

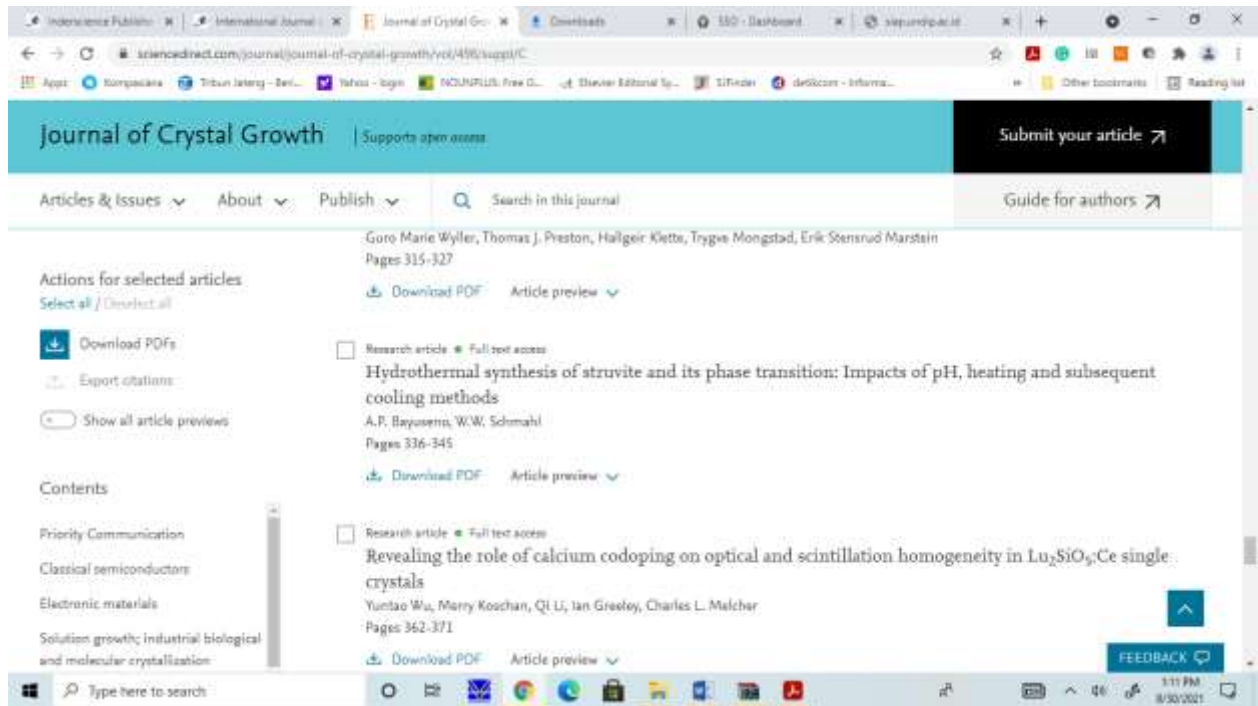
Judul : Hydrothermal synthesis of struvite and its phase transition: Impacts of pH, heating and subsequent cooling methods

Journal: Journal of Crystal Growth

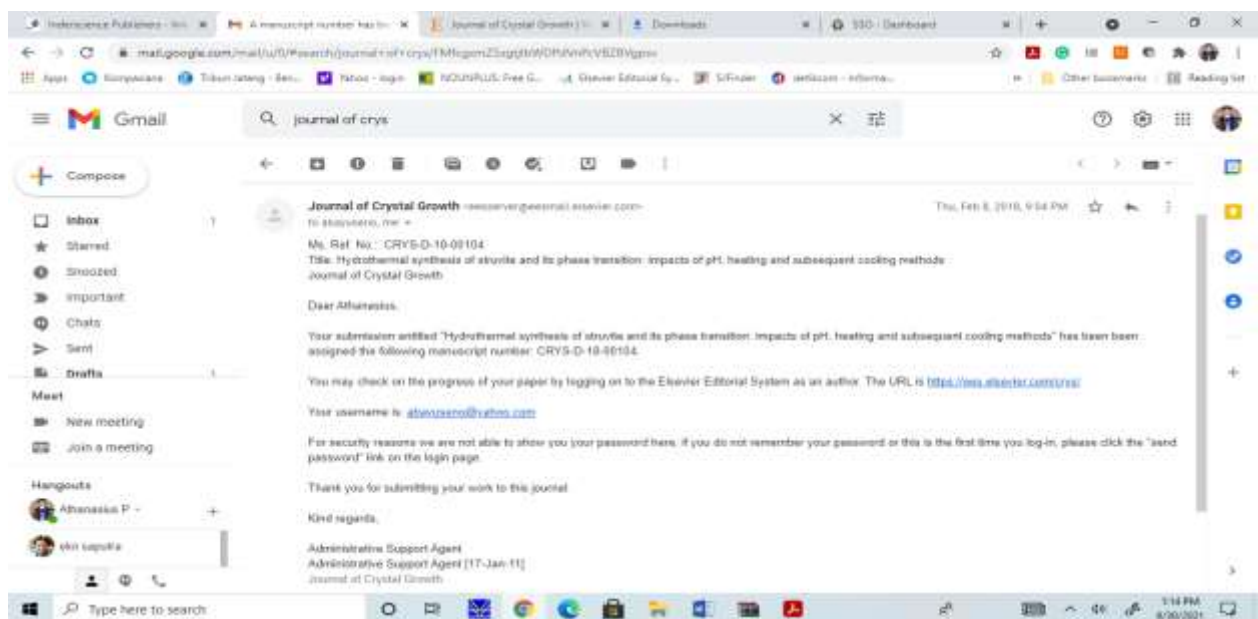
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URL: <https://www.sciencedirect.com/journal/journal-of-crystal-growth>

