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Employment of ^{31}P MAS NMR for the Identification of Amorphous Precipitation Products Obtained from the MAP Process

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In order to recover aqueous ammonium (NH_4^+) and phosphate (PO_4^{3-}) from wastewater, these ions were immobilized with MgO and $MgCl_2$ into an insoluble solid. Analysis by X-ray diffraction (XRD) showed that the insoluble solid was a single phase of ammonium magnesium phosphate ($Mg(NH_4)PO_4 \cdot 6H_2O$: MAP). Therefore, the present process has been commonly known as the MAP process. However, analysis by the solid-state ^{31}P magic-angle spinning nuclear magnetic resonance (^{31}P MAS NMR) of the insoluble solid revealed that the solid contained various phosphate compounds together with crystalline MAP. The results indicated that the solids obtained from the MAP process should be carefully identified, since they are considered to be utilized as a slow-acting fertilizer.

Since aqueous phosphate and ammonia cause a significant nutrient load on wastewater treatment processes, various procedures for the removal of these compounds have been suggested. For the removal of these aqueous ions, the MAP process, which is based on the typical quantitative analytical procedure of PO_4^{3-}, has been suggested.[1] In the MAP process using MgO or $MgCl_2$ as an immobilization reagent, both of the aqueous phosphate and ammonium ions can be simultaneously removed from the aqueous solution. In the process, those ions were immobilized as insoluble ammonium magnesium phosphate ($Mg(NH_4)PO_4 \cdot 6H_2O$: MAP or struvite) through the following dissolution–precipitation mechanism:

(1) Dissolution process: Eq. 1 for MgO and Eq. 2 for $MgCl_2$

$$MgO(solid) + H_2O \rightarrow Mg^{2+}(aq) + 2OH^-(aq), \qquad (1)$$

$$MgCl_2(solid) \rightarrow Mg^{2+}(aq) + 2Cl^-(aq). \qquad (2)$$

(2) Precipitation process both for MgO and $MgCl_2$

$$Mg^{2+}(aq) + PO_4^{3-}(aq) + NH_4^+(aq) + 6H_2O \rightarrow Mg(NH_4)PO_4 \cdot 6H_2O. \qquad (3)$$

The present process has received attractive attention and is now being extensively examined by various researchers in wide fields, such as chemistry,[2–4] civil engineering,[5] environmental engineering,[6–8] and so on.[9,10] On a commercial scale, a plant in which 25000 kL/day of wastewater containing 100 and 250 mg L^{-1} of aqueous phosphate is treated to remove 80 and 70% of the phosphate, respectively, is now in operation in Fukuoka, Japan.[11] Most researches have focused on the removal of aqueous phosphate and ammonia, based on environmental perspectives. However, it should be noted that a great amount of MAP is produced from the present process. The proposed utilization of the precipitation product obtained from this process is in the form of a slow-acting fertilizer.[12] Unfortunately, adequate identification of the precipitation product has not yet been carried out. X-ray diffraction (XRD) and the quantitative analyses have generally been employed for identifying the precipitation product. However, XRD does not provide any structural information about the amorphous product. The contamination of phosphate compounds rather than MAP is possible in products obtained from the MAP process. Indeed, it has already been reported that MgO extensively removes aqueous phosphate to afford $Ca_3(PO_4)_2$.[13] Since the applicability of the precipitation product as a fertilizer depends on the extent of contamination of the phosphates, the product should be carefully identified with other detectable procedures for the amorphous product. In the present paper, the precipitation product obtained from the MAP process was measured by XRD and ^{31}P magic-angle spinning nuclear magnetic resonance (^{31}P MAS NMR) to obtain structural information on the crystalline and amorphous products. In order to obtain a certain amount of the precipitation product required for a structural analysis, an aqueous solution containing rather greater concentrations of PO_4^{3-} and NH_4^+ was taken as model wastewater in the present study. Since the removal behaviors of PO_4^{3-} and NH_4^+ with magnesium compounds have been extensively studied, the removal behaviors with MgO and $MgCl_2$ are not deeply discussed in this paper. However, for identifying the source of the precipitation product, the removal behaviors of aqueous PO_4^{3-} and NH_4^+ using MgO and $MgCl_2$ were also investigated with and without a pH-adjustment. It should be noted that acidic conditions together with basic conditions, the latter of which were admitted as suitable conditions for the MAP process, are employed in the present study in order to obtain solids precipitated under various reaction conditions.

