Spatially Resolved Product Speciation during Struvite Synthesis from Magnesite (MgCO₃) Particles in Ammonium (NH₄⁺) and Phosphate (PO₄³⁻) Aqueous Solutions

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ABSTRACT: While population growth necessitates a significant increase in crop production, stringent environmental regulations require that it be done using sustainable nutrient sources. Nutrients in the form of NH₄⁺ and PO₄³⁻ are recovered from wastewater streams via precipitation, using water-soluble magnesium ions to form sustainable, slow-release fertilizer, struvite (MgNH₄PO₄·6H₂O). However, the magnesium needed is mainly incorporated in the crystal lattices of very low-solubility minerals. This work utilizes a combination of powder X-ray diffraction (pXRD) and ex situ Raman and energy-dispersive X-ray spectroscopies combined with ion chromatography to characterize transformation products of low-solubility MgCO₃ particles in NH₄⁺- and PO₄³⁻-containing aqueous solutions with and without Ca²⁺ ions present. Although pXRD showed struvite as the predominant solid product for the molar ratio [Mg²⁺/NH₄⁺/PO₄³⁻] of 0.2:1:1 and higher, ex situ Raman spectra evidenced formation of a dypingite-like phase along with struvite. Single-crystal Raman spectroscopy in combination with scanning transmission electron microscopy/energy-dispersive X-ray spectroscopy showed Ca²⁺ incorporation into the structure of struvite crystals as submicron crystallites at the Ca²⁺/Mg²⁺ ratio of 0.2, from both CaCO₃ and CaCl₂ and at the Ca²⁺/Mg²⁺ ratio of 1, in the case of CaCO₃. Moreover, distinct solid product speciation was observed when Ca³⁺ was present in aqueous solutions when using CaCl₂; for example, hydroxyapatite was observed for Ca²⁺/Mg²⁺ = 1 when CaCl₂ was used. The results reported here unravel the effect of the physicochemical solution parameters, such as concentration of MgCO₃, pH, Ca²⁺ concentration, and solubility of Ca-containing precursors, on the formation of struvite crystals. This shows that recovery of nutrients containing N and P from wastewater streams is possible in the form of a slow-release fertilizer (struvite) using low-solubility, abundant magnesium-containing minerals.

INTRODUCTION

The importance of sustainable, slow-release fertilizers is highlighted by the fact that increasing crop and livestock production has resulted in a major influx of nitrogen (N) and phosphorus (P) into the environment because of increased synthetic fertilizer use.¹ N fertilizers have a large environmental footprint, as they are produced via NH₃ synthesis, which consumes about 1–2% of the total global energy and 3–5% of total natural gas.¹² Such N fertilizers are highly water soluble and lead to release of large amounts of soluble forms of N to the soil upon application. The surplus N is lost to the environment in the form of greenhouse gas emissions, such as ammonia (NH₃), nitrous oxide (N₂O), nitric oxide (NO),² or aqueous NH₄⁺ and NO₃⁻ ions, whereas surplus P, being much less soluble, enters the watershed causing hazardous eutrophication or accumulates in soil.³–⁹ Additionally, large amounts of wastewater enters watershed in the form of sewage effluents and agricultural runoff. Such wastewater is rich in NH₄⁺ and PO₄³⁻, which then encounter natural mineral surfaces containing magnesium (Mg) and calcium (Ca) and can potentially react to form solid products.

