in the range of  $[\text{CO}_2]_{\text{w}0} \cong 3.39 \text{ mmol}\cdot\text{L}^{-1}$  to  $[\text{CO}_2]_{\text{w}0} \cong 33.9 \text{ mmol}\cdot\text{L}^{-1}$ , adding solid  $\text{CaCO}_3$  to the equilibrium system  $\text{H}_2\text{O}-[\text{CO}_2]_{\text{w}0}$  resulted in the final experimentally measured pH value lower than 7. The main source of protons in this range of  $[\text{CO}_2]_{\text{w}0}$  is  $\text{H}_2\text{CO}_3$ .

After the pH of the equilibrium system  $\text{H}_2\text{O}-[\text{CO}_2]_{\text{w}0}$  had stabilized following  $\text{CaCO}_3$  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  $\text{NH}_x\text{-N}$  in the reject water [15,18,19]. Consistently, as shown in Fig. 2, at the initial concentration of  $[\text{CO}_2]_{\text{w}0} \cong 3.39 \cdot 10^{-5} \text{ mmol}\cdot\text{L}^{-1}$ , the pH value decreased after  $\text{NH}_4\text{Cl}$  was added to the initial system  $\text{H}_2\text{O}-([\text{CO}_2]_{\text{w}0}-\text{CaCO}_3)$  from  $9.89 \pm 0.03$  to  $7.65 \pm 0.02$ . The change in the pH value was  $2.24 \pm 0.02$  units. In the system  $\text{H}_2\text{O}-[\text{CO}_2]_{\text{w}0}-\text{CaCO}_3-\text{NH}_x\text{-N}$ , at lower initial concentrations of  $[\text{CO}_2]_{\text{w}0}$ , the main source of protons is  $\text{NH}_4^+$  ions. However, at higher initial concentrations of  $[\text{CO}_2]_{\text{w}0}$  in the range



**Fig. 2.** Experimentally measured pH values of the closed equilibrium system  $\text{H}_2\text{O}-[\text{CO}_2]_{\text{w}0}-\text{CaCO}_3-\text{NH}_x\text{-N}$  at a concentration range from  $[\text{CO}_2]_{\text{w}0} \cong 3.39 \times 10^{-5}$  to  $33.9 \text{ mmol}\cdot\text{L}^{-1}$  at  $t = 25 \text{ }^\circ\text{C}$ .



**Table 3.** Experimental and model-predicted concentrations of  $[\text{Ca}^{2+}]$  and the corresponding final pH values in the closed  $\text{H}_2\text{O}$ – $[\text{CO}_2]_{\text{w}}$ – $\text{CaCO}_3$ – $\text{NH}_x$ – $\text{N}$  equilibrium system

$[\text{CO}_2]_{\text{w0}}$ ( $\text{mmol}\cdot\text{L}^{-1}$ )	$[\text{Ca}^{2+}]$ measured ( $\text{mmol}\cdot\text{L}^{-1}$ )	$[\text{Ca}^{2+}]$ theoretically predicted ( $\text{mmol}\cdot\text{L}^{-1}$ )	pH value measured after addition of $\text{NH}_4\text{Cl}$	pH value theoretically predicted
$3.39\times 10^{-5}$	$0.11 \pm 0.01$	0.10	$7.65 \pm 0.06$	7.59
$1.32\times 10^{-2}$	$0.12 \pm 0.01$	0.11	$7.60 \pm 0.03$	7.58
$3.39\times 10^{-1}$	$0.37 \pm 0.01$	0.36	$7.52 \pm 0.04$	7.48
3.39	$2.07 \pm 0.02$	2.09	$7.18 \pm 0.06$	6.80
$1.02\times 10^1$	$3.62 \pm 0.04$	3.57	$6.52 \pm 0.05$	6.36
$3.39\times 10^1$	$5.82 \pm 0.04$	5.78	$6.08 \pm 0.04$	5.95

from  $[\text{CO}_2]_{\text{w0}} \cong 3.39 \text{ mmol}\cdot\text{L}^{-1}$  to  $\cong 33.9 \text{ mmol}\cdot\text{L}^{-1}$ , the pH values of the system rose up to the value of  $7.18 \pm 0.03$  after  $71 \text{ mmol}\cdot\text{L}^{-1}$   $\text{NH}_4\text{Cl}$  was added to the initial system  $\text{H}_2\text{O}$ – $(\text{CO}_2)_{\text{w0}}$ – $\text{CaCO}_3$ , with the maximum change in the pH being  $0.54 \pm 0.03$  at  $[\text{CO}_2]_{\text{w0}} \cong 3.39 \text{ mmol}\cdot\text{L}^{-1}$ . This indicates that the final pH values of the system were affected by higher  $[\text{CO}_2]_{\text{w0}}$  concentrations in the solution.