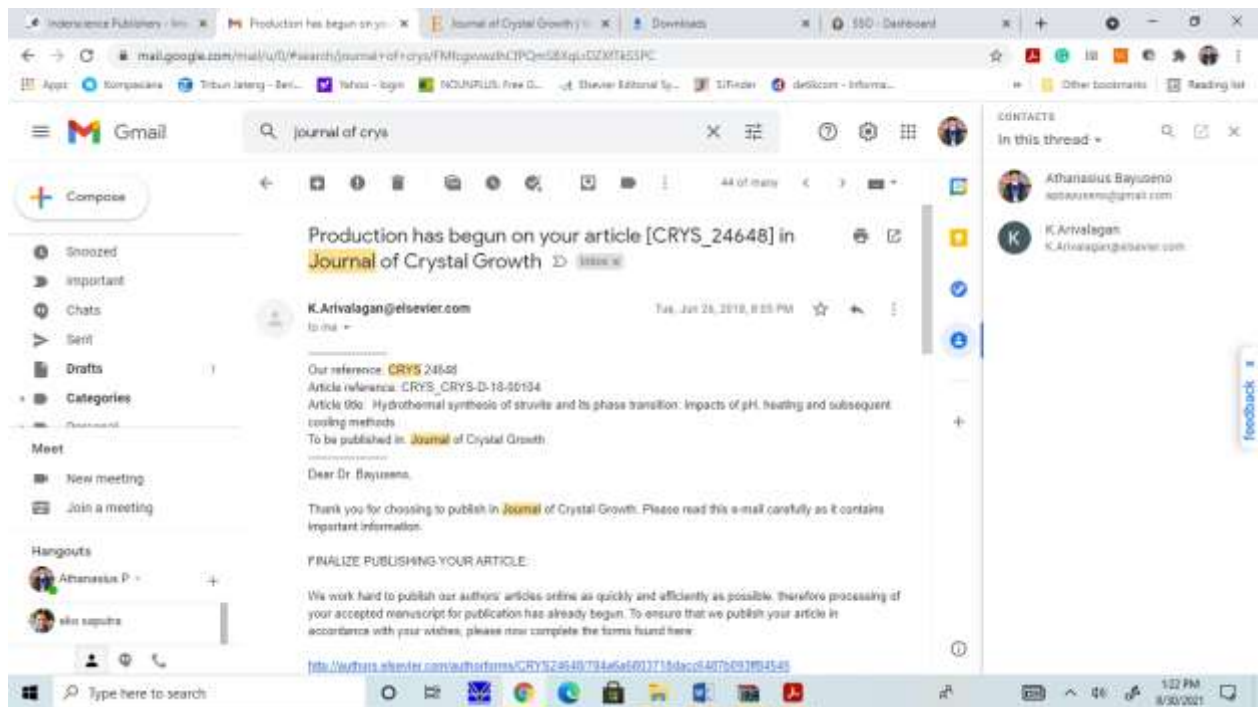
DOI: <https://doi.org/10.1016/j.jcrysgr.2018.06.026>



The screenshot shows the Journal of Crystal Growth website. The header includes the journal name, a search bar, and a 'Submit your article' button. The main content area displays a list of articles. The first article is 'Hydrothermal synthesis of struvite and its phase transition: Impacts of pH, heating and subsequent cooling methods' by A.P. Bayuseno, W.W. Schmahl, and Goro Marie Wyller, Thomas J. Preston, Halgeir Klette, Trygve Mongstad, Erik Sørensrud Marstein. The second article is 'Revealing the role of calcium codoping on optical and scintillation homogeneity in Lu₂SiO₅:Ce single crystals' by Yuntao Wu, Merry Koschan, Qi Li, Ian Greeley, Charles L. Melcher. The left sidebar contains navigation options like 'Articles & Issues', 'About', 'Publish', and 'Contents'.



The screenshot shows a Gmail inbox. The selected email is from 'Journal of Crystal Growth' with the subject 'Hydrothermal synthesis of struvite and its phase transition: impacts of pH, heating and subsequent cooling methods'. The email body contains the following text: 'Dear Athanasios, Your submission entitled "Hydrothermal synthesis of struvite and its phase transition: impacts of pH, heating and subsequent cooling methods" has been been assigned the following manuscript number: CRYSD-18-00104. You may check on the progress of your paper by logging on to the Elsevier Editorial System as an author. The URL is <https://ees.elsevier.com/jcrg>. Your username is athanasios@rathos.com. For security reasons we are not able to allow you your password here, if you do not remember your password or this is the first time you log-in, please click the "used password" link on the login page. Thank you for submitting your work to this journal. Kind regards, Administrative Support Agent Administrative Support Agent [17-Jan-19] Journal of Crystal Growth'.



