

# Unified thermodynamic methodology for modeling chemical reactions in heterogeneous equilibria applied to wastewater treatment and reuse

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## INTRODUCTION & AIM

This paper presents a thermodynamic approach for investigating complex chemical equilibria in both homogeneous and heterogeneous multicomponent systems, applied here to optimize wastewater conditions for maximum struvite precipitation. The method evaluates key processes such as metal ion hydrolysis, ligand protonation, and complex formation, with particular focus on the influence of pH on these thermodynamic functions. By integrating a complete set of thermodynamic functions with unique mass balance equations for insoluble species, the model estimates the amount of struvite formed based on initial concentrations and soil solution pH.

Through the process of struvite precipitation, it becomes possible to effectively remove the ammonium and phosphate content from various types of wastewater. This precipitate, characterized by its chemical properties, serves as a valuable slow-release fertilizer abundant in multiple nutrients essential for the growth of vegetables and plants.

Thermodynamic modeling has been highly effective in clarifying the formation mechanisms of magnesium phosphates and their interactions with other precipitates. Thermodynamic models rely on the equilibrium between liquid and solid phases, taking into account various ions and species involved, including  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{PO}_4^{3-}$ ,  $\text{H}_3\text{PO}_4$  and  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . However, other ionic species like  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{MgPO}_4^-$ ,  $\text{MgOH}^+$  and  $\text{MgH}_2\text{PO}_4^+$  as well as soluble species as  $\text{MgHPO}_4$  also contribute to the precipitation process.

## METHOD

This study examines various minerals with the general formula  $\text{Me}_m\text{H}_n(\text{OH})_p\text{A}_q\text{L}_r(\text{s})$ , representing insoluble species. Their solubility is influenced by the dissolution-precipitation equilibrium described as follows:

$$\frac{1}{m} \text{Me}_m\text{H}_n(\text{OH})_p\text{A}_q\text{L}_r(\text{s}) + \frac{p}{m} \text{H} = \text{Me} + \frac{n+p}{m} \text{H} + \frac{p}{m} \text{OH} + \frac{q}{m} \text{A} + \frac{r}{m} \text{L}, \quad K_S \quad (1)$$

For simplicity, the charges of species are excluded. In this formula, A and L represent two inorganic ligands, such as ammonium and phosphate ions in the slightly soluble mixed salt struvite,  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$ . The general formula also accounts for the formation of minerals such as metal hydroxides  $\text{Me}(\text{OH})_n(\text{s})$  and mixed salts like hydroxyapatite  $\text{Ca}_5(\text{PO}_4)_3\text{OH}(\text{s})$ , monetite  $\text{CaHPO}_4(\text{s})$ , etc. To compare the total Gibbs energy values for different minerals, equation (1) references one mole of the heavy metal Me.

The overall Gibbs energy change ( $\Delta G$ ) for the analyzed processes has been calculated using a more holistic approach:

$$\Delta G_S = -RT \ln \frac{C_{\text{Me}}^r}{C_{\text{Me}}^0} - \frac{q}{m} RT \ln \frac{C_{\text{A}}^r}{C_{\text{A}}^0} - \frac{r}{m} RT \ln \frac{C_{\text{L}}^r}{C_{\text{L}}^0} \quad (2)$$

The sign and value of  $\Delta G_S$  indicate the potential for the formation of sparingly soluble salts and the completeness of precipitation under specified conditions. If  $\Delta G_S > 0$ , precipitation occurs. Conversely, if  $\Delta G_S < 0$ , no solid phase forms. When  $\Delta G_S = 0$ , it signifies the onset of precipitation or dissolution of the sparingly soluble salt. In this equation,  $C_i^0$  represents the total (initial) concentration of the “i” species in the heterogeneous mixture, while  $C_i^r$  denotes its residual concentration in the solution.

Including all precipitates would increase the number of unknown parameters, thereby raising the model complexity. The three MB equations take the following form:

$$\begin{aligned} C_{\text{Mg}^{2+}}^0 &= \Delta C_{\text{MgNH}_4\text{PO}_4} + \Delta C_{\text{Mg}(\text{OH})_2} + C_{\text{Mg}^{2+}}^r \\ C_{\text{PO}_4^{3-}}^0 &= \Delta C_{\text{MgNH}_4\text{PO}_4} + \sum_{j=0}^{j=3} [\text{H}_j\text{PO}_4^{j-3}] + \sum_{n=0}^{n=2} [\text{MgH}_n\text{PO}_4^{2+n-3}] = \Delta C_{\text{MgNH}_4\text{PO}_4} + C_{\text{PO}_4^{3-}}^r \\ C_{\text{NH}_4^+}^0 &= \Delta C_{\text{MgNH}_4\text{PO}_4} + \text{NH}_4^+ + \text{NH}_3 \end{aligned} \quad (3)$$

