

# Application of quantitative XRD on the precipitation of struvite from Brine Water

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**Abstract.** The present studies have been conducted to quantify the varied phases in struvite formation from brine water as the magnesium source. The quantitative X-ray Diffraction (QXRD) method was performed to quantitatively determine the crystal phases and amorphous content of struvite samples. Substantial phase samples were employed quantitative analysis to calibrate against known phase composition information by Rietveld refinement on powder XRD data. The results showed that brine water could be considered as magnesium source the formation of struvite products. The study demonstrated that in general, the high N:P molar ratio (both pH 9 and 10) might lead to the significant formation of struvite.

## 1. Introduction

Struvite (magnesium ammonium phosphate hexahydrate) is a phosphate mineral with formula:  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ . The struvite crystallization has been broadly used for simultaneous recovery of nutrients from human urine, swine wastewater, sludge supernatant and landfill leachate [1–5]. Its composition (i.e. Mg, N and P in equal molar concentrations) makes it a potentially marketable product for the fertilizer industry which can be further utilized as a valuable slow-release fertilizer [5-6].

In addition, precipitating struvite by recovery of phosphorus from wastewater has received much attention [7-10] due to struvite can provide both phosphorous and nitrogen nutrients simultaneously [11]. Examining the precipitation potential of struvite under different operational conditions [12-14] have been conducted.

Recently, Liu et al. [6] investigated the feasibility of using seawater and  $\text{MgCl}_2$  as magnesium sources for phosphorus recovery from source-separated urine to struvite crystallization. The results demonstrated that both seawater and brine were effective magnesium sources to recover phosphorus from hydrolyzed urine to struvite formation. In addition, he was found that the presence of calcium in the magnesium sources could compromise struvite purity. Higher struvite purity could be obtained with higher Mg/Ca ratio in the magnesium source. In the previous study, as magnesium source, Heraldy et al. [15] have been utilized the brine water for Mg/Al hydrotalcite synthesis with the good performance. Therefore, the above mentioned challenges prompt us to investigate the feasibility of using brine water as magnesium sources for struvite crystallization.



The purity of struvite was investigated by various analytical methods, MAS-NMR spectroscopy [16], IC and ICP analysis [6, 17-18]. These methods were commonly used to determine the total Mg, P and N concentrations in precipitates. However, these methods may not be suitable for quantifying the relative phase abundances in precipitates because precipitates usually contain crystal and amorphous phases with similar elemental compositions. Although XRD methods have been used for struvite phase identification, the use has been limited to qualitative confirmation of the presence of phosphate phases in precipitates [17, 19]. However, quantitative phase analysis using XRD data can further be approached with Rietveld refinement [20], which fits a complete experimental diffraction pattern with a calculated profile [21]. Rietveld refinements for quantitative analysis of the phase compositions were processed with the RIETICA crystallographic program, where the pseudo-Voigt function was selected as the profile fitting function.

## 2. Materials and methods

The materials of  $\text{H}_3\text{PO}_4$  and  $\text{NH}_3^+$  were added to 200 mL brine water (as magnesium source) in stoichiometric proportion (Mg:N:P molar ratio) 1:1:1; 1:2:1 and 1:1:2 respectively at pH 9, 10 and 11. The mixture of raw materials was then agitated at room temperature for 2 h. After that, allow to separate the solids, and the solution is then decanted. The precipitate obtained were washed several times using free chlorine aquadest to remove the remaining impurities, separated by centrifuge 2500 rpm for 15 min and dried at  $55^\circ\text{C}$  for 24 h. Powder X-ray diffraction (XRD) data were collected by a Bruker D8 Advance X-ray diffractometer using monochromatized  $\text{Cu-K}\alpha$  radiation from  $2\theta = 10^\circ$  to  $70^\circ$ . XRD analysis was used to quantify the phase compositions of the samples using the Rietveld refinement method by fitting the full-profile experimental XRD data with a calculated diffraction pattern [22-23]. The Le Bail refinements were performed using RIETICA program [24]. Peak profiles were modeled using a pseudo-voigt peak shape. Experimental parameters refined were the instrument zero, scale factor, the lattice parameters and the peak shape parameters  $u$ ,  $v$ ,  $w$ ,  $\gamma_0$  and  $\gamma_1$  [25].

