

Predicting struvite formation for phosphorus recovery from human urine using an equilibrium model

H. Harada*, Y. Shimizu**, Y. Miyagoshi***, S. Matsui*, T. Matsuda* and T. Nagasaka****

*Graduate School of Global Environmental Studies, Kyoto University, Yoshida-Honmachi, Sakyo-Ku, Kyoto 606-8501, Japan (E-mail: harada@eden.env.kyoto-u.ac.jp; matsui@eden.env.kyoto-u.ac.jp; matsuda@eden.env.kyoto-u.ac.jp)

**RCEQM, Graduate School of Engineering, Kyoto University, 1-2 Yumihama, Otsu 520-0811, Japan (E-mail: shimizu@biwa.eqc.kyoto-u.ac.jp)

***Graduate School of Engineering, Kyoto University, Yoshida-Honmachi, Sakyo-Ku, Kyoto 606-8501, Japan

****Central Laboratory, Maezawa Industry, Inc., 5-11 Naka-Cho, Kawaguchi 322-8556, Japan (E-mail: toshiki_nagasaka@maezawa.co.jp)

Abstract Interest in phosphorus recovery from urine diverted from faeces has been growing recently. Phosphorus in urine can be precipitated out as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) with addition of magnesium salt under alkaline conditions. Struvite formation, however, should be more well understood for its practical application. We predicted the struvite formation with a development of a new equilibrium model. The model considered the formation of eight different kinds of precipitates, including struvite, with effects of ionic strength and temperature. In addition, experiments on struvite formation in urine were conducted for the model validation. The model prediction of struvite formation had good agreement with the experimental results. The optimum pH to form struvite was predicted to be 9.4–9.7. In order to precipitate 99% of phosphate in urine with 1.5 fold Mg concentration to $\text{PO}_4\text{-P}$, the pH value was necessary to be more than 8.1 based on the model prediction.

Keywords Equilibrium model; phosphorus; struvite; urine diversion

Introduction

Phosphorus recovery from wastewater has been a growing concern (Baimer, 2004). Since human urine is one of the main sources of phosphorus (Larsen and Gujer, 1996), studies on phosphorus recovery from urine diverted from faeces have been undertaken. Ban and Dave (2004) and Lind *et al.* (2000) reported that phosphorus, most of which is in the form of phosphate, could be recovered as struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) from urine with addition of magnesium salt under alkaline conditions (i.e., struvite-recovery conditions). Although this reaction indicates that it may be possible to recover phosphorus from urine, chemical reactions related to struvite formation in urine should be well understood more to optimise and control the reaction for its practical application.

Equilibrium models are strong tools to understand such chemical phenomena. Although some models on struvite precipitation in urine are established (Scott *et al.*, 1991; Wringley *et al.*, 1992; Udert *et al.*, 2003a, b), they were not developed for struvite recovery but for preventing blockage of pipes by the precipitation of struvite. Therefore, precipitates such as magnesium hydroxide ($\text{Mg}(\text{OH})_2$), which may be formed in the struvite-recovery conditions, are not considered in those models and little is known about an optimum condition for the struvite formation.

In this research, we developed an equilibrium model to predict struvite formation in urine in struvite-recovery conditions, considering precipitates, which may be formed under the conditions. In addition, we carried out experiments on struvite formation for

the model validation. Then, we predicted struvite formation in urine with the various values of magnesium addition and pH, and eventually came up with the optimum condition.

Experimental methodology

In this research, we separate urine from faeces using a urine-diversion toilet constructed in our laboratory and stored it in a storage tank for a few months. The human urine (HU) stored in the tank was collected for the experiment. In addition, synthetic urine (SU) containing 7 major inorganic solutes of human urine was made for experiments. For SU, we assumed that urine was diluted two times by flushing water of a urine-diversion toilet. Also, we set ammonia concentration as 1.5 fold concentration of PO₄-P in SU for struvite recovery, as urea is decomposed to ammonia during urine storage. The compositions of HU and SU are shown in Table 1.

