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A MODEL OF CLOSED EQUILIBRIUM SYSTEMS $H_2O–CO_2–CaCO_3–NaH_2PO_4$

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Introduction

Limestone bedrock, which consists mainly of $CaCO_3$, affects wastewater treatment—including reject water generated in biogas plants. The variation in the concentration of dissolved carbon dioxide $[CO_2]_W$ changes $CaCO_3$ solubility and pH in equilibrium systems.

The equilibrium systems containing carbonaceous and phosphorous species are present in many waste–and reject waters of various types and origin. In an anaerobic digester, the gas phase contains CO_2 about ⅓ part.

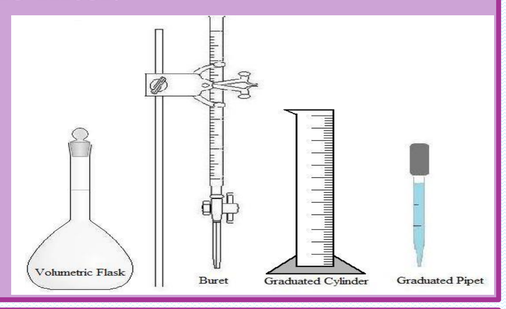
The landfill leachate and reject water from the anaerobic digestion of organic substrates contains high concentrations of phosphorous ions ($H_2PO_4^{2-}$ and HPO^{4-}), for example, the total phosphorous concentration is up to 100 mg $P_{tot}\cdot l^{-1}$ in the case of landfill leachate and up to 50-100 mg · $P_{tot}\cdot l^{-1}$ in the reject water that originates from the dewatering of digested sludge from anaerobic methane digesters.[1]

Objectives

The developed model of the equilibrium closed system $H_2O–(CO_2)_{W0}–CaCO_3–NaH_2PO_4$ can be used to determine concentrations of all components in the water phase over a wide range of natural and industrial conditions.

Materials and Methods

MilliQ water was purged with N_2 (99.999% pure) to remove any residual $(CO_2)_W$. The aqueous phase was saturated until a stable pH value was achieved. Measured pH values were registered using a Jenway type 3520 pH-meter and Dataway software. Temperature was 25.0±0.1°C using a thermostat equipped with a pH. The experiments were conducted in a closed system of $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ with 1000 mg of solid $CaCO_3$ (CAS # 471-34-1, 99.95% Sigma-Aldrich) and 344 mg of NaH_2PO_4 (CAS , 99.5% Acros Organics, US). The salts were added to the liquid in the reaction cell (volume of 1 litre, after purged with certain concentrations of $[CO_2]$ using gas bags from AGA). At the end of the experiment, samples were taken and filtered through a 0.45μm membrane filter.



Results

In this study of modelling the closed system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$, the system $H_2O–(CO_2)_W–CaCO_3$ 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.

The distribution of ions and molecules in the closed system $H_2O–(CO_2)_W–CaCO_3–NaH_2PO_4$ is described in terms of a structural scheme, **Fig. 1**. The calculated concentrations of $[CO_2]_{W0}$, $[Ca^{2+}]$, $[HCO^{3-}]$, and pH are presented in **Table 1.**

Fig.1 Structural scheme of the equilibrium distribution in the final closed system of $H_2O–[CO_2]_W–CaCO_3–NaH_2PO_4$, where Kh is the hydration constant of CO_2, K'a1 the true acid dissociation constant of H_2CO_3, Ka2 the acid dissociation constant of HCO^{3-}, K_{SP} is the solubility product constant of $CaCO_3$, K_W the ion-product constant of water, and Ka2,p the dissociation constant of $H_2PO_4^-$ ions, Ka3,p the dissociation constant of HPO_4^{2-}