Answer to review for the manuscript number: CRYS-D-18-00104

Title: Hydrothermal synthesis of struvite and its phase transition: impacts of pH, heating and subsequent cooling methods

Authors: A. P. Bayuseno and W. W. Schmahl

Article type: Research Paper

Summary:

In this manuscript, the authors carried out hydrothermal experiments for wide ranges in pH (7.0–10.0) and temperature (60, 80, and 120 °C) with two different cooling conditions (air-cooling and water quenching) in order to investigate the optimum condition for MAP (magnesium, ammonium, and phosphate) precipitation. The phases and morphologies of precipitates were investigated by XRPD and SEM analyses. They also calculated the saturation indexes (SI) of potential minerals except of dittmarite to compare their experimental results with the thermodynamic model. I think that their experimental data and findings are very precious for our knowledge on the renewable nutrient source from wastewater.

However, I think that this manuscript does not reach the standard for publication because of (i) lack of clear descriptions of motivation and originality, (ii) illogical discussions, (iii) conclusions not based on their experimental results, and (iv) incorrect descriptions. Their experimental results may be valuable if the originality of their experimental scheme is clearly explained. Unfortunately, I cannot catch the gist what the originality of their experimental scheme is when I read their Introduction session. In addition, I do not think that their discussions and conclusions were based on their experimental results. I recommend *major revision* before publication.

See following pages for my individual comments.

Dear Editor,

Thank you again for your letter on our manuscript. We would like to thank the reviewers for their constructive remarks. The manuscript has been improved accordingly. In the text we used track changes for the addition/revision of the manuscript. Following, we wrote in the font style of yellow for the answer of the reviewer.

Individual comments:

Line 103–110: The authors described the experimental scheme briefly. However, I have no idea what the originality of this experiment is. The wide pH range of 7–10 is new? But, the wider pH range has been already examined (6.5–11.5, [2, 5], see Line 56). The dynamic temperature condition is new? But, the struvite precipitation from the aqueous solution under dynamic

temperature condition has been already examined ([9], see Line 57). XRPD and SEM analyses are new? If so, why did the authors choose these analyses being examined? The motivation is unclear.

The authors should emphasize the originality and motivation more clearly in Introduction session. Otherwise, the readers cannot understand the importance of this experiment.

Response:

The Introduction has been revised to include this following information.

It is well known that struvite precipitation can occur in the different condition. Its crystallization or precipitation process is strongly related to the mother solution in which the process proceeds. Therefore, the struvite growth has been widely investigated in various mother solutions, for example, in the solution of artificial urine or in artificial wastewater. However, the investigation of crystallization in any solution cannot be used to draw out global conclusions. Therefore, what the introduced results on pH range [2, 5] and temperature [9] in the previous literature cannot directly be applied to the current work of hydrothermal synthesis. Moreover, there are likely mineralogical differences in the MAP (magnesium ammonium phosphate) precipitated by different mother solution. Moreover, there are certain known conditions in nature that a hydrothermal solution is, in fact, a fluid containing hot waters at varying temperatures from 50 to 300 °C and dissolved minerals from different sources converge. These characteristics of the solution may provide the different behavior of struvite precipitation.

Further, a chemical equilibrium model and phase characterization (qualitative and quantitative) and morphological analysis of precipitates was required to understand the mineral stability and transformation process involved in the complex hydrothermal systems. Additionally, the quantitative mineralogical characterization is required for an efficient quality control in an abundant variety of morphologies and purity of struvite crystal. These characterization results also provide important insights into the ways for crystal growth at diverse natural and laboratory conditions.

Original version

The present work was undertaken to examine crystallization of struvite and its phase transition from the aqueous media using a hydrothermal autoclave reactor. The induced MAP precipitation within the reactor was examined at an initial pH, dynamic temperature condition and cooling method to

room temperature. Experimental material characterization of crystal growth, the phase change and morphological development from the hydrothermal synthesis were performed by XRPD (X-ray powder diffraction) and SEM analysis. These findings are expected to provide an approach in designing novel struvite-based hydrothermal synthesis and the subsequent controlled homogeneous particle size.

Revised version

The struvite growth has been widely investigated in various mother solutions, for example, in the solution of artificial urine or in artificial wastewater [2, 5, 9]. However, no report is found in the literature on crystallization of struvite and subsequent decomposition in the hydrothermal solution. Principally, the hydrothermal solution containing hot waters with varying temperatures from 50 to 300 °C in which struvite and other phosphate-bearing minerals could be crystallized by supersaturation and inducing nucleation [4].

The present work was undertaken to examine crystallization of struvite and its phase transition from the aqueous media using a hydrothermal autoclave reactor. The induced MAP precipitation within the reactor containing the hydrothermal solution was examined at an initial pH, dynamic temperature condition and cooling method to room temperature. An effort to understand the struvite stability and its phase transition involved in the complex hydrothermal systems requires a chemical equilibrium model and material characterization (qualitative and quantitative) and morphological analysis of the precipitating product. Here, the experimental material characterization of crystal growth, the phase change and morphological development from the hydrothermal synthesis were performed by XRPD (X-ray powder diffraction) and SEM analysis. These findings are expected to provide an approach in designing novel struvite-based hydrothermal synthesis and the subsequent controlled homogeneous particle size.