To produce sustainable, slow-release fertilizers for the ever-increasing demand, reactions of natural minerals, such as the magnesium-containing magnesite, (MgCO₃), with ammonium and phosphate (NH₄⁺ and PO₄³⁻) ions present in water streams to synthesize struvite (MgNH₄PO₄·6H₂O) are of major importance. In particular, struvite crystallizes if pH of the solution is 8.0–9.0.⁰¹¹ Struvite crystal growth using water-soluble magnesium salts depends on many conditions, including pH,¹² solution saturation with NH₄⁺ and PO₄³⁻,¹³ and presence of other cations, such as Ca²⁺.¹⁴ However, magnesium, although a common constituent of many complex
minerals comprising 2% of the Earth’s crust, is mostly incorporated in the crystal lattice of low-solubility minerals that typically undergo slow surface reaction/hydration. Interactions of these sparingly soluble magnesium oxides or carbonates with aqueous NH₄⁺ and PO₄³⁻ ions proceed via a surface reaction limited mechanism. There is a limited number of experimental studies that spectroscopically measured the surface reactivity of such sparingly soluble Mg-containing mineral surfaces toward NH₃, NH₄⁺, and PO₄³⁻ and studied the resulting solid product speciation. Sparingly soluble MgO has been studied for solution phase synthesis in various literature reports and has shown to be very reactive toward various anions in high relative humidity conditions. The reactivity of the MgO crystalline surface was explained by the presence of ~2 monolayers of adsorbed H₂O, as inferred from transmission Fourier-transform infrared spectroscopy measurements. The ideal MgO(100) surface is by far energetically predominant and only partially dissociates H₂O but the extended defects, such as mono- and diatomic steps, will readily chemisorb H₂O, yielding a series of one, two-, or four-fold coordinate hydroxyl groups. Although the strength of water adsorption is primarily driven by the coordination number of the surface acid–base pairs, the surface hydroxyl groups resulting from water dissociation are also considerably stabilized by the electrostatic interaction with coadsorbed protons. At low coverage, such an interaction, considerably stronger than hydrogen bonding, hinders any proton diffusion away from its neighboring hydroxyl groups. The diverse chemical environment produced as a result of these hydroxyl (OH⁻) groups alters MgO surface reactivity. Surface sites exhibiting varying degrees of basicity are formed, with water O–H bond breakage occurring only at strongly basic edge sites and nondissociative H₂O adsorption taking place on medium-strength basic terrace sites. Moreover, it is known that hydroxyl groups will dominate the MgO and MgCO₃ surfaces in aqueous solutions and act as hosts for the struvite precursor ions, such as NH₄⁺ and PO₄³⁻. At pH 9 under room temperature, equal amounts of NH₃ and NH₄⁺ are present in an aqueous environment. Moreover, under such conditions, NH₃/NH₄⁺ will be weakly adsorbed on hydrated MgO or MgCO₃ by hydrogen-bonding of the nitrogen atom to hydroxyl groups exposed on the surface.

On the other hand, strong PO₄³⁻ adsorption in the infrared spectrum was observed on MgO from aqueous solutions with a spectral peak at 1060 cm⁻¹ assigned to PO₄³⁻ stretch, likely via surface inner-sphere complexation, surface electrostatic attraction, and precipitation mechanisms. Magnesite (MgCO₃) fundamental interactions with NH₄⁺ and PO₄³⁻ ions are much less studied and understood compared to MgO. Recent work by Kirinovic et al. utilized ex situ Raman spectroscopy of the solid phase struvite formed using MgCO₃ containing mineral surfaces toward NH₃, NH₄⁺, and PO₄³⁻ (fixed 1:1 molar ratio). Ion Chromatography (IC) was utilized to evaluate temporal concentration of the residual ions in solution. Ex situ Raman spectroscopy was used to spatially resolve the solid products, whereas pXRD was employed to evaluate the crystallinity of the solid phase. Finally, Raman/pXRD/energy dispersive X-ray spectroscopy (EDXS) in conjunction with scanning transmission electron microscopy (STEM) studies were performed to examine how calcium ions from either soluble CaCl₂ or very low-solubility CaCO₃ alter reactive intermediates and affect the resulting solid product speciation.

### EXPERIMENTAL METHODS

**Ion Chromatography.** The Metrohm Eco 925 IC system (Herisau, Switzerland) was used in all experiments. The separation columns used were Metrosep A supp 4/5 guard column (5 × 4 mm) and Metrosep A supp 5 (4 × 150 mm) for anion analysis and Metrosep C 4 guard column (5 × 4 mm) and Metrosep C 4 (4 × 150 mm) for cation analysis. The sample-loop volume was 10 μL in the cation system and 20 μL in the anion system, and the eluted species were measured using a conductivity detector. HNO₃ (1.75 nM) and dipicolinic acid (DPA, 0.7 mM) was used as eluent for Metrosep C 4, whereas 3.2 mM NaHCO₃ and 1.0 mM NaHCO₃ were used for Metrosep A supp 5. All samples were measured at room temperature. Error bars are provided for triplicate in selected experiments. The system was computer controlled through MagIC Net 3.2 software.

**Powder X-ray Diffraction.** Crystalline nature of all reactants and products was confirmed using pXRD (Empyrean, PANalytical B.V.). The applied current was 40 mA, and the applied voltage was 45 kV. The X-ray mirror that was used was a graded, flat Bragg–Brentano HD mirror, and the step size that was used for the measurements was 0.0131°.

**Scanning Transmission Electron Microscopy.** The morphology of the catalyst particles was investigated using a dedicated Scanning Transmission Electron Microscope (Hitachi 2700C) operating at 200 kV. The EDXS signals were collected using a Bruker SDD EDX detector with a 30 mm² collection window.