In this case, a system of three equations with five unknowns is achieved:  $\Delta C_{\text{MgNH}_4\text{PO}_4}$ ,  $\Delta C_{\text{Mg}(\text{OH})_2}$ ,  $[\text{Mg}^{2+}]$ ,  $[\text{PO}_4^{3-}]$  and  $[\text{NH}_4^+]$ .

In all examined cases it is necessary to solve a set of non-linear equations, including equilibrium and mass balance equations.

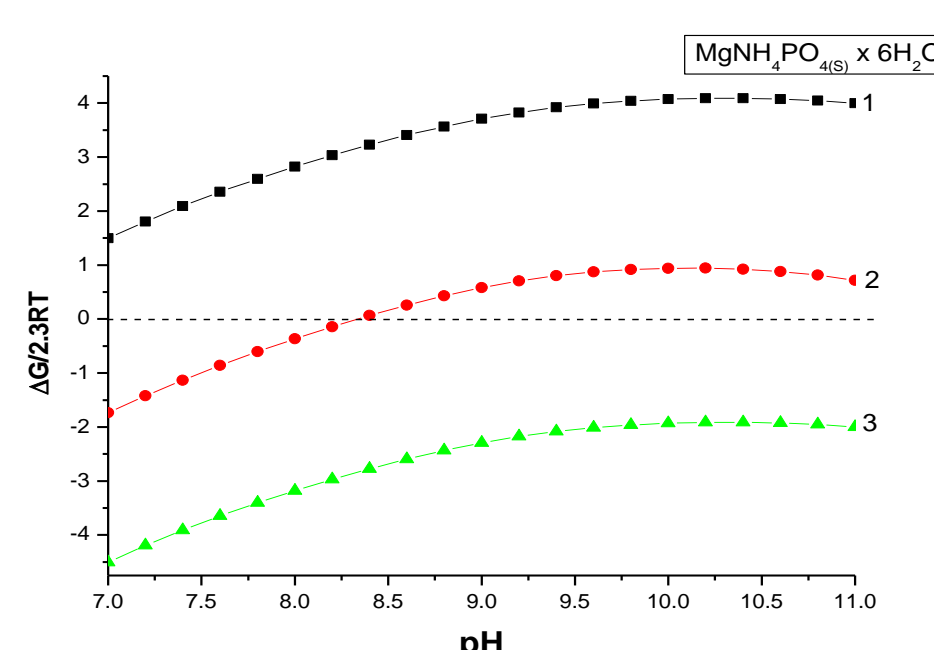
## CONCLUSION

The methodology enables the prediction of mineral formation as a function of initial wastewater composition and environmental parameters, offering valuable insight into the conditions favorable for contaminant removal through controlled precipitation. Application of the model to real wastewater systems confirms its effectiveness in identifying optimal pH values and ionic conditions for maximizing mineral recovery. Furthermore, the enhanced buffering capacity observed in the heterogeneous systems is attributed to synergistic effects arising from the formation of mixed ligand insoluble phases, particularly in the case of struvite. Overall, this thermodynamic framework provides a robust predictive tool for optimizing wastewater treatment processes. It reduces the need for extensive laboratory experimentation and supports the development of sustainable treatment strategies that promote resource recovery and ensure chemical stability in treated effluents.

## RESULTS & DISCUSSION

In our calculations, the formation of all the aforementioned soluble species is taken into account. To simulate the short-term precipitation of solid phases based on experimental results and a literature review, the following insoluble species have been considered: struvite  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$ , brucite  $\text{Mg}(\text{OH})_2(\text{s})$ , newberyite  $\text{CaHPO}_4(\text{s})$  and monetite  $\text{CaHPO}_4$ . In the presence of potassium and sodium ions the formation of insoluble species  $\text{MgKPO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  and  $\text{MgNaPO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  was also considered. Precipitates like octacalcium phosphate, tricalcium phosphate, whitlockite, dolomite, huntite, and calcite have been excluded from the model due to their slow formation rates. Ionic strength may affect struvite precipitation depending on chemical interactions and concentrations, but it is considered negligible in this study.