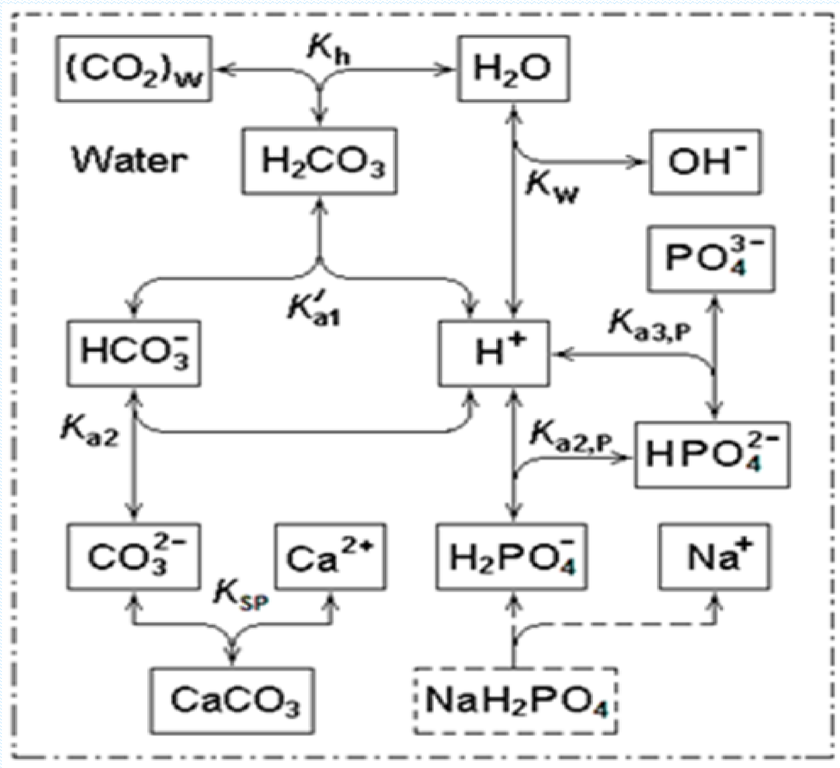


Table 1. Results of the calculations of the equilibrium parameters after adding 344 mg/l NaH_2PO_4 (containing 100 mg/l of phosporous) to the closed initial system of $H_2O–(CO_2)_{W0}–CaCO_3$ containing $[CO_2]_{W0} \cong 3.39\cdot10^{-7}$ to 33.9 $mmol\cdot l^{-1}$ at a t = 25°C. **Δ** – amount of H^+ ions released from dissociation of water, H_2CO_3, CO_3, H_2PO_4 respectively.

$[CO_2]_{W0}$ mmol·L⁻¹	$\Delta[H^+]_{H_2O}$ mmol·L⁻¹	$\Delta[H^+]_{H_2CO_3}$ mmol·L⁻¹	$\Delta[H^+]_{CO_3^{2-}}$ mmol·L⁻¹	$\Delta[H^+]_{H_2PO_4^-}$ mmol·L⁻¹	pH	$[HPO_4^{2-}]$ mmol·L⁻¹	$[Ca^{2+}]$ mmol·L⁻¹	$[HCO_3^-]$ mmol·L⁻¹
$3.39\cdot10^{-7}$	$3.63\cdot10^{-4}$	$-6.85\cdot10^{-2}$	-1.28	1.35	7.59	1.35	1.28	1.21
$1.00\cdot10^{-6}$	$3.63\cdot10^{-4}$	$-6.85\cdot10^{-2}$	-1.28	1.35	7.59	1.35	1.28	1.21
$1.02\cdot10^{-5}$	$3.63\cdot10^{-4}$	$-6.84\cdot10^{-2}$	-1.28	1.35	7.59	1.35	1.28	1.21
$2.37\cdot10^{-5}$	$3.63\cdot10^{-4}$	$-6.84\cdot10^{-2}$	-1.28	1.35	7.59	1.35	1.28	1.21
$3.39\cdot10^{-5}$	$3.63\cdot10^{-4}$	$-6.83\cdot10^{-2}$	-1.28	1.35	7.59	1.35	1.28	1.21
$3.39\cdot10^{-4}$	$3.63\cdot10^{-4}$	$-6.78\cdot10^{-2}$	-1.28	1.35	7.59	1.35	1.28	1.21
$3.05\cdot10^{-3}$	$3.62\cdot10^{-4}$	$-6.47\cdot10^{-2}$	-1.28	1.34	7.58	1.34	1.28	1.21
$1.32\cdot10^{-2}$	$3.59\cdot10^{-4}$	$-5.43\cdot10^{-2}$	-1.28	1.331	7.58	1.33	1.28	1.22
$3.39\cdot10^{-2}$	$3.52\cdot10^{-4}$	$-3.44\cdot10^{-2}$	-1.28	1.310	7.57	1.31	1.28	1.24
$3.39\cdot10^{-1}$	$2.70\cdot10^{-4}$	$2.41\cdot10^{-2}$	-1.30	1.052	7.48	1.052	1.29	1.53
2.01	$1.29\cdot10^{-5}$	1.40	-1.77	$3.78\cdot10^{-1}$	7.03	$3.78\cdot10^{-1}$	1.77	3.18
2.15	$3.29\cdot10^{-8}$	1.47	-1.82	$3.52\cdot10^{-1}$	7.00	$3.52\cdot10^{-1}$	1.82	3.29
2.45	$-2.54\cdot10^{-7}$	1.61	-1.92	$3.11\cdot10^{-1}$	6.94	$3.11\cdot10^{-1}$	1.92	3.53
3.39	$-9.27\cdot10^{-5}$	1.99	-2.22	$2.26\cdot10^{-1}$	6.80	$2.26\cdot10^{-1}$	2.22	4.21
$1.02\cdot10^{1}$	$-4.12\cdot10^{-4}$	3.51	-3.63	$1.21\cdot10^{-1}$	6.36	$1.21\cdot10^{-1}$	3.63	7.14
$3.39\cdot10^{1}$	$-1.12\cdot10^{-3}$	5.76	-5.79	$3.17\cdot10^{-2}$	5.95	$3.17\cdot10^{-2}$	5.79	11.56

Conclusions

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.

References

1. Tenno, T., Uiga, K., Mashirin, A., Zekker, I., and Rikmann, E. Modelling closed equilibrium systems of H_2O–dissolved CO_2–solid $CaCO_3$. J. Phys. Chem. A., 2017, 121, 3094–3100.