Line 204–206: The authors described “*struvite was the major phase in the sample obtained at in the pH range of 7–8 and the temperature of 80 °C. However, at the same condition, the presence of dittmarite and newberyite were observed.*” This description is inconsistent with Table 2, which suggests no newberyite at the corresponding condition. At pH = 7, the sum of the wt% of dittmarite, struvite and sylvite becomes 100%. At pH = 8, the sum becomes 99.9%. Where is newberyite?

Response:

The statement in line 204-206 has been re-written. The sum of each phase composition had been re-calculated and adjusted accordingly. The reason for the absence of newberyite could be related to the concentration of magnesium ions and pH of the system [18]. The newberyite could be formed as a product of decomposition of struvite or directly precipitated in association with struvite. The formation of dittmarite crystals from the dissolution of struvite crystals mainly depends on the concentration of hydrogen ions during the hydrothermal reaction between the ionic species [9]. At pH 7 and 8, the condition may be still rich in ammonia and magnesium which is not favorable for newberyite formation.

[18] V. Babic-Ivancic, J. Kontrec, L. Brecevic, Formation and transformation of struvite and newberyite in aqueous solutions under conditions similar to physiological. *Urol Res* 32 (2004) 350–356.

[9] M.I.H. Bhuiyan, D.S. Mavinic, F.A. Koch, Thermal decomposition of struvite and its phase transition. *Chemosphere* 70 (2008) 1347–1356.

Original version

It is noticeable in Table 2 that struvite was the major phase in the sample obtained at in the pH range of 7-8 and the temperature of 80 °C. However, at the same condition, the presence of dittmarite and newberyite were observed.

Revised version

It is noticeable in Table 2 that struvite was the major phase in the sample obtained in the pH range of 7-8 and the temperature of 80 °C. However, at the same condition, the presence of dittmarite and newberyite were observed at pH of 9 and 10. The reason for the absence of newberyite in the pH 7 and 8 could be related to the concentration of magnesium ions and pH of the system [18]. In general, newberyite could be formed as a product of decomposition of struvite or directly precipitated in association with struvite. Conversely, dittmarite may be formed from the dissolution of struvite, of which the concentration of hydrogen ions controls the reaction between the ionic species [9]. In this case, the solution with a pH of 7 and 8 was proposed to be still rich in ammonia and magnesium, which is favorable for dittmarite formation rather than newberyite.

[9] M.I.H. Bhuiyan, D.S. Mavinic, F.A. Koch, Thermal decomposition of struvite and its phase transition. *Chemosphere* 70 (2008) 1347–1356.

Line 216–218: The authors described “As a consequence of increasing initial pH, the amount of dittmarite increased, suggesting a decomposition of the struvite product to dittmarite assisted by the pH solution and air-cooling of the hydrothermal reactor.” As the authors suggested, with temperature of 80 °C, the amount of struvite was significantly decreased from 58.4 wt% (pH = 8) to 10.4 wt% (at pH = 9). However, such notable decrease of struvite was not observed at 60 or 120 °C. The authors also said “no further change of phase composition in the sample” at 120 °C (Line 239). Why did the decomposition of struvite occur ONLY around 80 °C? It would be useful for readers to mention authors’ idea on that.

Response:

The line 216-218 has been revised to include this following reason.

It was reported previously that struvite decomposition in the excess water that occurred in the solid state was due to the loss of water and ammonium at the increasing temperatures (> 55 °C) [9]. At the temperature of 80 °C, heating of the mixtures undertaken in the sealed conditions yielded that most of ammonia, if not all, was transformed into NH₃ species resulting from dissolution. The rest of NH₄ concentration may form dittmarite. Correspondingly, dittmarite and newberyite may be formed from the struvite decomposition and would be found as the crystal product after cooling. With the hydrothermal condition at 120 °C, the orthophosphate activity made increasing in the excess water, implying that dittmarite other than struvite was present (Stumm and Morgan, 1970). Subsequently, dittmarite is more likely to be hydrated in the solution during air cooling, but not all being transformed to struvite in the course time of reaction.

Stum W and Morgan, J.J., 1970. *Aquatic chemistry*. Wiley-Interscience, New York, NY, p583.

Original version

As a consequence of increasing initial pH, the amount of dittmarite increased, suggesting a decomposition of the struvite product to dittmarite assisted by the pH solution and air-cooling of the hydrothermal reactor.

Revised version

As a consequence of increasing initial pH, the amount of dittmarite increased, suggesting a decomposition of the struvite product to dittmarite assisted by the pH solution and air-cooling of the hydrothermal reactor. It has been reported previously that a product of struvite transformation in

the presence of excess water, could be contributed by the loss of ammonium and water at the increasing temperatures ($> 55\text{ }^{\circ}\text{C}$) [9]. At the temperature of $80\text{ }^{\circ}\text{C}$, heating of the mixtures in the sealed conditions resulted in most of the ammonia, if not all, being transformed into NH_3 species. The simultaneous release of both NH_3 and H_2O molecules corresponded to the formation of dittmarite and newberyite, in which struvite could have decomposed in the solution with the pH of 9 and 10. They would subsequently be found as the crystal product after air-cooling.