## 3. Result and discussions

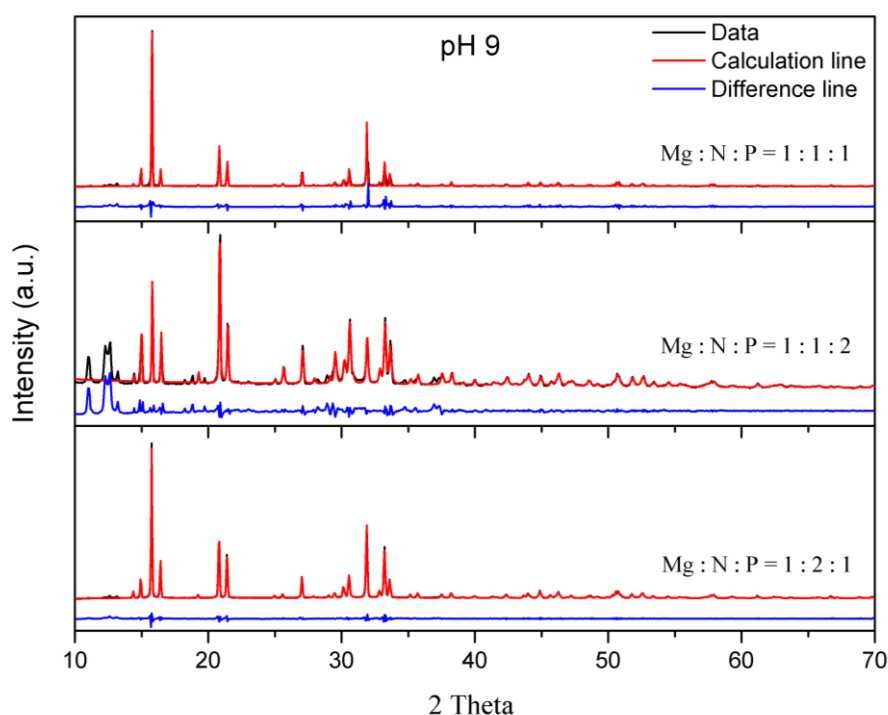
Rietveld refinement method was carried out for both samples using the lattice parameters from JCPDS standard as initial values. The refinement had been done as follow order zero, histogram parameter, lattice parameter and instrumental peak shape. For each step were used 30 cycles. In Fig. 1, the Struvite sample at pH 9 with molar ratio 1:1:1 was showed differently with JCPDS standard. The Rietveld analysis result which is shown in blue line is the differently between struvite and standard at  $2\theta$   $33^\circ$  and  $16^\circ$ . It is implied on the values of reability index parameters, i.e. the pattern factor ( $R_p$ ), the weighted pattern factor ( $R_{wp}$ ), and the goodness of fit ( $\chi^2$ ). The limitation of values of reability index parameters for  $R_p$  and  $R_{wp}$  closed to 8,0 [25] while for  $\chi^2$  closed to 4,0 [18, 27]. In Table 1, the struvite at pH 9 with molar ratio 1:1:1 have low reability values so as possible the high struvite content.

When the phosphor molar ratio in struvite was increased, appearing more new peaks nearby at  $11^\circ$ ,  $13^\circ$  and around  $30^\circ$ , which are possible as the other phase of struvite like potassium cyclo-triphosphate ( $\text{K}_3\text{P}_3\text{O}_9$ ) and hydroxylapatite [ $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ]. Because of any other phase in struvite make it value of the reability index become higher (Table 1) and consequently can possible the content of struvite becoming lower. Therefore, the molar ratio Mg : P must be 1:1 to avoid the formation another phase in the formation of struvite. In addition, any other material will affect it. As is known in the brine water containing  $\text{Ca}^{2+}$  ions that will compete with  $\text{Mg}^{2+}$  ions to binding to P or N. Wang et al. [11] was stated the slightly amount of  $\text{Ca}^{2+}$  ions can afford reduces formation struvite. In according to Hao et al. [28], at pH higher than 10 will be a formation of Calcium compounds ( $\text{Ca}_3\text{PO}_4$ ,  $\text{CaHPO}_4$ , etc.) so it will have an impact on the formation of struvite crystals.