Experimental

All of the required chemicals were purchased from Wako Pure

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Chemicals, Osaka and were used as supplied. Standard solutions for inductively coupled plasma (ICP) measurements were obtained from Kanto Kagaku, Tokyo. An aqueous solution (100 mL) containing a known quantity of NH_4^+ and PO_4^{3-} as NH_4Cl and H_3PO_4, together with a 5 mol L^{-1} NaOH solution for adjusting the pH in the initial solution, was introduced into a 200 mL Erlenmeyer flask with a stopper. The flask was shaken at 120 rpm in a constant temperature bath at 298 K for 20 min. Then, a known quantity of MgO or $MgCl_2 \cdot 6H_2O$ was added to the solution. After a specified period, the solution was filtered and analyzed by ICP (Seiko SPS1500). The concentration of NH_4^+ was analyzed using absorptiometry (Shimadzu UV-2500PC) with indophenol.[14] The solution pH was monitored with a pH meter (Horiba F-22). The removal rate of NH_4^+ and PO_4^{3-} was calculated from the corresponding concentrations before and after immobilization (C_{before} and C_{after}, respectively), as follows:

$$\text{Removal rate (\%)} = 100 \times (1 - C_{\mathrm{after}}/C_{\mathrm{before}}). \tag{4}$$

When the solution pH was adjusted to be a constant value during immobilization, the solution (100 mL) containing NH_4^+ and PO_4^{3-} together with NaOH for adjusting the initial pH was introduced into an automatic titrator (Metrohm-Shibata 718 STAT Titrino). The other procedures were the same as those described above. With this titrator, in which the solution was stirred, but not shaken, the solution can be adjusted to the desired pH within 1 min after the start of immobilization. In the present work, the pH value after 1 min was employed as the pH of the solution. In the titrator, the pH was controlled with 1 mol L^{-1} HCl for immobilization with MgO or 1 mol L^{-1} NaOH for that with $MgCl_2$. The surface areas were calculated from adsorption isotherms obtained with a conventional BET nitrogen adsorption apparatus (Shibata P-700). Scanning electron microscopy (SEM) was measured with a JXA-840A electron probe microanalyzer (JEOL, Tokyo). Powder X-ray diffraction (XRD) patterns of solids dried at 333 K overnight were recorded with a Rigaku RINT2500X using monochromatized Cu Kα radiation at 40 kV and 100 mA. Solid-state ^{31}P magic-angle spinning nuclear magnetic resonance (MAS NMR) was obtained with a Bruker AVANCE DSX300wbs, with an internal reference of $(NH_4)_2HPO_4$ at 1.33 ppm at room temperature and a spinning rate of 7 kHz.