With the hydrothermal condition at $120\text{ }^{\circ}\text{C}$, the orthophosphate activity appeared also increasing in the excess water, implying that dittmarite other than struvite was present [23] (Stumm and Morgan, 1970). Subsequently, dittmarite was slowly hydrated in the solution during air cooling, but not all being transformed to struvite in the course time of reaction. As discussed in the next section, however, dittmarite hydration could not be observed in the precipitate during the water-quenching. This shorter time duration may not allow dittmarite to transform to struvite.

[9] M.I.H. Bhuiyan, D.S. Mavinic, F.A. Koch, Thermal decomposition of struvite and its phase transition. *Chemosphere* 70 (2008) 1347–1356.

Line 264–266: The authors described “*the increase in temperature of the reactor system (from 80 to 120 °C), lead to struvite to transform into dittmarite soon afterward.*” This transformation seems very effective because most of all precipitates are dittmarite (see Table 3). On the other hand, with air-cooling, the major precipitates are struvite at temperatures of 80 and $120\text{ }^{\circ}\text{C}$ with $\text{pH} = 7\text{--}8$, suggesting that this transformation did not occur efficiently with air-cooling. Why this transformation occurred ONLY with water-quenching, and did not occur with air-cooling? If the transformation occurred before cooling, it ought to occur regardless of the cooling method. If the transformation occurred during cooling phases, the efficiency with air-cooling should be higher rather than that with water-quenching because of the longer cooling duration. The authors also said “*the subsequently dropped temperature in the system by water-quenching made a crystal growth of dittmarite being now the only process*” (Line 266–267). This explanation seems insufficient to answer the above question.

Response:

The line 264–266 has been revised to include this following information.

The possible transformation mechanisms of various phases associated with struvite have been reported by Bhuiyan et al. (2008) [9]. It has been suggested that struvite precipitation is based on both supersaturation and ammonia activity in the solution. It is assumed here that struvite decomposition occurs by increasing temperature and pH. In contrast, the possible returning structure of phase is related to rehydration during subsequent cooling. With gradually cooling from high temperature to room temperature, some ammonia molecules were still present in the solution, which leads dittmarite to transform into struvite in the sealed condition of hydrothermal solution. However, with quenching method, dittmarite has not enough time to return struvite. [9] M. Iqbal H. Bhuiyan , D.S. Mavinic, F.A. Koch, Thermal decomposition of struvite and its phase transition, Chemosphere 70 (2008) 1347–1356

Original version

Thus, the increase in temperature of the reactor system (from 80 to 120 °C), lead to struvite to transform into dittmarite soon afterward.

Revised version

Thus, the increase in temperature of the reactor system (from 80 to 120 OC), lead to struvite to transform into dittmarite soon afterward. The possible transformation mechanisms of various phases associated with struvite precipitation have been previously reported by Bhuiyan et al. [9] and suggested that struvite decomposition depended on both supersaturation and ammonia activity in the solution. When the reactor was heated from temperatures of 80 to 120 °C, some ammonia and water molecules were simultaneously released. At these temperatures, struvite was entirely transformed into dittmarite, but it was slowly hydrated in the hydrothermal solution during air cooling, where the resulting hydration product was struvite at room temperature. Conversely, the quenching method of the reactor did not allow dittmarite to return to struvite in the short time duration of the reaction.

[9] M. Iqbal H. Bhuiyan , D.S. Mavinic, F.A. Koch, Thermal decomposition

Line 284–285: The authors described “*there are optimum pH values for crystallization of bobbierite and brucite, with an optimum pH value be around 9.0–10 for both minerals.*” At this condition, SI values for bobbierite and brucite are greater than 0 and equal to 0, respectively

(see Fig 8a). This suggests that this aqueous solution is supersaturated at least for bobierrite. If so, why bobierrite was not detected in the hydrothermal experiment? The authors explained “*This was probably bobierrite and cattite, which were reported to have a low precipitation rate in the order of days*” (Line 349–351). However, I cannot judge whether this hypothesis is plausible or not because no reference was cited.

If possible, the authors should examine other experiments with hydrothermal reaction time longer than 24 h. The results will help to verify their hypothesis.

Response:

The statements in line 284-285 and line 349–351 have been amended accordingly. We had also conducted the experiments with longer reaction time than 24 h. However, bobierrite was still not formed at temperature of 120 °C hold for 96 h and subsequent air-cooling (Figure 9; Table 4).