Samples of 250 ml of both SU and HU were used in the experiment on struvite formation. The concentration of magnesium in each sample was adjusted, corresponding to 20 mmol-Mg/litre-SU or 10 mmol-Mg/litre-HU, respectively, and the pH was adjusted to 6–10. After mixing them for 24 h at 20 °C, the supernatant of each sample was separated from the precipitates by filtration (0.4 μm) and analyzed for NH₄-N, PO₄-P, Na, K, Ca and Mg, followed by Standard Methods for sewage (JSWA, 1997a, b). Filtered precipitates were dried at 105 °C for 2 h and then dissolved in sulfuric acid or hydrochloric acid. Dissolved precipitates were analyzed in the same manner as the supernatant.

Model formation

Assumptions

The equilibrium model was formulated with the following four assumptions:

- Species in urine are ammonia, phosphate, sodium, potassium, calcium, magnesium, citrate, carbonate, chloride, protons and hydroxyl ions.
- Precipitates, which may be formed in urine in struvite-recovery conditions, are the following eight precipitates: struvite (MgNH₄PO₄·6H₂O), calcium phosphates (Ca₃(PO₄)₂ and (CaHPO₄), magnesium hydroxide (Mg(OH)₂), calcium hydroxide (Ca(OH)₂), magnesium carbonate (MgCO₃), calcium carbonate (calcite) (CaCO₃) and dolomite (CaMg(CO₃)₂).
- All reactions are in an equilibrium state.
- All reactions proceed in an open system.

The assumptions (a) and (b) are included with consideration of the precipitates in urine in struvite-recovery conditions. The precipitates, which were not considered to thermodynamically precipitate in the conditions, such as CaH₂PO₄ are not included in the model. Although species of Na, K and Cl do not affect any precipitation directly in this model, they are present at high concentrations in urine and may affect ionic strength. The assumption (c) is valid to predict struvite formation for its practical application using urine diversion toilets. The validity of assumption (d) is discussed in this paper.

Table 1 Composition of synthetic urine (SU) and human urine (HU) stored in the storage tank

Item	PO ₄ -P (mmol/L)	NH ₄ -N (mmol/L)	Na (mmol/L)	Mg (mmol/L)	K (mmol/L)	Ca (mmol/L)	Cl (mmol/L)
Synthetic urine	13.45	20.18	69.60	1.85	21.30	1.21	90.30
Human urine in the storage tank (N = 13)							
Avg. (S.D.)	5.85 (0.14)	191.23 (5.86)	57.66 (7.58)	0.04 (0.00)	11.78 (2.94)	0.47 (0.05)	– (–)

Equations

This model considers mass balance, electro-neutrality, acid–base equilibrium and solubility equilibrium and vapour–liquid equilibrium as the model equations. Equilibrium constants, except vapour–liquid equilibrium, at 25 °C are shown in Table 2. The constant of struvite formation is measured as various values between 12.6–13.26 (Ohlinger *et al.*, 1998), which is discussed further in the next section. Vapour–liquid equilibrium is applied to calculate H_2CO_3^* concentration in urine. It is calculated as $10^{-5.0}$ using Henry's constant of $10^{-1.5}$ mol/L/atm and CO_2 partial pressure of $10^{-3.5}$ atm (1 atm = 1.013×10^5 Pa).

Although we consider the eight solubility equilibria, not all of the eight precipitates are formed all the time and the model does not need to satisfy the equilibria of the precipitates which are not formed. Therefore, the necessary equations used for the model calculation differ from the combination of the precipitates formed in each condition. In the consideration of the reaction in urine in struvite-recovery conditions, the combination of precipitates could be classified into 14 patterns. This model calculates these 14 patterns and selects one appropriate pattern. In inappropriate patterns, there are negative values of calculated-solute concentrations and/or ionic products values exceeding solubility product constants.

Effects of temperature

We consider the effect of temperature on equilibrium constants in this model. It is known that the change of equilibrium constants accords to the Van't Hoff equation {Equation (1)}, which can be transformed into Equation (2),

$$\frac{\partial K}{\partial T} = \frac{\Delta H}{RT^2} \quad (1)$$

$$K = K_0 \cdot \exp\left(\frac{\Delta H}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad (2)$$

In Equations (1) and (2), K is the equilibrium constant of a reaction. T is temperature (K), ΔH is the enthalpy change of the reaction (kJ/mol), R is the gas constant (8.314 J/K/mol), K_0 is the equilibrium constant of a reaction at 298 K and T_0 is 298 K.