Results and Discussion

Employment of MgO with and without a pH Adjustment during Immobilization. Although it has been known that the formation of MAP proceeds favorably under basic conditions,[15] there are rather few reports that compare the efficiency with and without adjusting the pH of the solution during immobilization. Furthermore, in using MgO as an immobilization reagent, additional effects of the pH on immobilization should be considered, since acidic conditions are suitable for the dissolution of magnesia. Table 1 gives the results of immobilization for 0.5 and 1.0 h using MgO (0.223 g, 5.54 mmol) from a solution (100 mL) containing NH_4^+ (49.2 mmol L^{-1}) and PO_4^{3-} (51.6 mmol L^{-1}) at 298 K and initial pH values of 4.9, 6.8, and 8.8. It should be noted that only the initial pH was adjusted while the pH was not controlled during immobilization. In the case of pH 8.8, which is the typical pH condition generally employed in the MAP process, both NH_4^+ and PO_4^{3-} were removed from the solution during the initial 0.5 h by 17.3 and 19.4%, respectively. Under those conditions, the immobilization for 1.0 h resulted in removal rates of 23.5 and 26.9% for NH_4^+ and PO_4^{3-}, respectively. The solution pH gradually increased from 8.8 to 9.9 during a 4.0 h period due to the formation of basic compounds, such as $Mg(OH)_2$. After a duration of 4.0 h, removal rates of 38 and 35% for NH_4^+ and PO_4^{3-} were observed, respectively (not shown in the Table). Since more acidic conditions were thought to favor the dissolution of MgO, immobilizations at pH 4.9 and 6.8 were examined. It is of interest to note that, at pH values of 4.9 and 6.8, the removals of both NH_4^+ and PO_4^{3-} together with the solution pH were essentially constant after 0.5 and 1.0 h of immobilization, respectively, indicating completion of the immobilization process at 0.5 h. The immobilization conditions at the initial solution pH of 4.9 are unfavorable for the precipitation of MAP, but favorable for the formation of compounds not containing NH_4^+, such as magnesium hydrogenphosphate. Therefore, the removal rate for PO_4^{3-} (32.3%) at 0.5 h was evidently greater than that for NH_4^+ (23.1%). As shown in Table 2, it is interesting to note that both ammonium and phosphate ions were not immobilized when the solution pH was kept constant at 5.0 during immobilization, but other conditions were the same as those in Table 1. Table 2 indicates that MAP was not precipitated at all under the acidic conditions. The maintenance of a constant solution pH of 7.0 and 9.0 during immobilization (Table 2) resulted in greater removal rates of both NH_4^+ and PO_4^{3-}, as compared to the case adjusting only the initial pH (Table 1). The shifting of the pH to basic conditions, as shown in Table 1, hinders the dissolution of MgO, followed by a decrease of the removal rate. Therefore, the removal rate given in Table 2 is greater than that in Table 1. Based on the dissolution–precipitation mechanism, it seems to be possible that the surface of MgO dissolves first,

Table 1. Effects of the Initial Solution pH on the Removal Rate (%) and the Resulting pH after Immobilization of Aqueous NH_4^+ and PO_4^{3-} with MgO at 298 K[a)]

	Immobilization time					
Initial	0.5 h			1.0 h		
pH	NH_4^+	PO_4^{3-}	pH	NH_4^+	PO_4^{3-}	pH
4.9	23.1	32.3	6.3	33.9	38.6	6.4
6.8	37.3	36.4	7.8	36.3	37.4	7.8
8.8	17.3	19.4	9.4	23.5	26.9	9.6

a) Immobilization conditions: MgO (5.54 mmol), NH_4Cl (4.92 mmol), and H_3PO_4 (5.16 mmol) in 100 mL solution.

Table 2. Effects of Solution pH, which was Controlled for Keeping Constant, on the Removal Rate (%) after Immobilization of Aqueous NH_4^+ and PO_4^{3-} with MgO at 298 K[a)]

	Immobilization time			
	0.5 h		1.0 h	
pH	NH_4^+	PO_4^{3-}	NH_4^+	PO_4^{3-}
5.0	0	0	0	0
7.0	44.6	46.6	47.7	47.2
9.0	26.0	22.8	31.2	27.3

a) Immobilization conditions: MgO (5.54 mmol), NH_4Cl (5.31 mmol), and H_3PO_4 (5.40 mmol) in 100 mL solution.