The reason of the absence of bobierrite formed in the solution is due to the fact that it is well known as a slow forming mineral (Frazier et al., 1963), while AQION program does not account for the kinetic analysis of the possible mineral formation. It has been reported in the literature that struvite could decompose to the more stable octahydrate, bobierrite occurring in water of an open container or when struvite stands in water for a long time (about two months) (Frazier et al., 1963). The present result of a long time (96 h) for hydrothermal synthesis of struvite at the 120 °C confirmed that dittmarite was a still major crystalline phase (Figure 9; Table 4). In the solution with a pH of 7, struvite and dittmarite were still observed as a major phase, but with the increasing pH (8-10), struvite was totally replaced by dittmarite during heating at the temperature of 120 °C, while the more stable octahydrate, bobierrite was not detected. Longer reaction time and high temperature (> 100 °C) may be favorable for dittmarite formation.

Original version

It is noticed that there are optimum pH values for crystallization of bobierrite and brucite, with an optimum pH value be around 9.0-10 for both minerals. Within the scope of optimum pH value, the SI values turn on to be SI brucite < SI bobierrite.

Revised version

The statements in line 284-285 was added as follows;

It is noticed that there are optimum pH values for crystallization of bobierrite and brucite, with an optimum pH value be around 9.0-10 for both minerals. Within the scope of optimum pH value, the SI values turn on to be SI brucite < SI bobierrite. It should bear in mind that the AQION software program did not account for the kinetics of the possible mineral precipitation. In the present study, struvite would presumably precipitate in a short reactor residence time, whereas bobierrite would precipitate in the order of days or months (Celen et al., 2007; Frazier et al., 1963). Therefore, it was proposed that the slow-forming minerals (e.g., bobierrite) with having SI positive value might be not identified in the subsequent XRPD analysis.

Line 349–351; the statement was added in the following.

Further, this hypothesis for the lower precipitation rate of bobierrite may be supported by the experimental evidence of hydrothermal synthesis for longer reaction time. The present outcome of the hydrothermal synthesis for a long time (96 h) at the temperature of 120 °C and subsequent air cooling showed that the more stable octahydrate, bobierrite did not grow, while dittmarite was the major crystalline phase obtained in the solution with any pH condition (Figure 11; Table 4). In the solution with a pH of 7, struvite was partially transformed to dittmarite. However, with the increasing pH (8-10) at this temperature, struvite was totally replaced by dittmarite during heating. Obviously, the longer reaction time at high temperature (> 100 OC) has the significant effect on the change of struvite structure, in which there was a loss of five water molecules providing for struvite decomposition as dittmarite [9]. Subsequently, dittmarite was likely to be the more stable phase during long time heating, thereby, in turn, remains stable during air-cooling. Further research should be done in the synthesis of bobierrite with varying temperatures of the hydrothermal solution for the longer reaction time. This term may allow struvite to transform to bobierrite at the certain hydrothermal condition.

W. Frazier, J. R. Lehr, J P. Smith. The magnesium phosphates hannayite, schertelite and bobierrite. The American Mineralogist, Vol 4E, May-June, 1963.

I.Celen, John R. Buchanan, R.T. Burns, R. B. Robinsonc, D. R. Raman. Using a chemical equilibrium model to predict amendments required to precipitate phosphorus as struvite in liquid swine manure. Water Research 41 (2007) 1689-1696.

Line 291: The authors described “*The crystallization of struvite and newberyite is under equilibrium with $SI = 0$* ”. This description is correct only at pH = 7. At larger pH values, SI for newberyite is smaller than 0. The authors should specify the pH condition of the above description.

Response:

We agree with the reviewer. It is suggested from a previous research that the precipitation of both of struvite and newberyite can occur simultaneously and coexist under certain conditions. We had amended accordingly

Kontrec J, Babic-Ivancic V, Brecevic, L. Formation and Morphology of Struvite and Newberyite in Aqueous Solutions at 25 and 37 °C Coll. Antropol.. 29 (2005) 1: 289–294

Original version

The crystallization of struvite and newberyite is under equilibrium with $SI = 0$, while, bobierrite grew gradually under supersaturated solution, reaching the peak at pH 8.

Revised version

The crystallization of struvite and newberyite is below equilibrium with $SI = 0$ at pH 7 and tends to be undersaturation when pH value increased from 8 to 10. In contrast, bobierrite grew gradually under supersaturated solution, reaching the peak at pH 8. However, struvite and newberyite could precipitate simultaneously and coexist under certain pH conditions [9].

Line 294–295: The authors described “*In this case of increasing pH, the SI value of newberyite decreased, while the SI value of bobierrite increased accordingly.*” This description is inconsistent with Fig 8b regarding bobierrite. With a pH value ranging from 8 to 10, the SI value of bobierrite also decreased with the increase of pH.

Response:

We agree with reviewer. The statement has been corrected accordingly.

Original version

In this case of increasing pH, the SI value of newberyite decreased, while the SI value of bobierrite increased accordingly.

Revised version

In this case of increasing pH, the SI value of newberyite decreased, while the SI value of bobierrite decreased accordingly.

Line 303–304: The authors described “*The pH value in the hydrothermal synthesis should be adjusted to be within 8-9.*” However, I have no idea how this conclusion comes from the thermodynamic modeling results. For example, SI of bobierrite has peak at this pH range for all temperatures (Figs 8a–c), however, bobierrite has not been detected in any experimental conditions. With temperature of 60 °C and pH = 8, the solution is equilibrium with newberyite and under-saturated for brucite, but I have no idea why this condition is suitable for the hydrothermal synthesis. Many possibilities can be considered from Fig 8. The authors should describe the reason why the pH value of 8–9 is suitable for hydrothermal synthesis more clearly.