**Raman Spectroscopy.** Ex situ Raman spectra and spectral maps were acquired using WITec alpha300R confocal Raman microscope using 532 nm laser and a ×100 objective. Laser intensity at the sample was ~54 mW. Spectral maps were typically acquired using 2 s exposure time per single scan point. Two types of Raman spectral maps were obtained. In particular, for MgCO₃/NH₄H₂PO₄ experiments, 2-D spectra maps were acquired in the x–y plane, for example, perpendicular to the laser beam. To elucidate homogeneity of a single crystal formed using MgCO₃/NH₄H₂PO₄ in the presence of Ca²⁺ ions from CaCO₃, 2-D spectral maps were...
acquired in the x−z plane, for example, parallel to the direction of the beam.

The true component analysis (TCA) was used to create spectral intensity distribution images of different spectra components. It is the utilization of linear combination of the spectral components using the basis analysis algorithm via eq 1

\[ \mathbf{S}_i = \mathbf{B} \mathbf{H}_i + \mathbf{E}_i \]  

where \( \mathbf{S}_i \) — spectrum i from the spectral dataset, \( \mathbf{B} \) — matrix of basis spectra, \( \mathbf{H}_i \) — mixing values of spectrum i, and \( \mathbf{E}_i \) — error spectrum. The mixing values are fitted using least squares minimization methods following the expression 2

\[ (\mathbf{S}_i - \mathbf{B} \mathbf{H}_i)^2 = \text{minimum} \]  

**REAGENTS AND SOLUTIONS**

Stock solution of ammonium (1.0 g/L), magnesium (1.0 g/L), and phosphate (1.0 g/L) were prepared from monoammonium phosphate, NH₄H₂PO₄ (99.9%, Fisher Scientific) and MgCl₂ (99.9%, Fisher Scientific). Appropriate amounts of individual salts were weighted into a volumetric flask (100 mL) and dissolved in deionized (DI) water. Working standard solution of ammonium, magnesium, and phosphate were prepared by measuring the appropriate volume of standard solutions into a 100 mL volumetric flask, which was afterwards filled with DI water. Working eluent solutions were prepared by appropriate dilution of standard eluent solution with DI water. An 18.2 MΩ/cm DI water (Millipore, Bedford, MA, USA) was used for dilution in all cases.

MgCO₃, CaCO₃, CaCl₂, Mg(OH)₂, and Ca(OH)₂ powders (99%+) were obtained from Sigma-Aldrich and used as received.

MgCO₃ Reactive Experiments to Form Struvite. All reactions were performed using MgCO₃ (Brunauer−Emmett−Teller surface area 94 m²/g) as the magnesium source. Simulated NH₄⁺ and PO₄³⁻-containing aqueous solution was prepared by adding 600 ppm of NH₄H₂PO₄ (Fisher Scientific, Certified A.C.S.) at room temperature with constant stirring at 350 rpm, which resulted in a solution with pH of ∼5.4. Concentrations between 300 and 1500 ppm of MgCO₃ were added to the aqueous solution containing NH₄⁺ and PO₄³⁻ and stirred for up to 120 min. The total volume of the reactive solution was 500 mL. The solution (1 mL) was sampled periodically and filtered through a 13 mm diameter polyethersulfone (PES) filter (0.22 μm pore size) to remove solid material and analyzed using IC. Unless specified otherwise, the starting pH was 5.4 before the solid MgCO₃ was added in all cases.

Detailed experiments, for example, 300, 1000, and 1500 ppm MgCO₃ and 600 ppm NH₄H₂PO₄ used in this work correspond to molar [Mg²⁺]/[NH₄⁺]/[PO₄³⁻] ratios of: [0.7:1:1], [2.3:1:1], and [3.4:1:1], respectively. [Mg²⁺]/NH₄⁺/PO₄³⁻ ratios of [0.5−1.5:1:1] have previously been tested, and it was concluded that lower ratios lead to a lesser N,
PO₄ and chemical oxygen demand removal. A 600 ppm NH₄H₂PO₄ represents PO₄³⁻ and NH₄⁺ values found in municipal, animal, and industrial wastewater while maintaining the molar 1:1 ion ratio needed for struvite formation. Therefore, a slight excess of Mg²⁺ was preferred in the previous works to circumvent this issue and ensure efficient precipitation of P and N from the solution. Further, CaCl₂ or CaCO₃ were introduced with 1000/600 ppm 0.2 to assess the change in the MgCO₃.

NH₄⁺ and PO₄³⁻ Adsorption Kinetics. Pseudo-first-order kinetic models were used to analyze the obtained NH₄⁺ and PO₄³⁻ adsorption data according to the pseudo-first-order model, summarized in eq 3.

\[ \ln[q_e - q_t] = \ln[q_e] - k_1 t \]  

where \( q_t \) (mg g⁻¹) and \( q_e \) (mg g⁻¹) are the amounts of NH₄⁺ or PO₄³⁻ adsorbed at time \( t \) (min) and at equilibrium, respectively, whereas \( k_1 \) (min⁻¹) is the rate constant of pseudo-first-order kinetic models. Equation 3 can be rearranged to make it suitable for a linear plot as follows.

\[ \ln[q_e - q_t] = k_1 t \]  

where the right hand side of the equation is \( y \) and \( k_1 \) is the slope.