followed by the precipitation of MAP on the surface of the oxide. It is possible that the formation of MAP on the surface disturbs the additional dissolution of MgO. Therefore, it can be expected that the immobilization proceeds further when MAP is removed from the surface of the recovered solid. In order to confirm the effect of MAP precipitated on the surface of MgO, the solid employed in obtaining the results shown in Table 2 at pH 7.0 was finely ground, and then added into a 100 mL solution of the initial concentration of NH_4Cl (2.84 mmol) and H_3PO_4 (3.06 mmol). The removal rates for NH_4^+ and PO_4^{3-} reached to 52.6 and 34.0%, respectively, after 1 h of immobilization. It should be noted that, in employing the recovered solid without grinding, the rates were 13.2 and 5.5%, respectively, under identical conditions. Therefore, it is evident that the precipitation of MAP on the surface of MgO disturbs the immobilization. In order to check the influence of the surface area on the removal rate before and after grinding, MgO, which was previously ground for 30 min, was employed for immobilization. The surface areas of MgO before and after grinding were essentially identical, i.e. 4.1 and 4.3 $m^2 g^{-1}$, respectively. The removal rates of PO_4^{3-} and NH_4^+ with the non-ground MgO after 3.0 h of immobilization agreed roughly with those with the ground MgO within a 10% deviation under the conditions employed in Table 2, but at pH 7.0. The present results reveal that the effect of grinding the immobilization reagent on the surface area did not directly contribute to an enhancement of the removal rate to 52.6 and 34.0% of NH_4^+ and PO_4^{3-}, respectively, as described above. In order to re-confirm the dissolution–precipitation mechanism, SEM analyses of the solids before and after immobilization with MgO were carried out. As shown in Fig. 1A, before immobilization, an irregular surface on MgO was detected by SEM. However, a regular surface was detected on the solid after immobilization with MgO at pH = 7 for 4.0 h due to dissolution of the irregular MgO surface, followed by the precipitation of fine MAP particles over the surface (Fig. 1B). Therefore, immobilization proceeds through a dissolution–precipitation mechanism.

Employment of $MgCl_2$ with and without a pH Adjustment during Immobilization. It can be generally expected that the employment of $MgCl_2$ for MgO as an immobilization reagent is preferable due to the higher solubility of the chloride than that of the oxide. Table 3 gives the removal rates for NH_4^+ and PO_4^{3-} after 0.5 h with $MgCl_2 \cdot 6H_2O$ (1.127 g, 5.55 mmol) from a solution (100 mL) containing NH_4^+ (50.2 mmol L^{-1}) and PO_4^{3-} (46.0 mmol L^{-1}) at 298 K and various initial pH values. In Table 3, data both with and without pH-control during immobilization are described. Since the basic conditions are suitable for the precipitation of MAP, immobilization was observed in the basic solutions. Without any pH control during immobilization, the solution pH shifted to acidic conditions regardless of the initial solution pH. When the initial solution pH was only adjusted at 8.1 and 9.0, the removal rates of PO_4^{3-} were evidently greater than those of NH_4^+ (Table 3). At the same time, the pH values shifted to 6.0 and 6.2, respectively (Table 3). Under weak acidic conditions, $MgHPO_4$ is favorably formed through the immobilization of PO_4^{3-} with Mg^{2+}, while the immobilization of NH_4^+ with Mg^{2+} is rather suppressed.[15] Therefore, the removal rates for PO_4^{3-} were evidently greater than those of NH_4^+ at the initial pH of 8.1 and 9.0 (Table 3). In adjusting the initial pH only at 11.3 and 12.1, greater removal rates for PO_4^{3-} compared to those for NH_4^+ were again observed (Table 3), since formation of $Mg_3(PO_4)_2$ instead of MAP is possible under stronger basic conditions.[15] Maintaining of the initial pH alone at 10.1 produced an approximately 1:1 immobilization of NH_4^+ and PO_4^{3-} from the solution, indicating that the present conditions are very desirable for the MAP process without pH-control during immobilization. When the solution pH was controlled to be a constant

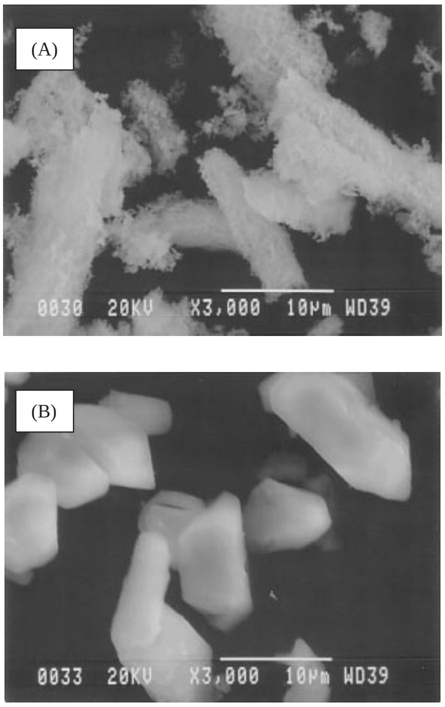

Fig. 1. SEM results obtained from MgO (A) and the solid previously employed for the results shown in Table 2 at pH = 7, but after 4.0 h immobilization (B).

