

# Removal of aqueous ammonium with magnesium phosphates obtained from the ammonium-elimination of magnesium ammonium phosphate

Shigeru Sugiyama<sup>a,\*</sup>, Masahiko Yokoyama<sup>a</sup>, Hisaaki Ishizuka<sup>a</sup>, Ken-Ichiro Sotowa<sup>a</sup>,  
Tahei Tomida<sup>a</sup>, Naoya Shigemoto<sup>b</sup>

<sup>a</sup> Department of Chemical Science and Technology, Faculty of Engineering, The University of Tokushima, Minamijosanjima,  
Tokushima 770-8506, Japan

<sup>b</sup> Shikoku Research Institute Inc., Yashima-nishi, Takamatsu 761-0192, Japan

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## Abstract

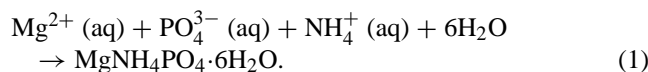
In order to recycle magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ : MAP) obtained from MAP process, which is one of the attractive processes for removal of aqueous ammonium and phosphate from wastewater, ammonium elimination from MAP to magnesium phosphates and ammonium incorporation into the magnesium phosphates have been investigated in the present study. It is confirmed that magnesium hydrogen phosphate ( $\text{MgHPO}_4$ ) is favorably obtained from the ammonium elimination from MAP at temperatures greater than 353 K, although magnesium phosphate ( $\text{Mg}_3(\text{PO}_4)_2$ ) and magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ) have been suggested as possible candidates. Based on the dissolution–precipitation mechanism for the removal of aqueous ammonium with magnesium phosphates, three magnesium phosphates were employed for the removal of aqueous ammonium. The order of the removal rate of the aqueous ammonium was  $\text{MgHPO}_4 > \text{Mg}_3(\text{PO}_4)_2 > \text{Mg}_2\text{P}_2\text{O}_7$ , as expected from the solubility of those magnesium phosphates. The removability of the solid obtained from ammonium elimination of MAP is also confirmed. The present results show that MAP can be employed as an advanced material for the removal/recovery of ammonium, although it is generally accepted that an excess of MAP obtained from the wastewater treatment can be only used as a slow-acting fertilizer.

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**Keywords:** Recycle; Aqueous ammonium; MAP; Magnesium phosphates; Removal/recovery process

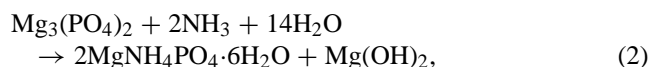
## 1. Introduction

As one of the attractive processes for the removal of phosphate and ammonium from wastewater, the MAP process has been received attention [1–5]:



Since magnesium ammonium phosphate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ : MAP) is hardly soluble, aqueous phosphate and ammonium, both of which cause eutrophication, can be efficiently separated from wastewater. A plant on commercial

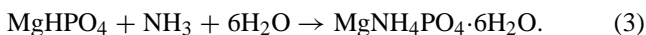
scale is now in operation in Fukuoka, Japan, partly due to the employment of MAP as a slow-acting fertilizer [6]. However, another utilization of MAP should be developed since an excess amount of MAP is continuously precipitated from the process. Stefanowicz et al. [7] and Inoue and Hayashi [8] showed that aqueous ammonium can easily be immobilized with the solid obtained from ammonium elimination of MAP to regenerate MAP, indicating that MAP may be used as a recycling material for the removal–recovery of ammonium. It should be noted that  $\text{Mg}_3(\text{PO}_4)_2$  was suggested as the solid obtained from ammonium elimination of MAP by the former group,



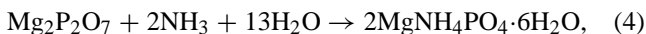
\* Corresponding author. Fax: +81 655 7025.

E-mail address: [sugiyama@chem.tokushima-u.ac.jp](mailto:sugiyama@chem.tokushima-u.ac.jp) (S. Sugiyama).

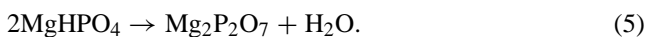
while  $\text{MgHPO}_4$  was suggested by the latter groups without any experimental evidences:



Magnesium pyrophosphate ( $\text{Mg}_2\text{P}_2\text{O}_7$ ) may be also one of the candidates,



since  $\text{Mg}_2\text{P}_2\text{O}_7$  can easily be obtained from the dehydration of  $\text{MgHPO}_4$ ,



In the present study, ammonium elimination from MAP to magnesium phosphates together with ammonium incorporation into the magnesium phosphates to MAP has been investigated to afford information on the recycling of MAP for the removal–recovery of ammonium.