Together with the equilibrium constant of each reaction at 298 K (Table 2), the model can estimate the constant at any temperatures using the enthalpy change of each reaction,

Table 2 Acid–base and solubility equilibria in the model and their constants (Stumm and Morgan, 1996; Snoeying and Jenkins, 1980; Ohlinger *et al.*, 1998)

Equation	pK
$\text{NH}_4^+ \leftrightarrow \text{NH}_3 + \text{H}^+$	9.3
$\text{H}_3\text{PO}_4 \leftrightarrow \text{H}_2\text{PO}_4^- + \text{H}^+$	2.1
$\text{H}_2\text{PO}_4^- \leftrightarrow \text{HPO}_4^{2-} + \text{H}^+$	7.2
$\text{HPO}_4^{2-} \leftrightarrow \text{PO}_4^{3-} + \text{H}^+$	11.3
$\text{H}_2\text{CO}_3 \leftrightarrow \text{HCO}_3^- + \text{H}^+$	6.3
$\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$	10.2
$\text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{H}^+$	14.0
$\text{Mg}^{2+} + \text{NH}_4^+ + \text{PO}_4^{3-} \leftrightarrow \text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	12.6–13.26
$3\text{Ca}^{2+} + 2\text{PO}_4^{3-} \leftrightarrow \text{Ca}_3(\text{PO}_4)_2$	25.0
$\text{Ca}^{2+} + \text{HPO}_4^{2-} \leftrightarrow \text{CaHPO}_4$	6.57
$\text{Mg}^{2+} + 2\text{OH}^- \leftrightarrow \text{Mg}(\text{OH})_2$	8.22
$\text{Mg}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{MgCO}_3$	5.0
$\text{Ca}^{2+} + 2\text{OH}^- \leftrightarrow \text{Ca}(\text{OH})_2$	4.59
$\text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3$	16.7
$\text{Mg}^{2+} + \text{Ca}^{2+} + 2\text{CO}_3^{2-} \leftrightarrow \text{MgCa}(\text{CO}_3)_2$	5.3

which can be calculated using Hess's Law {Equation (3)}, as follows:

$$\Delta H = \sum \Delta H_f(\text{formations}) - \sum \Delta H_f(\text{reactions}) \quad (3)$$

In Equation (3), ΔH_f (formation) is the enthalpy of formation (kJ/mol), ΔH_f^0 (reaction) is the enthalpy of reaction (kJ/mol). The standard enthalpy change of each reaction can be calculated using the standard enthalpy of formation shown in Table 3. Thus, the model can simulate the effect of temperature on equilibrium constants except for struvite. We could not find the standard enthalpy of formation for struvite. In addition, the equilibrium constant of struvite differs among researchers, as mentioned in the previous section. Therefore, we calibrated the constant based on the experiment on struvite formation for SU and the calibrated constant is $\text{pK} = 13.0$ at 20°C .

Effects of ionic strength

In order to consider the effects of ionic strength, activity coefficients are introduced in this model. There are many theoretical methods to calculate activity coefficients. It is acknowledged that the values of activity coefficients depend on ionic strengths {Equation (4)}, where I is the ionic strength (mol/L), C_i is the molarity of species i (mol/L) and Z_i is the charge of species i (dimensionless).

$$I = \frac{1}{2} \sum C_i Z_i^2 \quad (4)$$

When ionic strength is less than 0.5 mol/L, activity coefficients can be estimated by the Davies approximation {Equations (5) and (6)} of the Debye–Huckel equation (Stumm and Morgan, 1996):

$$\log_{10} \gamma_i = -AZ_i^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.2I \right) \quad (5)$$

$$A = 1.82 \times 10^6 (\epsilon T)^{-\frac{3}{2}} \quad (6)$$

In Equations (5) and (6), γ_i is the activity coefficient of species i (dimensionless) and ϵ is the dielectric constant (F/m). In this model, the value of A was approximated to 0.5 because urine was in water solution. Thus, activity coefficients are calculated. Due to the applicable range of the ionic strength in this approximation, the applicable pH range of this model was set as less than 10 for SU and HU in struvite-recovery conditions.