Table 3. Effects of Initial Solution pH on the Removal Rate (%) and the Resulting pH after Immobilization of Aqueous NH_4^+ and PO_4^{3-} for 0.5 h with $MgCl_2$ at 298 K

Initial pH[a)]														
8.1 (8.1)			9.0 (9.0)			10.1 (9.9)			11.3 (10.9)			12.1 (11.9)		
NH_4^+	PO_4^{3-}	pH	NH_4^+	PO_4^{3-}	pH	NH_4^+	PO_4^{3-}	pH	NH_4^+	PO_4^{3-}	pH	NH_4^+	PO_4^{3-}	pH
22.3	42.5	6.0	42.7	55.0	6.2	77.3	84.2	6.7	56.4	94.2	10.5	68.9	99.5	11.7
(81.9	98.5	—)	(85.8	99.5	—)	(95.2	99.9	—)	(80.3	85.6	—)	(50.2	87.2	—)

a) Values without parenthesis indicate the results when only the initial pH was adjusted. Values in parenthesis indicate the results when pH was kept constant during immobilization.

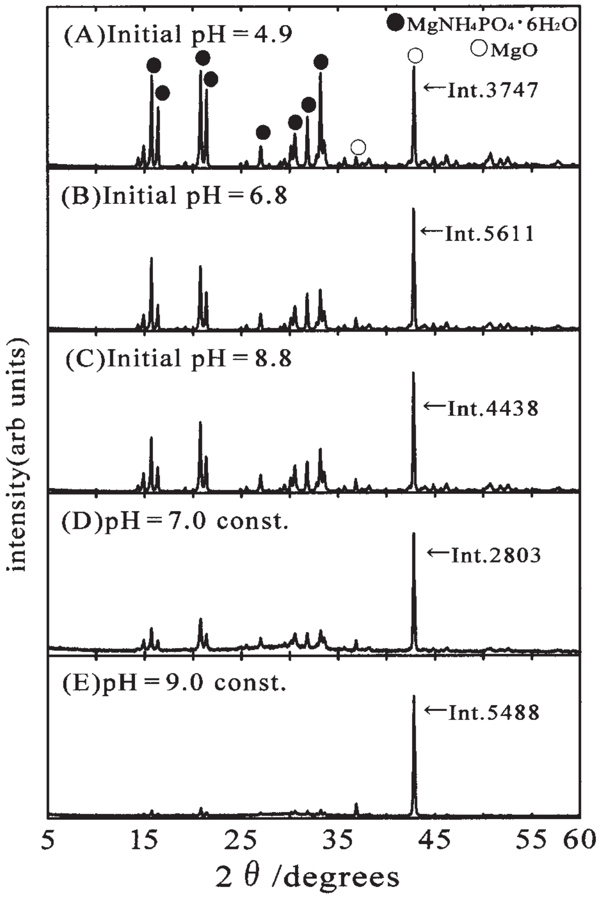

Fig. 2. XRD patterns of the solids previously employed in obtaining the results shown in Tables 1 and 2, but after 4.0 h immobilization.