## 2. Experimental

All the chemicals were purchased from Wako Pure Chemicals, Osaka, Japan and used as supplied. Standard solutions for inductively coupled plasma analysis (ICP; Seiko SPS 1500) were obtained from Kanto Kagaku, Tokyo, Japan. The preparation procedure of MAP was essentially identical to that reported previously [9]. Into aqueous solution (100 ml) containing  $\text{NH}_4^+$  (50.2 mmol/L) and  $\text{PO}_4^{3-}$  (46.0 mmol/L) as  $\text{NH}_4\text{Cl}$  and  $\text{H}_3\text{PO}_4$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (1.127 g, 5.55 mmol) was added and stirred at 298 K and pH 10 for 0.5 h. The XRD pattern of the solid thus obtained was matched with the reference date for  $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$  (JCPDS 15-0762). Powder X-ray diffraction (XRD) was recorded with a Rigaku RINT2500X using monochromatized  $\text{CuK}\alpha$  radiation at 40 kV and 100 mA. Particle size of each phosphate was measured in ethanol solution by a laser diffraction/dispersion method (Microtrac FRA, Niliso, Tokyo). Commercially available MAP (hexahydrate) was also employed in the present study. In order to examine ammonium elimination from MAP, commercially available MAP was calcined for 3 h at various temperatures and the solids recovered were analyzed with XRD. Since amorphous phases were detected from some solid samples with XRD, solid state  $^{31}\text{P}$  magic angle spinning nuclear magnetic resonance ( $^{31}\text{P}$  MAS NMR) was also employed (Bruker AVANCE DSX300) with an external reference of  $(\text{NH}_4)_2\text{HPO}_4$  at 1.33 ppm and a spinning rate of 7 kHz. Differential thermal analysis–thermogravimetric analysis (DTA–TGA) of MAP was performed with a thermal analyzer (Rigaku TAS-100). The ammonium incorporation into magnesium phosphates, that is, the removal of aqueous ammonium with magnesium phosphates, was examined as follows. Aqueous solution (100 ml) containing  $\text{NH}_4^+$  (8.15 mmol) as  $\text{NH}_4\text{Cl}$  together with NaOH for adjustment of initial pH was introduced into an automatic titrator (Metrohm-Shibata 718 STAT Titrino). The solution was

stirred for 20 min at 298 K. Then  $\text{Mg}_3(\text{PO}_4)_2$  (4.08 mmol, particle size 10.7  $\mu\text{m}$ ),  $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$  (8.15 mmol, particle size 150  $\mu\text{m}$ ),  $\text{Mg}_2\text{P}_2\text{O}_7$  (4.08 mmol, particle size 16.9  $\mu\text{m}$ ), or magnesium phosphates obtained from ammonia elimination of both commercial and synthesized MAP (8.15 mmol, particle size 17.0 and 21.0  $\mu\text{m}$ , respectively) was added into the solution stirred at 298 K. It should be noted that atomic ratio of N/P in the aqueous solution was adjusted to be unity. Therefore the amount of those magnesium phosphates was adjusted to be the same molar number regarding P. During the ammonium incorporation into magnesium phosphates, the solution pH and the reaction temperature were controlled to be constant. After a specified period of time, the solution was filtered and the filtrate was analyzed with ICP for  $\text{Mg}^{2+}$  and  $\text{PO}_4^{3-}$  and ion chromatography for  $\text{NH}_4^+$  (Shimadzu PIA-1000). The removal rate of  $\text{NH}_4^+$  was calculated from the concentration before and after the removal experiment ( $C_{\text{before}}$  and  $C_{\text{after}}$ , respectively), as follows:

$$\text{removal rate (\%)} = 100 \times (1 - C_{\text{after}}/C_{\text{before}}). \quad (6)$$

The solids recovered after the filtration were analyzed with XRD.

## 3. Results and discussion

### 3.1. Ammonium elimination from MAP

In order to recycle MAP for the removal/recovery process of aqueous ammonium, it is evident that the solid obtained from ammonium elimination of MAP should be characterized. However, the formation of  $\text{Mg}_3(\text{PO}_4)_2$  and  $\text{MgHPO}_4$  from the ammonium elimination was suggested from two research groups without any experimental evidence [7,8]. Based on the reverse reactions described in Eqs. (2)–(4), which corresponded to the ammonium elimination from MAP, the candidates for the solid are suggested to be  $\text{MgHPO}_4$  and  $\text{Mg}_2\text{P}_2\text{O}_7$ . The formation of  $\text{Mg}_3(\text{PO}_4)_2$  from MAP itself is essentially impossible, as shown in Eq. (2), while the stoichiometric addition of  $\text{Mg}(\text{OH})_2$  to MAP resulted in the easy formation of  $\text{Mg}_3(\text{PO}_4)_2$  after the calcination at 473 K as shown in Fig. 1. It should be noted that continuous addition of  $\text{Mg}(\text{OH})_2$  is needed for the recycle removal/recovery system for ammonium if  $\text{Mg}_3(\text{PO}_4)_2$  is employed as one of the candidates. Fig. 2 shows DTA–TGA curves obtained from the decomposition of commercially available MAP. Decrease of the weight corresponded to the elimination of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  from MAP to  $\text{MgHPO}_4$  observed at a temperature of approximately 500 K. The employment of a decomposition temperature higher than 500 K appears to result in the dehydration of  $\text{MgHPO}_4$  to  $\text{Mg}_2\text{P}_2\text{O}_7$  described in Eq. (5). In order to characterize the solid after the decomposition, the solids were calcined at 373–1073 K for 3 h to be analyzed with XRD (Fig. 3). The decomposition at 373 and 423 K resulted in the dehydration from hexahydrate to monohydrate ( $\text{MgNH}_4\text{PO}_4 \cdot \text{H}_2\text{O}$ ,

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