At the beginning of the calculation, all activity coefficients are set at 1.0 temporarily. Using these temporary coefficients ($= 1.0$), the model estimates solute concentrations

Table 3 The standard enthalpy of formation used in the model (Stumm and Morgan, 1996; CSJ, 2004)

Species	ΔH_f^0 (kJ/mol)	Species	ΔH_f^0 (kJ/mol)
CO ₂ (g)	-393.5	Mg ²⁺ (aq)	-466.8
H ₂ CO ₃ (aq)	-699.6	Mg(OH) ₂ (s)	-924.5
HCO ₃ ⁻ (aq)	-692.0	MgCO ₃ (s)	-1112.944
CO ₃ ²⁻ (aq)	-677.1	MgNH ₄ PO ₄ ·6H ₂ O(s)	-
Ca ²⁺ (aq)	-542.83	NH ₃ (aq)	-80.29
Ca(OH) ₂ (s)	-986.0	NH ₄ ⁺ (aq)	-132.5
CaCO ₃ (s)	-1207.4	OH ⁻ (aq)	-230.0
CaMg(CO ₃) ₂ (s)	-2324.5	PO ₄ ³⁻ (aq)	-1277.4
CaHPO ₄ (s)	-1814.39	HPO ₄ ²⁻ (aq)	-1292.1
Ca ₃ (PO ₄) ₂ (s)	-4131.9	H ₂ PO ₄ ⁻ (aq)	-1296.3
H ⁺ (aq)	0	H ₃ PO ₄ (aq)	-1288.3
H ₂ O(l)	-285.83		

and the ionic strength. Based on the estimated ionic strength, new activity coefficients are then calculated. Using newly calculated coefficients, the model re-estimates solute concentrations again. Repeating this procedure, the calculated coefficients eventually reach a stable value.

Model calculation

The model formulated can calculate the concentration of each solute in urine and the amount of each precipitate formed in a litre of urine. A calculation flow of this model is shown in Figure 1. In this model, we use Newton's method to find the approximate value.

By giving total concentrations of $\text{PO}_4\text{-P}$, $\text{NH}_4\text{-N}$, Mg, Ca, Na, K in SU or HU and temperature (20°C), the model predicted the amount of precipitates formed from a litre of each urine in the experiments in the range of pH 6.0 to 10.0. The total concentration of Mg means the summation of concentrations of initial Mg present in each urine and Mg added in the experiment. In addition, changing the total concentration of Mg, the model calculated the recovery ratio of $\text{PO}_4\text{-P}$ to initial $\text{PO}_4\text{-P}$ in each urine with the various values of magnesium addition and pH.

Results and discussion

For synthetic urine

For the comparison between the modeled and experimental results for SU, the amounts of $\text{PO}_4\text{-P}$, Mg, Ca and $\text{NH}_4\text{-N}$ precipitated in a litre of SU are shown in Figure 2. A good agreement was observed between the measured and modeled results of $\text{PO}_4\text{-P}$ and $\text{NH}_4\text{-N}$