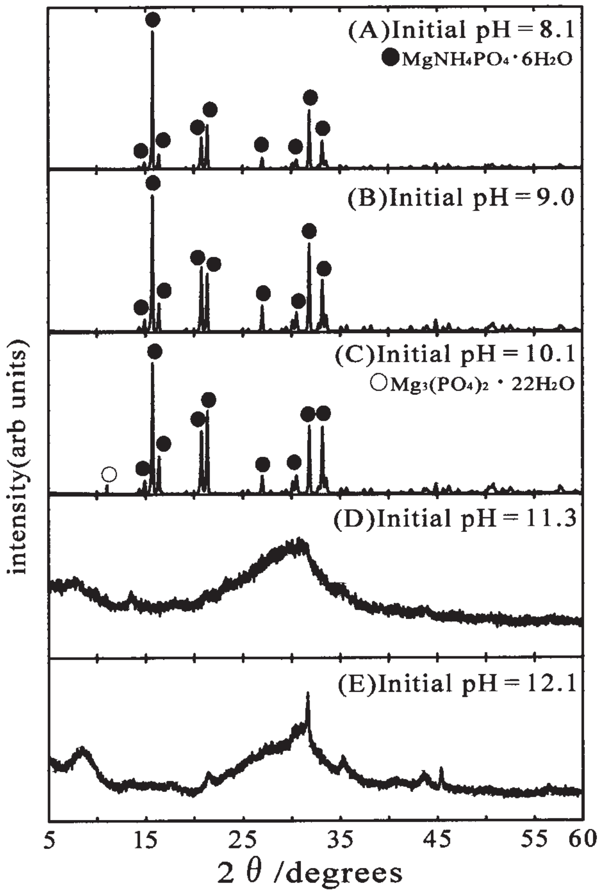

Fig. 3. XRD patterns of the solids previously employed in obtaining the results shown in Table 3 but in the case without the adjustment of the solution pH during the immobilization.

value at 8.1, 9.0, and 9.9 during immobilization, the removal rates for both NH_4^+ and PO_4^{3-} were evidently greater than those without control of the pH (Table 3). Furthermore, the ratio of ammonia to phosphate, both of which were immobilized from the solution, was rather close to unity under those pH conditions (Table 3). However, a further shift of the pH to basic conditions (pH 11.9) resulted in a decrease of the removal rate, particularly that of NH_4^+. It is generally accepted that specific types of phosphate anions ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) are mainly formed in aqueous solution under acidic-neutral, neutral-basic, and strong basic conditions, respectively.[16] Therefore, there is no doubt that no-controlling of the solution pH during the immobilization of NH_4^+ and PO_4^{3-} results in the formation of complex mixtures consisting of not only MAP, but also a solid not-containing N-species, the latter of which is not suitable for re-use as a slow-acting fertilizer.

Structure of a Solid Recovered after Immobilization. It is suggested that the solid recovered from the immobilization of NH_4^+ and PO_4^{3-} with Mg^{2+} can be used as a fertilizer.[11] However, the formation of magnesium hydrogenphosphate and magnesium phosphate together with MAP is also possible, as described in the previous section. In previous research on the MAP process, the XRD measurement was mainly employed for identifying the recovered solid as MAP. However, it should be noted that XRD can not provide any structural information on amorphous compounds. In order to re-use the recovered solid as a fertilizer containing nitrogen and phosphorus, it is necessary to determine whether the recovered solid consists of pure MAP only, or a mixture of MAP and other phosphates. Therefore, the employment of other analytical procedures for the identification of the solids recovered from the present process would be important. Figures 2A–C and D and E show XRD patterns of the solids corresponding to Tables 1 and 2, respectively, but after 4.0 h of immobilization. As shown in Table 1, when the solution pH was not controlled during immobilization, the removal rates at the initial pH of 6.8 were greater than those at pH 4.9 and 8.8. Therefore, it is generally expected that XRD signals due to MAP with great intensity are detected from the solid produced at the initial pH 6.8. However, the XRD signals with the highest intensity due to $Mg(NH_4)PO_4\cdot6H_2O$ (MAP; JCPDS 15-0762), together with those due to MgO (JCPDS 45-0946), were detected from the solid produced at the initial pH 4.9 (Figs. 2A–C). As shown in Figs. 2D and E on the solids recovered after immobilization at controlled pH values of 7.0 and 9.0, XRD signals due to MAP were rather weaker than those recovered after immobilization at un-controlled pH (Figs. 2A–C). It should be noted that the removal rates obtained at the controlled pH (Table 2) were significantly greater than those obtained at the un-controlled pH (Table 1). Therefore, it is evident that the