Response:

The statement is to explain that the pH control with the highest reduction in the orthophosphate (OP) concentration toward the optimized struvite precipitation by hydrothermal experiment. This paragraph has been added accordingly. The reason is that the model at pH 8 and 9 of the solution at any temperature (60, 80, and 120°C) provided the estimation for the high reduction in the OP concentration. Significant ammonia losses were also possibly found with increasing pH (8 and 9). Model simulations showed that increasing pH to 8 with magnesium induced into the hydrothermal solution made a reduction in the soluble phosphorus. Based on the observed Mg^{2+} reduction is likely that a MAP compound was formed.

Original version

The pH value in the hydrothermal synthesis should be adjusted to be within 8–9.

Revised version

The pH value in the hydrothermal synthesis should be adjusted to be within 8–9. Model simulations showed that increasing pH to 8 and 9 with the induced magnesium into the hydrothermal solution made the reduction in the soluble phosphorus. In this case, the pH 8 and 9 of the hydrothermal solution at any temperature (60, 80, and 120°C) were estimated for the condition with the highest reduction in the orthophosphate (OP) concentration. Moreover, the significant ammonia losses were also shown with increasing pH (8 and 9). Based on the observed MAP ion reduction, it is more likely that a high amount MAP compound could be formed as struvite or dittmarite in the solution within a pH of 8 and 9.

Line 309–311: The authors described “*With the pH value ranging from 7.0 to 9.0 and the temperature of 60 °C, the Mg^{2+} and PO^{3-}_4 declined sharply (Fig 9a).*” This description is inconsistent with Fig 9a regarding PO^{3-}_4 . The total concentration of PO_4 is decreased slightly (not sharply!) with the increase of pH from 7 to 8, but increased slightly with the increase of pH from 8 to 9. The concentration of PO^{3-}_4 may be different from that of PO_4 , but there is no information on that in Fig 9a.

Response:

We agree with the reviewer. The statement has been rewritten accordingly. We had added in the figure 9 MAP ions is presented as MAP (Mg^{2+} , NH_4^+ and PO^{3-}_4) ions

Original version

With the pH value ranging from 7.0 to 9.0 and the temperature of 60 °C, the Mg^{2+} and PO^{3-}_4 declined sharply (Fig 9a).

Revised version

With the pH value ranging from 7.0 to 9.0 and the temperature of 60 °C, the Mg^{2+} and PO^{3-}_4 declined slightly (Fig 9a).

Line 312–313: The authors described “*With the increase in pH from 8 to 10,*”. Is this typo of “*pH from 9 to 10*”? The Mg^{2+} concentration does not seem stagnant at $\text{pH} = 8$ (see Fig 9a).

Response:

We agree with the reviewer. The statement has been rewritten accordingly.

Original version

With the increase in pH from 8 to 10, the reaction products of NH_4^+ and PO_4^{3-} was not so high, while the Mg^{2+} concentration remained stagnant.

Revised version

With the increase in pH from 8 to 10, the reaction products of NH_4^+ and PO_4^{3-} was not so high, while the Mg^{2+} concentration reduced gradually.

Line 325–326: The authors described “*Across the pH range (7–10) and temperature (80 and 120 °C) and time (24 h) examined, the model predicted Mg^{2+} and PO_4^{3-} to be most reactive ions, followed by NH_4^+ (Figs 9b,c).*” However, I have no idea how we can reach this conclusion from Figs 9b and c. Why this conclusion was not applied for temperature of 60 °C? I think that the concentration profile is not so different between temperatures of 60, 80, and 120 °C.

Response:

We agree with the reviewer. The statement has been rewritten by including temperature of 60 °C accordingly

Original version

Across the pH range (7-10) and temperature (80 and 120 °C) and time (24 h) examined, the model predicted Mg^{2+} and PO_4^{3-} to be most reactive ions, followed by NH_4^+ (Figs 9b,c).

Revised version

Across the pH range (7-10) and temperature (60, 80 and 120 °C) and time (24 h) examined, the model predicted Mg^{2+} and PO_4^{3-} to be most reactive ions, followed by NH_4^+ (Figs 9b,c).

Line 334–335: The authors described “*the experimental results were in close agreement with the predictions of the thermodynamic model.*” I have no idea how the authors reached this

conclusion. For example, with temperature of 80 °C and subsequent air-cooling, newberyite was detected at pH = 9–10 (see Table 2). However, SI of newberyite at this condition is less than 0 (see Fig 9b). Precipitation of newberyite from UNDER-saturated solution seems thermodynamically inconsistent. The authors mentioned the possibility “*struvite can decompose to newberyite at room temperature of 20 °C [15, 16].*” If so, why the same decomposition did not occur at temperatures of 60 and 120 °C, in which no newberyite was detected? I will give another example. At temperatures of 80 and 120 °C, dittmarite was the major phase under both of air-cooling and water-quenching (Tables 2 and 3). However, SI of dittmarite is not available (see Line 276–277). This indicates that we cannot mention the consistency between experiments and thermodynamic modeling at these conditions. In my opinion, the above conclusion was not based on the experimental results.