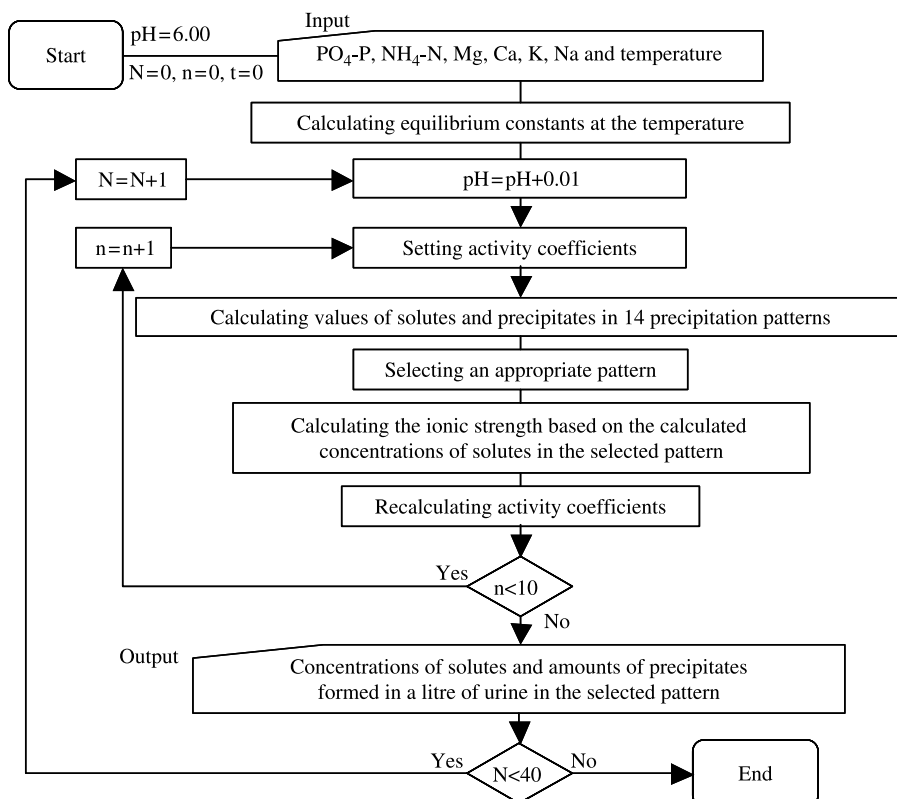


Figure 1 A flow of the model

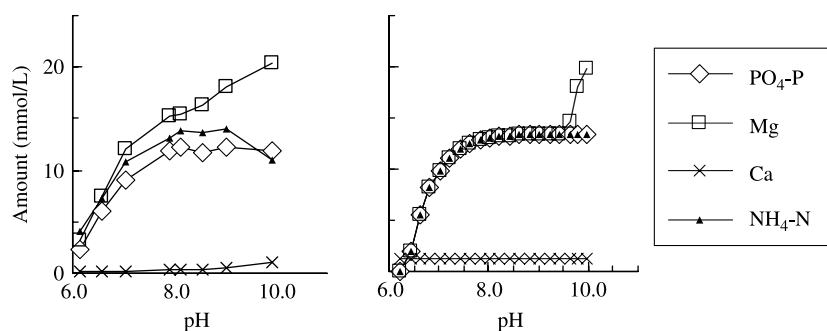


Figure 2 Measured (left) and modeled (right) amounts of $\text{PO}_4\text{-P}$, Mg, Ca, $\text{NH}_4\text{-N}$ precipitated in a litre of SU

at each pH. The measured amount of $\text{PO}_4\text{-P}$ corresponded to $\text{NH}_4\text{-N}$. As most phosphate precipitates in a form of struvite in struvite-recovery conditions (Lind *et al.*, 2000; Ban and Dave, 2004), the correspondence means that most phosphate precipitated as struvite in the experiment. In addition, the model predicted that phosphate precipitated as only struvite. Thus, it is indicated that the model prediction of struvite formation was valid for SU.

Additionally, the model predicted the excess precipitates of Mg compared to $\text{PO}_4\text{-P}$ at pH greater than 9.5, although the precipitate amount of Mg exceeded that of $\text{PO}_4\text{-P}$ at pH greater than 7 in the experiment (Figure 2). The excess of the model was due to the formation of MgCO_3 . The excess may be derived from MgCO_3 formation at pH lower than that pH at which the model predicted the formation. However, the difference of MgCO_3 formation between the model and the experimental had insignificant effects on prediction of struvite formation. The reason for the insignificance may be why there was enough Mg to form struvite in the urine.

In contrast to Mg, the model predicted the precipitates of Ca derived from CaCO_3 at any pH, although the precipitate of Ca were little formed in the experiment (Figure 2). The little Ca precipitates in the experiment is noteworthy, because Ca was one of the major components of precipitates in urine of a urine-collecting system (Udert *et al.*, 2003a, b). The difference between this research and the literature is not considered to be derived from the difference between synthetic and human urines, as mentioned in the next section. It may depend on the conditions for struvite formation. The difference in Ca precipitation between the model prediction and the experiment results may be explained using Assumption (4) of the model: all reactions are in the equilibrium state. The actual state might not be at equilibrium, and the reaction related to Ca might not proceed fast enough due to the low concentration of Ca. In spite of the difference between the model and the experiment, it is considered that the formation of Ca does not have a big influence on the struvite formation due to its low concentration.