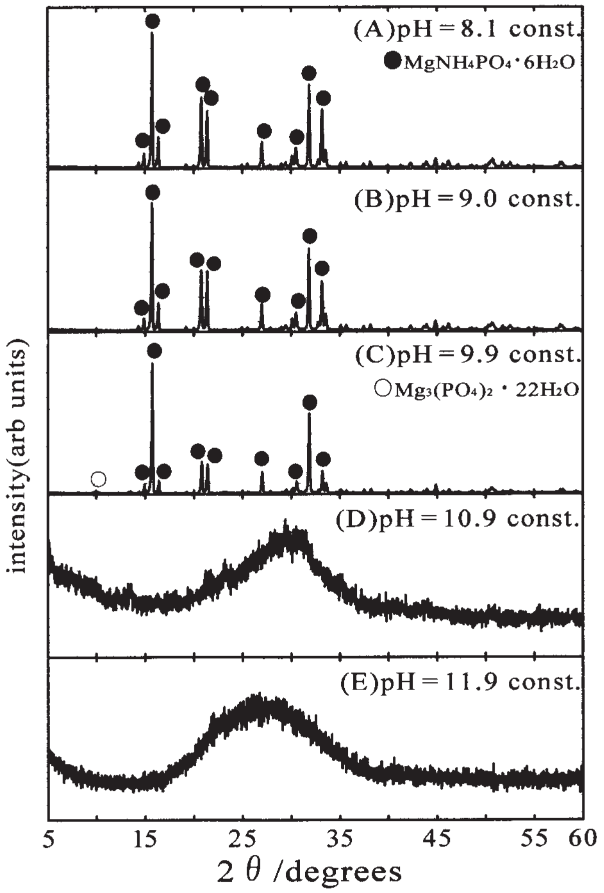

Fig. 4. XRD patterns of the solids previously employed in obtaining the results shown in Table 3 but in the case with the adjustment of the solution pH during the immobilization.

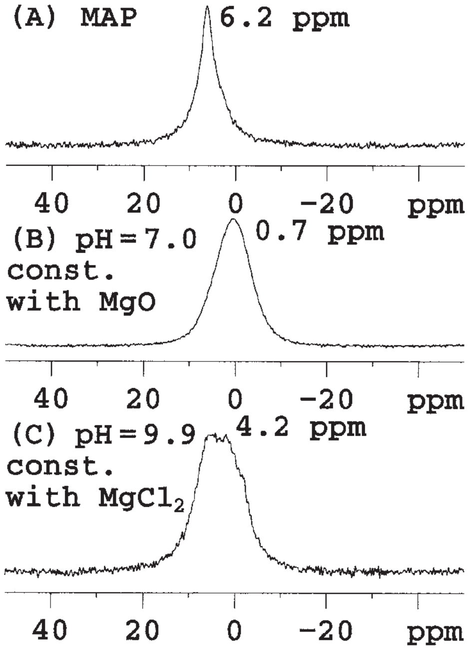

Fig. 5. ^{31}P MAS NMR of commercially available MAP (A) and those of the solid recovered from the immobilization for 4.0 h by MgO at constant pH 7.0 (B) and for 0.5 h by $MgCl_2$ at constant pH 9.9 (C).