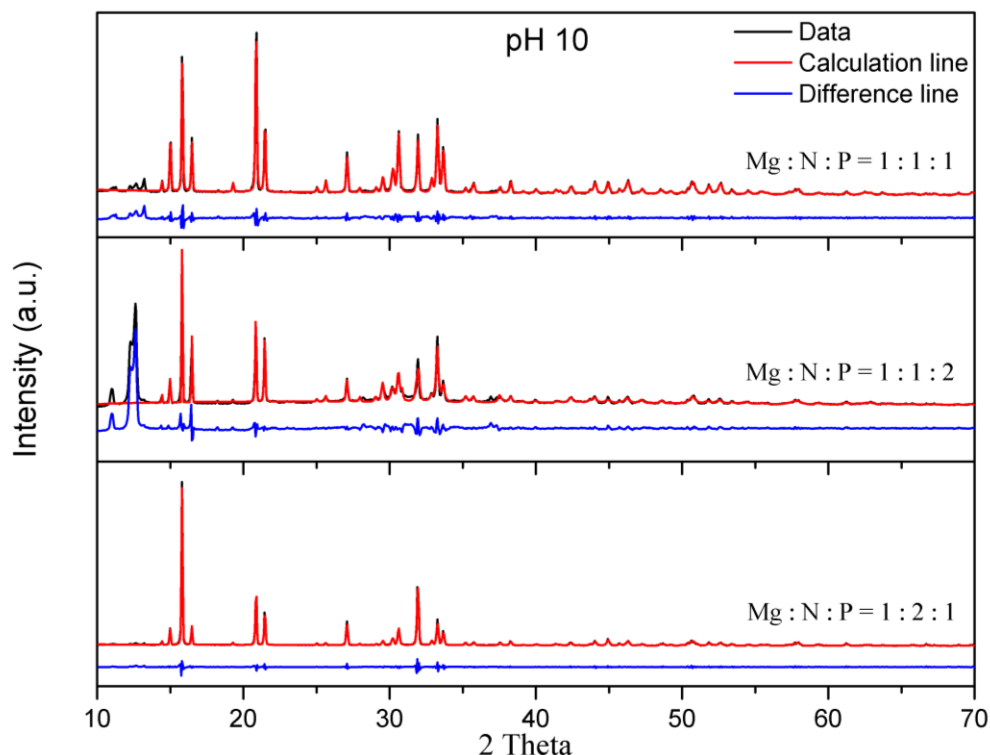
Similarly, when the nitrogen mole was increased shows that the struvite crystallization was growing larger. It was proved in Fig. 1 and Fig. 2 which did not show new peaks and in the difference line no high peak as well as in Table 1 the  $R_p$  value closer to reliable value. Teddeo et al. [29] in his research was mentioned that the excessive nitrogen content are able to make newberyite [ $\text{MgHPO}_4(\text{H}_2\text{O})_3$ ] react

to form struvite, so as to decrease the number of another phase than struvite formation. However, at pH 11 (Fig. 3) appears the new peaks in 11-13°. Hao et al. [28] were stated that when approaching pH 10.5 the content of  $\text{NH}_4^+$  to struvite formation will be reduced from the deposition process and decreases rapidly when the pH exceeds 10.5 due to the equilibrium process to form  $\text{NH}_3$ . This is why in Fig. 3 at pH 11 struvite with molar ratio 1:1:2 tend to amorphous form. However when there is still excessive nitrogen content, is able to form struvite.

Molar ratio and pH is one of the parameters in struvite crystallization. When the pH is raised into pH 10 and pH 11, did not show significant changes in the XRD spectra. However, at pH 10 showed the formation of struvite higher than at pH 11. It can be seen in Fig. 2 where the formation of another phase besides struvite is lower than at pH 11 (Fig. 3) and also demonstrated in Table 1 at pH 10 is showed good quality in comparison to struvite at pH 11. Harrison et al. [30] were stated that the struvite crystallization could take place at a pH of between 7-11. Along with the increase of pH, struvite crystals was formed there will be more crystalline [30]. In accordance with Xia et al. [31] at pH 9, P total in solution tend to be in the form of  $\text{HPO}_4^{2-}$  that will produce a precipitate  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{H}^+$ , while at  $\text{pH} > 10$  P total tend to be in the form of  $\text{PO}_3^{2-}$  that will produce  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  only. It is indicated that pH range 9-10 favorable for phosphate recovery. Similar trends were reported by Liu et al. [6].



