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

E Heraldy¹,², F Rahmawati¹,², Heryanto¹, and DP Putra¹

¹ Department of Chemistry, Faculty of Mathematics and Natural Sciences, Sebelas Maret University
² Porous Materials Research Group
Jl. Ir. A. Sutami 36A, Kentingan, Surakarta 57126, Indonesia

Email: eheraldy@mipa.uns.ac.id

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: MgNH₄PO₄·6H₂O. 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 MgCl₂ 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 H₃PO₄ and NH₄⁺ 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°C for 24 h. Powder X-ray diffraction (XRD) data were collected by a Bruker D8 Advance X-ray diffractometer using monochromatized Cu-Kα radiation from 20 = 10° to 70°. 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, γ₀ and γ₁ [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° and 16°. It is implied on the values of reability index parameters, i.e. the pattern factor (Rp), the weighted pattern factor (Rwp), and the goodness of fit (χ²). The limitation of values of reability index parameters for Rp and Rwp closed to 8.0 [25] while for χ² 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°, 13° and around 30°, which are possible as the other phase of struvite like potassium cyclo-triphosphate (K₃P₃O₁₀) and hydroxylapatite [Ca₅(PO₄)₃(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 Ca²⁺ ions that will compete with Mg²⁺ ions to binding to P or N. Wang et al. [11] was stated the slightly amount of Ca²⁺ 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 (Ca₅PO₄, CaHPO₄, 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 Rp value closer to reliable value. Teddeo et al. [29] in his research was mentioned that the excessive nitrogen content are able to make newberyite [MgHPO₄(H₂O)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 NH₄⁺ 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 NH₃. 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 HPO₄²⁻ that will produce a precipitate MgNH₄PO₄.6H₂O and H⁺, while at pH > 10 P total tend to be in the form of PO₄³⁻ that will produce MgNH₄PO₄.6H₂O only. It is indicated that pH range 9-10 favorable for phosphate recovery. Similar trends were reported by Liu et al. [6].

![Figure 1](image-url)

**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 pH | Molar ratio Mg : N : P | Phase composition | 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 = MgNH_4PO_4 \cdot 6H_2O ; B = K_3(PO_4)_3 ; C = CaHPO_4 ; D = MgHPO_4(\text{H}_2\text{O})_3 ; \ E = Ca(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.

References
[1] Ganrot Z, Dave G, Nilsson E 2007 Recovery of N and P from human urine by freezing, struvite precipitation and adsorption to zeolite and active carbon, *Bioresour. Technol.* 98, 3112–3121.
[2] Huang H, Xu C, and Zhang W 2011 Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology, *Bioresour. Technol.* 102, 2523–2528.
[3] Shu L, Schneider P, Jegatheesan V and Johnson J 2006 An economic evaluation of phosphorus recovery as struvite from digester supernatant, *Bioresour. Technol.* 97, 2211–2216.
[4] Huang H, Xiao D, Zhang Q, and Ding L 2014 Removal of ammonia from landfill leachate by struvite precipitation with the use of low-cost phosphate and magnesium sources, *J. Environ. Manage.* 145, 191–198.
[5] Le Corre KS, Valsami-Jones E, Hobbs P, and Parsons SA 2009 Phosphorus recovery from wastewater by struvite crystallization: a review, *Crit. Rev. Environ. Sci. Technol.* 39, 433–477.
[6] Liu B, Giannis A, Zhang J, Chang VWC, and Wang J-Y 2013 Characterization of induced struvite
formation from source-separated urine using seawater and brine as magnesium sources, Chemosphere 93, 2738–2747.

[7] Battistoni P, Paci B, Fatone F, and Pavan P 2006 Phosphorus removal from anaerobic supernatants: start-up and steady-state conditions of a fluidized bed reactor full-scale plant, Ind. Eng. Chem. Res. 45 (2), 663-669.

[8] Karabegovic L, Uldal M, Werker A, Morgan-Sagastume F 2013 Phosphorus recovery potential from a waste stream with high organic and nutrient contents via struvite precipitation, Environ. Technol. 34 (7), 871-883.

[9] Lahav O, Telzhensky M, Zewuhn A, Gendel Y, Gerth J, Calmano W, and Birn hack L 2013 Struvite recovery from municipal-wastewater sludge centrifuge supernatant using seawater NF concentrate as a cheap Mg (II) source, Sep. Purif. Technol. 108, 103-110.

[10] Xie M, Nghiem LD, Price WE, and Elimelech M 2014 Toward resource recovery from wastewater: extraction of phosphorus from digested sludge using a hybrid forward osmosis–membrane distillation process, Environ. Sci. Technol. Lett. 1 (2), 191-195.