As shown in Table 3, experimentally measured final stabilized pH values of the closed equilibrium system  $\text{H}_2\text{O}$ – $[\text{CO}_2]_{\text{w}}$ – $\text{CaCO}_3$ – $\text{NH}_x$ – $\text{N}$  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  $\text{Ca}^{2+}$  ions in the range of  $\cong 0.11$ – $5.82 \text{ mmol}\cdot\text{L}^{-1}$  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  $\text{H}_2\text{O}$ – $(\text{CO}_2)_{\text{w}}$ – $\text{CaCO}_3$ – $\text{NH}_4\text{Cl}$  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  $[\text{CO}_2]_{\text{w0}}$  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  $\text{H}_2\text{O}$ – $(\text{CO}_2)_{\text{w}}$ – $\text{CaCO}_3$ – $\text{NH}_4\text{Cl}$ , the system  $\text{H}_2\text{O}$ – $(\text{CO}_2)_{\text{w}}$ – $\text{CaCO}_3$  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  $\text{H}_2\text{O}$ – $(\text{CO}_2)_{\text{w}}$ – $\text{CaCO}_3$  by the dissolution of  $\text{CaCO}_3$ ,  $\text{CO}_3^{2-}$  ions will release and accept protons ( $\Delta[\text{H}^+]_{\text{CO}_3^{2-}}$ ) originating from two sources: the dissociation of water ( $\Delta[\text{H}^+]_{\text{H}_2\text{O}}$ ) or  $\text{H}_2\text{CO}_3$  ( $\Delta[\text{H}^+]_{\text{H}_2\text{CO}_3}$ ). The smaller the initial concentration of  $[\text{CO}_2]_{\text{w0}}$ , 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  $[\text{CO}_2]_{\text{w0}}$  gives the main amount of protons to form the equilibrium of the system. As a result, protons will be bound to  $\text{CO}_3^{2-}$  ions and the pH of the formed equilibrium system will increase.

In the system  $\text{H}_2\text{O}$ – $[\text{CO}_2]_{\text{w}}$ – $\text{CaCO}_3$ – $\text{NH}_x$ – $\text{N}$ , at lower initial concentrations of  $[\text{CO}_2]_{\text{w0}}$  the main source of protons is  $\text{NH}_4^+$  ions. Experimentally measured data coincided well with the theoretically calculated values.

At higher initial concentrations of  $[\text{CO}_2]_{\text{w0}}$  the main source of protons is  $\text{H}_2\text{CO}_3$ . The concentration of toxic  $[\text{NH}_3]$  in the system is affected by the interaction between carbonaceous and ammoniacal equilibrium processes. The developed model of the equilibrium closed system  $\text{H}_2\text{O}$ – $(\text{CO}_2)_{\text{w0}}$ – $\text{CaCO}_3$ – $\text{NH}_4\text{Cl}$

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  $[\text{CO}_2]_{\text{W}0}$  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  $[\text{CO}_2]_{\text{W}}$  and  $[\text{NH}_3]$  concentrations in water.

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### **Protoni ülekandel põhinev uudne mudel suletud tasakaaluliste süsteemide $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3-\text{NH}_x$ modelleerimiseks**

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On käsitletud uutset protoni ülekandel põhinevat täiendatud mudelit suletud tasakaalulise süsteemi  $\text{H}_2\text{O}-\text{CO}_2-\text{CaCO}_3-\text{NH}_x$  modelleerimiseks matemaatilise iteratsiooni abil, mille aluseks on võetud varasemates uurimustes käsitletud süsteem  $\text{H}_2\text{O}-(\text{CO}_2)_w-\text{CaCO}_3$ . Loodud mudel võimaldab arvutada vees teadaolevate  $[\text{CO}_2]_{w0}$  ja  $[\text{NH}_x]$  kontsentratsioonide põhjal kõigi antud tasakaalulises süsteemis moodustuvate ionide ja molekulide sisalduse ning sellele vastava pH väärtuse. Samuti saab väljatöötatud mudelit kasutada nii inimtegevusest tulenevate mõjude hindamiseks looduslikele veekogudele kui ka tööstuslike protsesside ja teiste analoogsete süsteemide modelleerimiseks.