Response:

We agree with the reviewer. The statement has been rewritten accordingly. So far, no solubility data of dittmarite has been reported in the literature. Correspondingly dittmarite was not included in the AQION model. When it contacts with the excess water, however, dittmarite could be rehydrated into struvite before dissolution (Bhuiyan et al., 2008) and it would obey struvite solubility closely.

Bhuiyan, M.I.H., D.S. Mavinic, and F.A. Koch. 2008. Thermal decomposition of struvite and its phase transition. Chemosphere 70:1347–1356.

Original version

The thermodynamic modeling of MAP precipitation in the hydrothermal experiments on various pH value and temperature has been verified, providing that the experimental results were in close agreement with the predictions of the thermodynamic model.

Revised version

The thermodynamic modeling of MAP precipitation in the hydrothermal experiments on various pH value and temperatures has been verified, providing that the experimental results were in close agreement with the predictions of the thermodynamic model except for pH of 9 and 10 at the temperature of 80 OC. Although newberyite was modeled to be undersaturated with struvite, it was identified by XRPD method. This is because the gradual loss of ammonium during heating made a low activity of ammonium in the solution, of which struvite became a metastable phase and was likely to transform to newberyite during heating of the reactor (Kontrec et al., 2005).

Further, at temperatures of 80 and 120 °C, dittmarite was the major phase under both of air-cooling and water-quenching (Tables 2 and 3), though it was not modeled in the AQION program. **Up to**

now, no solubility data of dittmarite has been described in the literature. However, it was proposed that dittmarite could be hydrated in the excess water and then formed into struvite before dissolution (Bhuiyan et al., 2008). Thus its solubility would obey close struvite solubility.

Line 335–336: The authors described “*The optimum pH range for MAP precipitation was 9.0–10.0.*” This description seems inconsistent with the description “*the appropriate pH value should be controlled to be between 8.0–9.0 during MAP crystallization under hydrothermal reaction*” (Line 329–330).

Response:

We agree with the reviewer. The statement has been rewritten accordingly

Original version

The optimum pH range for MAP precipitation was 9.0-10.0.

Revised version

Established along the model of OP reduction in the solution, the optimum pH range for MAP precipitation was 8.0-9.0. However, the XRPD analysis verified that the cooling method has significantly influenced on the struvite decomposition rather than the pH control.

Fig 10: This figure is quite misleading. For example, in the case of 120 °C, struvite and dittmarite are displayed on the air-cooling path, and dittmarite is displayed on the water-quenching path. Does this suggest that these minerals crystallize during cooling phases? What does the arrow mean? The struvite and dittmarite crystallized in air-cooling transform to dittmarite in water-quenching? (it does not make sense!) In addition, in the case of 80 °C, the minerals are displayed at temperature higher than the cases of 60 and 120 °C. Does this suggest that the crystallization temperature for the 80 °C case is higher than other cases?

Response:

We proposed here that the cooling method plays an important role in the struvite precipitation process. A literature review was conducted on each of these minerals to determine the likelihood of formation in a short period of time and subsequent mineral stabilities achieved after cooling of the

reactor (Bhuiyan et al., 2008; Kontrec et al., 2005). The loss of water and ammonium at the increasing temperature in the closed condition are important factors for struvite decomposition, while cooling method may be related to the rehydration of struvite structure in which it may take time. The arrow means the tendency of mineral formation or decomposition. The paragraphs have been added accordingly. During cooling, the precipitation or decomposition of struvite may occur.

Revised version

The cooling mode of the hydrothermal reactor has a substantial role in the performances of struvite production. A literature review had been carried on each of the phosphate minerals to determine the likelihood of formation in a period of time and subsequent mineral stabilities achieved after cooling of the reactor (Bhuiyan et al., 2008; Kontrec et al., 2005). It has been demonstrated that struvite, newberyite, and dittmarite can be precipitated in the short period of time, while bobierrite and cattite could be formed at longer time duration of the reaction. With the chemical equilibrium model in the AQION program, the precipitation of those minerals is possible. Despite the possibility of struvite formation in the different condition, the model could predict its formation more successfully for an increasing pH and temperatures. However, the precipitation kinetics of all minerals were not counted in the AQION program. Therefore, the model simulations provided underprediction for the potential of bobierrite precipitated in the hydrothermal solution as can be seen in Fig. 8a-c.

Furthermore, the loss of water and ammonium at the increasing temperature and pH in the sealed condition are important factors for struvite decomposition, while the cooling method may contribute to the rehydration of struvite structure (Montes et al., 2009). It was shown that the general trend of struvite formation or its phase decomposition during cooling is signified by an arrow. Presumably, the transformation of dittmarite to struvite could have resulted from the slow hydration in the solution. Here struvite was the major phase obtained from the air-cooling. With the quenching method, however, the major phase obtained was dittmarite.

F. Montes, C.A. Rotz, H. Chaoui, Process modeling of ammonia volatilization from ammonium solution and manure surfaces: a review with recommended models, *Trans. ASABE* 52 (2009) 1707–1719.