Analysis of the computed data indicates that the thermodynamic stability areas of the examined mineral expand notably with higher total (initial) concentrations. Therefore, the key parameters involved in struvite solution chemistry are pH and the initial concentration of the reactants. Thermodynamic examination of complex chemical equilibria in the analyzed mixtures suggests that at low concentrations of magnesium ions and inorganic ligands, the formation of solid phases resembling struvite does not occur (see Fig. 1).

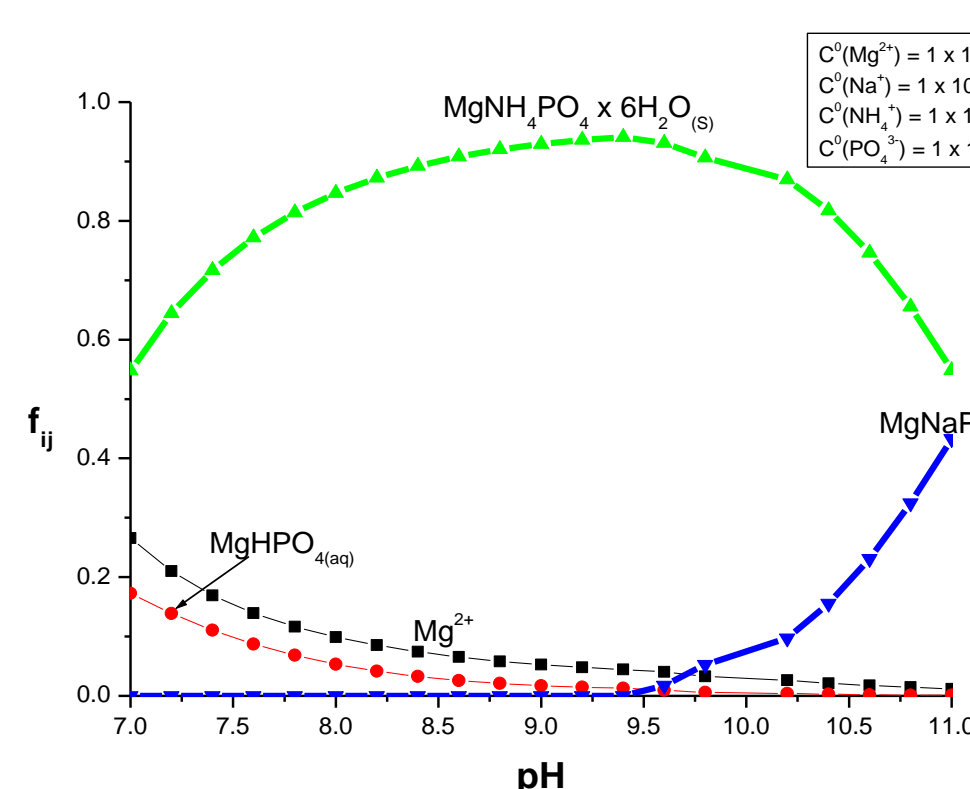


**Fig. 1.** Variation of the overall Gibbs energy as a function of pH for the process of precipitation dissolution in the system:  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  - saturated aqueous solution.  $C_i$ , mol  $\text{L}^{-1}$ :