**Figure 1.** Graphic output of the Rietveld refinement of struvite at pH 9 in molar ratio Mg:N:P. The black line (---) represent XRD data; the red line (---) represents Rietveld calculated and the blue line (---) represent the difference line between XRD data and struvite standard

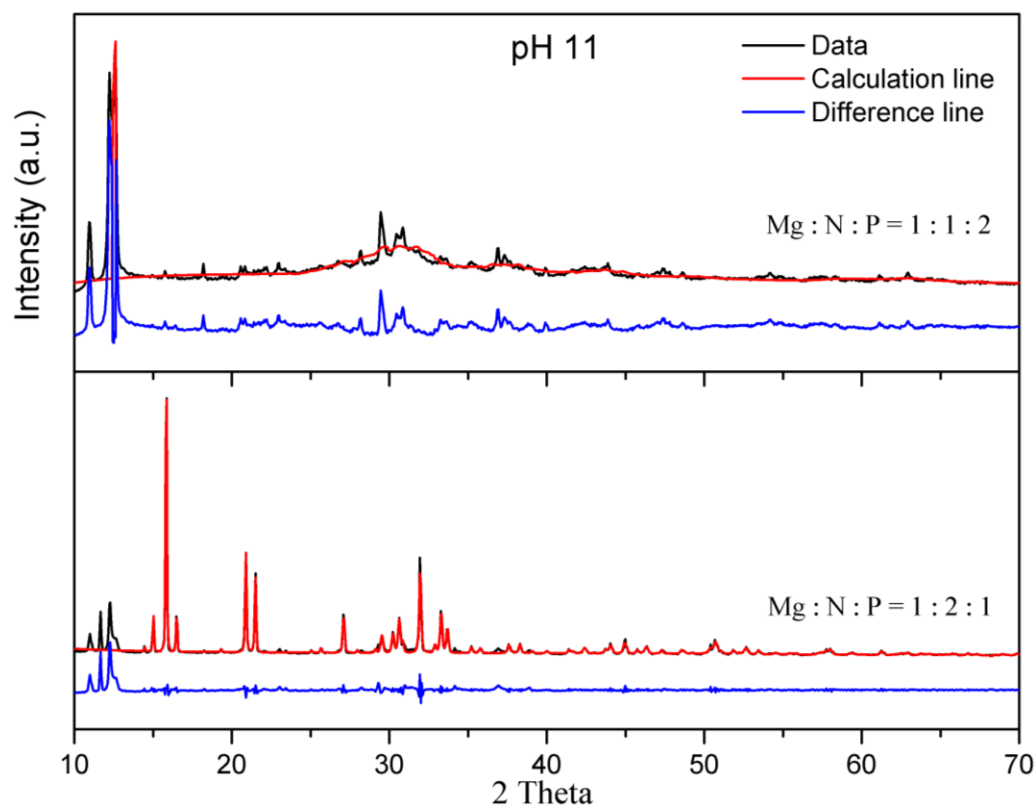


**Figure 2.** Graphic output of the Rietveld refinement of struvite at pH 10 in molar ratio Mg:N:P. The black line (---) represent XRD data; the red line (---) represents Rietveld calculated and the blue line (---) represent the difference line between XRD data and struvite standard

**Table 1. Rietveld reliable factors, and phase composition of sample**

Sample		Phase composition					Rietveld reliable factors		
pH	Molar ratio Mg : N : P						Rp	Rwp	$\chi^2$
9	1 : 1 : 1	A					17.66	26.62	134.5
	1 : 1 : 2	A	B	C	D	E	11.32	19.39	60.77
	1 : 2 : 1	A					7.71	11.55	25.56
10	1 : 1 : 1	A					8.46	12.16	22.59
	1 : 1 : 2	A	B	C	D	E	16.01	30.10	156.4
	1 : 2 : 1	A					6.97	9.52	12.45
11	1 : 1 : 2	A	B	C	D	E	15.50	25.78	91.45
	1 : 2 : 1	A	B	C			11.95	21.00	72.42

A =  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  ; B =  $\text{K}_3(\text{PO}_3)_3$  ; C =  $\text{CaHPO}_4$  ; D =  $\text{MgHPO}_4(\text{H}_2\text{O})_3$  ; E =  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$



**Figure 3.** Graphic output of the Rietveld refinement of struvite at pH 11 in molar ratio Mg:N:P. The black line (---) represent XRD data; the red line (---) represents Rietveld calculated and the blue line (---) represent the difference line between XRD data and struvite standard

#### 4. Conclusions

The present study showed that brine water could be considered as magnesium source in a formation of struvite products. The study demonstrated that in general, the high N:P molar ratio (both pH 9 and 10) might lead to the significant formation of struvite. The quantitative XRD technique is powerful and effective to determine the content of struvite in struvite products.

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