For human urine in the storage tank

For the comparison between the modeled and experimental results for HU, the amounts of $\text{PO}_4\text{-P}$, Mg, and Ca precipitated in a litre of HU are shown in Figure 3. A good agreement was observed between the measured and modeled results of $\text{PO}_4\text{-P}$ and Mg. The measured amount of $\text{PO}_4\text{-P}$ corresponded to Mg. Likewise to the discussion for SU, it is considered that most phosphate precipitated as struvite in the experiment. In addition, the model predicted that phosphate precipitated as only struvite (Figure 4). Thus, it is indicated that the model prediction of struvite formation was also valid for HU.

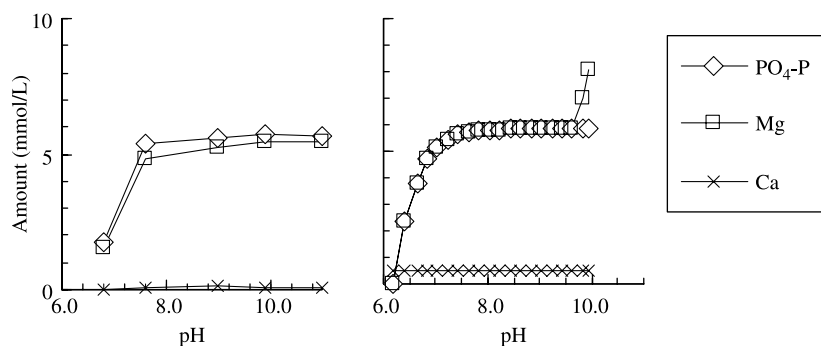


Figure 3 Measured (left) and modeled (right) amounts of $\text{PO}_4\text{-P}$, Mg and Ca precipitated in a litre of SU

Different from the results for SU, the precipitated amount of Mg did not exceed that of $\text{PO}_4\text{-P}$ at any pH in the experiments, although the model predicted the excess at pH greater than 9.5 (Figure 3). The Mg excess in the model result was due to the formation of MgCO_3 (Figure 4). The reason of the no-Mg-excess in the experiment is considered to be the difference between SU and HU. HU contains many kinds of inorganic and organic compounds, which are not contained in SU. Some of them may inhibit the formation of MgCO_3 . However, the difference in MgCO_3 formation between model prediction and experimental results had insignificant effect on the prediction of struvite formation. Likewise to SU, the reason for the insignificance may be due to the sufficient presence of Mg to form struvite in the urine.

Corresponding to the result of SU, the precipitates of Ca were little formed in the experiment, although the model predicted the precipitates of Ca derived from CaCO_3 at any pH (Figure 3). It was confirmed that Ca precipitates were not the main components of precipitates in urine in struvite-recovery conditions, which is different from the urine-collecting system (Udert *et al.*, 2003a, b). In addition, the difference in Ca precipitates between the model and the experiment may be derived from the assumption of equilibrium, as mentioned previously for SU. In spite of the difference, it was considered that the precipitates of Ca do not have big influences on the struvite formation due to its low concentration.

The amount of total precipitates in the experiment is shown in Figure 4, together with the amount of each precipitate predicted by the model. The amount of struvite in the model was calculated as that of MgNH_4PO_4 since the hydrated water of struvite was removed during drying at 105°C in the experiment. It was predicted that three kinds of precipitates such as struvite, MgCO_3 and CaCO_3 were formed, although it was considered