crystallinity of the immobilized MAP is strongly influenced by not only the adjustment of the pH during immobilization, but also by the initial pH. From the solids recovered without and with pH control during immobilization with $MgCl_2$ (in both cases, initial pH at approximately 8, 9, and 10), XRD signals due to MAP were detected, as shown in Figs. 3A–C and Figs. 4A–C, respectively. However, the growth behaviors of each plane were dependent on the initial pH and the adjustment procedure of the pH. The compositions of the solids estimated from Table 3 are different from those of MAP and $Mg_3(PO_4)_2 \cdot 22H_2O$ detected by XRD (Figs. 3A–C and Figs. 4A–C). For example, in the case without any adjustment of the pH, the removal rates for NH_4^+ and PO_4^{3-} were 22.3 and 42.5%, respectively, at pH 8.1, while 77.3 and 84.2%, respectively, at pH 10.1 (Table 3). However, XRD showed the formation of MAP ($Mg(NH_4)PO_4 \cdot 6H_2O$) at pH 8.1 and a trace amount of $Mg_3(PO_4)_2 \cdot 22H_2O$ together with MAP at pH 10.1 (Figs. 3A and C, respectively). Since XRD dose not afford any structural information on amorphous compounds, Figures 3A–C and Figures 4A–C reveal the formation of various non-crystalline compounds. At an initial pH higher than approximately 11, but with and without a pH adjustment during immobilization (Figs. 3D–E and Figs. 4D and E, respectively), amorphous compounds were detected by XRD. Based on the results from immobilization (Tables 1–3), the presence of compounds undetectable by XRD is evident. In order to analyze those compounds, solid-state ^{31}P MAS NMR was employed in the present study. Figure 5 shows the ^{31}P MAS NMR of commercially available MAP (A) together with those of the solid recovered from immobilization for 4.0 h by MgO at a constant pH 7.0 (B) and for 0.5 h by $MgCl_2$ at a constant pH 9.9 (C). A single signal of ^{31}P MAS NMR was observed at 6.2 ppm from the commercially available MAP. However, ^{31}P MAS NMR of the solids after immobilization using MgO and $MgCl_2$ afforded symmetric and broad signals at 0.7 and 4.2 ppm, respectively. Therefore, those recovered solids were not pure MAP. The main signals from ^{31}P MAS NMR of commercially available $Mg_3(PO_4)_2 \cdot 8H_2O$, $MgHPO_4 \cdot 3H_2O$, and $Mg_2P_2O_7$ were detected at 4.7, −7.5, and −18.5 ppm, respectively (not shown). Therefore, based on Fig. 5, the complex mixtures were formed particularly from immobilization with $MgCl_2$. It should be noted that the evident XRD signals mainly due to MAP were obtained form the solid after immobilization using $MgCl_2$ (Fig. 4C). Those results show that analysis by XRD is insufficient for identifying the solids obtained from the MAP process. As shown in Fig. 3E and Fig. 4E, amorphous compounds were detected with XRD after immobilization using $MgCl_2$ at an initial solution pH of approximately 12. Therefore, the solids recovered from the solution with the pH controlled to be constant at 11.9 together with 8.1 and 9.9 were analyzed with ^{31}P MAS NMR (Fig. 6). Although those compounds were confirmed as phosphate compounds, but not pure MAP by solid-state ^{31}P MAS NMR, the shape of the signals was strongly dependent on the solution pH (Fig. 6). Those results obtained with XRD and solid-state ^{31}P MAS NMR reveal that the quality of the MAP recovered from the present process would be dependent on how the solution pH was adjusted.

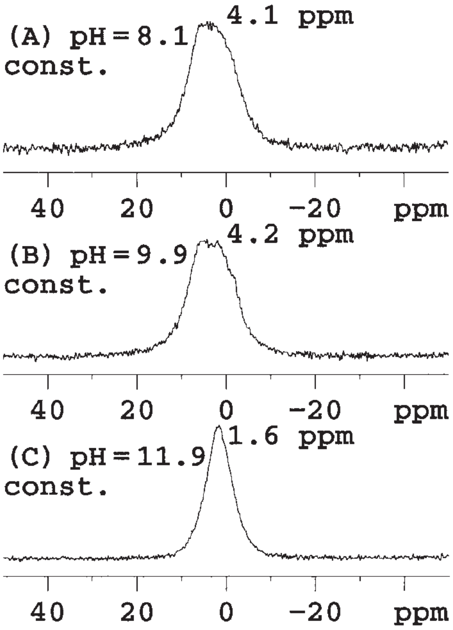

Fig. 6. ^{31}P MAS NMR of the solids recovered from the immobilization with $MgCl_2$ with the control of the solution pH at 8.1 (A), 9.9 (B), and 11.9 (C).

Conclusion

1. In employing MgO as the immobilization reagent, a neutral solution pH produced a rather greater immobilization of NH_4^+ and PO_4^{3-} due to the balance of the favorable dissolution of MgO under acidic conditions with the facile formation of MAP under basic conditions.

2. Although the basic conditions at approximately pH 10 are suitable for the formation MAP with $MgCl_2$ as the immobilization reagent, the employment of basic conditions stronger than pH 11 resulted in a suppression of the immobilization with $MgCl_2$.

3. Except for most basic conditions at pH 12 with $MgCl_2$, the adjustment of the solution pH to be constant during immobilization with MgO and $MgCl_2$ produced a rather greater immobilization than that without an adjustment.

4. The identification with XRD and solid-state ^{31}P MAS NMR reveals that the structure and composition of the solids recovered after immobilization were strongly influenced by the adjustment procedure of the solution pH.

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