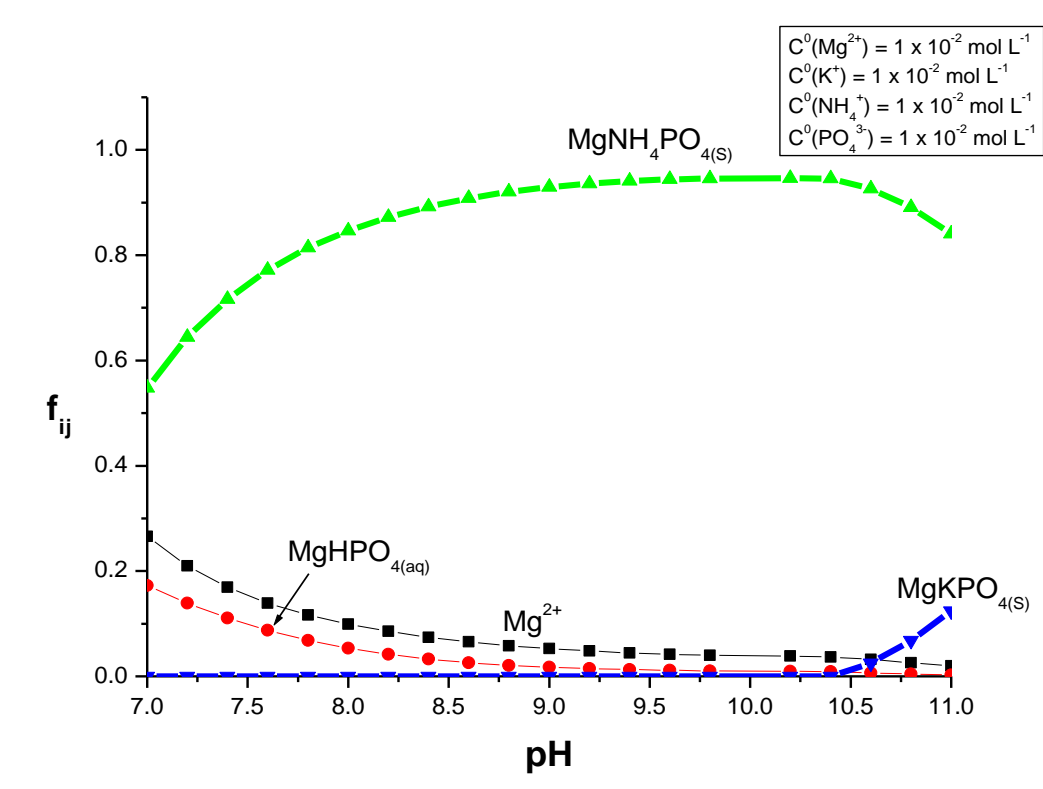
1.  $C^0(\text{Mg}^{2+}) = 1 \cdot 10^{-2}$ ;  $C^0(\text{NH}_4^+) = 1 \cdot 10^{-2}$ ;  $C^0(\text{PO}_4^{3-}) = 1 \cdot 10^{-2}$ ;
2.  $C^0(\text{Mg}^{2+}) = 1 \cdot 10^{-3}$ ;  $C^0(\text{NH}_4^+) = 1 \cdot 10^{-3}$ ;  $C^0(\text{PO}_4^{3-}) = 1 \cdot 10^{-3}$ ;
3.  $C^0(\text{Mg}^{2+}) = 1 \cdot 10^{-4}$ ;  $C^0(\text{NH}_4^+) = 1 \cdot 10^{-4}$ ;  $C^0(\text{PO}_4^{3-}) = 1 \cdot 10^{-4}$ .

The presence of competitive ions has a substantial effect on the struvite precipitation process. Newberyite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ) and bobierrite ( $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) are the primary magnesium phosphate compounds that can precipitate, although their formation is highly dependent on the operating conditions. Newberyite requires a high  $\text{Mg}^{2+}/\text{P}$  ratio and a relatively low pH (below 6) to precipitate significantly, whereas bobierrite precipitation occurs more slowly and may take several days to form.

Figures 2-3 illustrate the coexistence of two phases: struvite and  $\text{MgNaPO}_4(\text{s})$ ,  $\text{MgKPO}_4(\text{s})$ , respectively. In each case, the formation of a second phosphate-containing solid phase alongside struvite does not significantly affect the degree of struvite formation.



**Fig. 2.** Diagram of distribution for the heterogeneous system  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  -  $\text{MgNaPO}_4(\text{s})$  - saturated aqueous solution. Chemical composition, mol  $\text{L}^{-1}$ :  $C^0(\text{Mg}^{2+}) = C^0(\text{NH}_4^+) = C^0(\text{PO}_4^{3-}) = C^0(\text{Na}^+) = 1.00 \cdot 10^{-2}$ .



**Fig. 3.** Diagram of distribution for the heterogeneous system  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}(\text{s})$  -  $\text{MgKPO}_4(\text{s})$  - saturated aqueous solution. Chemical composition, mol  $\text{L}^{-1}$ :  $C^0(\text{Mg}^{2+}) = C^0(\text{NH}_4^+) = C^0(\text{PO}_4^{3-}) = C^0(\text{K}^+) = 1.00 \cdot 10^{-2}$ .

Our analysis indicated that the suitable pH for struvite precipitation likely fell within the range of 9.0 - 9.5 and for pH values exceeding 9.5, the likelihood of struvite precipitation compared to other salts was considerably reduced. Based on our calculations, it appears that adding Mg in a lower molar ratio compared to P does not induce struvite precipitation. However, it may lead to the formation of other solid phases, containing magnesium ions and phosphates.

In conclusion, the obtained outcomes of the thermodynamic modeling elucidated the mechanisms of struvite crystallization associated with precipitation reactions and prevailing conditions.

## ACKNOWLEDGMENT

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