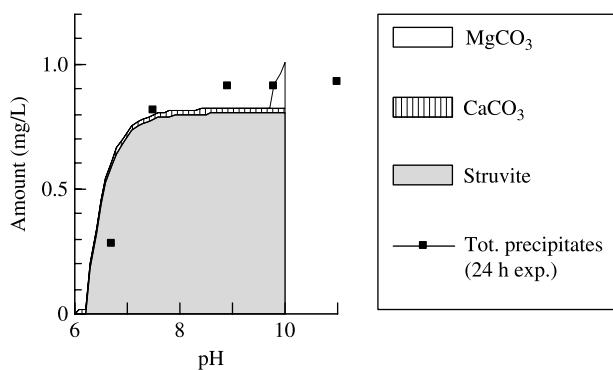


Figure 4 The amount of the precipitates predicted by the model and the total precipitates in the experiment

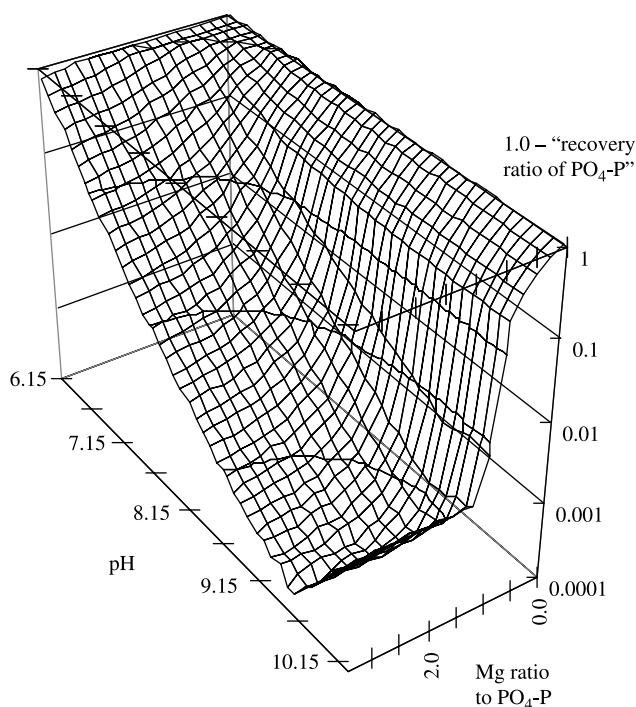


Figure 5 Modeled ratio of $\text{PO}_4\text{-P}$ recovery in HU at each pH and Mg ratio to $\text{PO}_4\text{-P}$

that little MgCO_3 and CaCO_3 were formed in the experiment. The total amount in the experiment corresponded to the amount of struvite at low pH, and it exceeded the amount of struvite at the high pH. It is considered that most of precipitates are composed of struvite and the precipitates contain other kinds of precipitates as well, which is not predicted.

Optimum condition for struvite formation from urine

It was confirmed that the model could predict struvite formation with enough accuracy. Then, we calculated the $\text{PO}_4\text{-P}$ recovery ratio to initial $\text{PO}_4\text{-P}$ concentration for HU as shown in Figure 5. The minimum value of “1.0- ‘recovery ratio to $\text{PO}_4\text{-P}$ ’” was located at pH 9.4–9.7 with any Mg ratios. Therefore, the optimal pH to form struvite is considered to be pH 9.4–9.7. When the Mg ratio to $\text{PO}_4\text{-P}$ was 1.5 or 2.0, more than 99% of $\text{PO}_4\text{-P}$ was precipitated at pH higher than 8.1 or 7.9, respectively. It was considered that in order to precipitates 99% of $\text{PO}_4\text{-P}$ in urine with 1.5-fold or 2.0-fold Mg concentration to $\text{PO}_4\text{-P}$, the pH value should be more than 8.1 or 7.9, based on the model prediction.

Conclusions

The model developed in this research was confirmed to be valid to predict struvite formation from urine. In addition, it was confirmed that precipitates formed in urine in struvite-recovery conditions were composed of mainly struvite and contained little Ca precipitates. The optimum pH to form struvite was predicted to be 9.4–9.7. In order to precipitate 99% of phosphates in urine with 1.5 fold Mg concentration to $\text{PO}_4\text{-P}$, the pH value was necessary to be more than 8.1 based on the model prediction. These may be useful references to understand and control struvite formation in practical application. A pilot plant experiment to recover phosphorus from urine by struvite formation is ongoing based on the achievements of this research.

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