[11] Wang J, Burken JG, Zhand XJ, and Surampalli R 2005 Engineering struvite precipitation: impact of component-ion molar ratios and pH, J. Environ. Eng. 131, 1433-1440.

[12] Etter B, Tilley E, Khadka R, and Udert KM 2011 Low-cost struvite production using source-separated urine in Nepal, Water Res. 45 (2), 852-862.

[13] Lew B, Phalah S, Sheindorf C, Kummel M, Rebhun M, and Lahav O 2010 Favorable operating conditions for obtaining high-value struvite product from sludge dewatering filtrate, Environ. Eng. Sci. 27 (9), 733-741.

[14] Warmadewanthi, and Liu JC 2009 Recovery of phosphate and ammonium as struvite from semiconductor wastewater, Sep. Purif. Technol. 64 (3), 368-373.

[15] Heraldy E, Santos JI, Triyono, Wijaya K 2015 Anionic and cationic dyes removal from aqueous solutions by adsorption onto synthetic Mg/Al hydrotalcite-like compound, Indones. J. Chem. 15(3), 234-241.

[16] Scrimgeour SN, Chudek JA, Cowper GA, Lloyd CH 2007 31P solid-state MAS-NMR spectroscopy of the compounds that form in phosphate-bonded dental casting investment materials during setting, Dent. Mater. 23 (8), 934-943.

[17] Wang CC, Hao XD, Guo GS, van Loosdrecht MCM 2010 Formation of pure struvite at neutral pH by electrochemical deposition, Chem. Eng. J. 159 (1-3), 280-283.

[18] Yan H and Shih K 2016 Effects of calcium and ferric ions on struvite precipitation: A new assessment based on quantitative X-ray diffraction analysis, Water Res. 95, 310-318.

[19] Kruk DJ, Elektorowicz M, Oleszkiewicz JA 2014 Struvite precipitation and phosphorus removal using magnesium sacrificial anode, Chemosphere 101, 28-33.

[20] Nguyen DD, Devlin L, Koshy P, and Sorrell CC 2015 Quantitative X-ray diffraction analysis of anhydrous and hydrated portland cement-paste 2: computer-based methods, Adv. Mater. Res. 1087, 498-503.

[21] Walenta G and Fullman T 2004 Advances in quantitative XRD analysis for clinker, cement, and cementitious additions, Powder Diff. 19, 40-44.

[22] Wiles DT and Young R 1981 A new computer program for Rietveld analysis of X-ray powder diffraction patterns, J. Appl. Crystallogr. 14 (2), 149-151.

[23] Young R 1993 The Rietveld Method, IUCr. Monographs on Crystallography. Oxford University Press, Oxford.

[24] Hunter BA and Howard CJ 2000 A Computer Program for Rietveld Analysis Of X-Ray and Neutron Powder Diffraction Patterns, Lucas Heights Research Laboratories, NSW, Australia, 1-27.

[25] Peterson VK 2005 Lattice parameter measurement using Le Bail versus structural (Rietveld) refinement: A caution for complex, low symmetry systems, Powder Diff. 20, 14–17.

[26] Fei L, Yanhuai L, Zhongxia S, Kewei X, Zhi Z, and Hong C 2015 Rietveld Study on Evolution of Crystalline Structure of YSZ Nanoparticles during Co-Precipitation Synthesis, Rare Met.
Lu X, Shih K, Li X, Liu G, Zeng EY, and Wang F 2016 Accuracy and application of quantitative X-ray diffraction on the precipitation of struvite product, *Water Res.* 90, 9–14.

Hao X, Wang C, Lan L, and Van Loosdrecht MCM 2008 Struvite formation, analytical methods and effects of pH and Ca$^{2+}$, *Water Sci. Technol.* 58, 1687–1692.

Teddeo R, Kolppo K, and Lepisto R 2016 Sustainable nutrients recovery and recycling by optimizing the chemical addition sequence for struvite precipitation from raw swine slurries, *J Environ. Manage.* 180, 52-58.

Harrison ML, Johns MR, White ET, and Mehta CM 2011 Growth rate kinetics for struvite crystallization, *Chem. Eng. Trans.* 25, 309–314.

Xia P, Wang X, Song J, Wang H, Zhang J, and Zhao J 2016 Struvite crystallization combined adsorption of phosphate and ammonium from aqueous solutions by mesoporous MgO–loaded diatomite, *Colloids Surf., A.* 506, 220–227.