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Figure 2. Kinetic modeling of experimental data using pseudo-first-order kinetics model for different starting concentrations of MgCO₃. (Left) Total PO₄³⁻ and (right) total NH₄⁺.

RESULTS AND DISCUSSION

Kinetic Studies of Aqueous NH₄H₂PO₄ Reaction with MgCO₃. IC was used to monitor the time-dependent anion (PO₄³⁻) and cation (NH₄⁺ and Mg²⁺) concentration change taking place in the liquid phase during the formation of solid products. Figure 1a shows the concentration profile of residual PO₄³⁻ ions with three different initial MgCO₃ concentrations of 300, 1000, 1500 ppm MgCO₃ and 600 ppm NH₄H₂PO₄ corresponding to molar \([\text{Mg}^2⁺]/[\text{NH}_4^+] / [\text{PO}_4^{3-}]\) ratios of: \([-0.7:1:1], [2.2:1:1], \) and \([3.3:1:1], \) respectively. The highest concentration of MgCO₃ exhibited the fastest rate of PO₄³⁻ removal from the solution, with the PO₄³⁻ concentration of 40 ppm at the equilibrium, after 2 h. Concentration profiles of Mg²⁺ in solution as a function of reaction time in Figure 1b showed that there was an immediate dissolution (mobilization) of Mg²⁺ ions from solid MgCO₃ within 5 min of the reaction for all MgCO₃ concentrations. Equilibrium was achieved rather fast for the unreactive case of 300/600 ppm MgCO₃/NH₄H₂PO₄ 1000/600 and 1500/600 ppm MgCO₃/NH₄H₂PO₄ experienced a very fast initial dissolution followed by slight decrease in the aqueous Mg²⁺ concentration between 10 and 25 min. The initial fast dissolution was associated with the undersaturated conditions when solid phases, such as struvite, could not form. It was followed by the rapid solid product precipitation accompanied by the corresponding Mg²⁺ concentration decrease. After the solid product formation was complete (similar with the literature reports of fast struvite precipitation within 5–10 min under similar conditions for MgO particles), an increase in Mg²⁺ concentration was observed to achieve equilibrium after around 2 h of reaction. Time-resolved plot of NH₄⁺ adsorption/reaction is shown in Figure 1c, with the inset summarizing removal as a function of MgCO₃ concentration. NH₄⁺ adsorption and reaction with MgCO₃ followed a very similar behavior as that of PO₄³⁻ with undersaturated solution of 300/600 ppm MgCO₃/NH₄H₂PO₄ not forming any solid products and higher concentrations resulting in ~80% NH₄⁺ removal from solution. This suggests a facile formation of solids, in contrast to a recent report, where at comparable conditions using MgO, struvite formation only took place under two MgO concentration regimes that is at \([\text{Mg}/\text{NH}_4^+/\text{PO}_4^{3-}]\) molar ratios of \(1.4:1:1\) (300 ppm MgO) and \(4.8:1:1\) (1000 ppm MgO). In the case of 300 ppm MgO, maximum removal of NH₄⁺ (80%) was achieved at equilibrium after 120 min, whereas in the case of 1000 ppm MgO, a very fast kinetic regime was observed 5 min after the reaction onset to achieve ~70% removal of NH₄⁺. Increase in the initial MgCO₃ concentration agreed well with the increasing pH of the solution shown in Figure 1d. Here, the initial 600 NH₄H₂PO₄ solution pH was 5.4, and the first measurement with MgCO₃ added was taken 1–2 min after the addition. Results show that although pH increased in all three cases, 300 ppm MgCO₃ had only gradual change from 6.4 to 7.2 pH units.

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over a the total time of 125 min, whereas 1000 and 1500 ppm MgCO₃ exhibited an increase to 8.3 and 8.7, respectively.

To further evaluate the observed kinetics, the NH₄⁺ and PO₄³⁻ decrease in concentration shown in Figure 1 was fitted to both pseudo-first⁴¹,⁴² and pseudo-second⁴⁶,²⁰,⁴³ (not shown here) order kinetics. The pseudo-first-order plot of ln \( q_e - \ln(q_e - q_t) \) versus \( t \), as shown in Figure 2 and summarized in Table 1, fit the experimental data better than pseudo-

Table 1. Summarized Data from Pseudo-First-Order Kinetic Fits, Shown in Figure 2

<table>
<thead>
<tr>
<th>MgCO₃ (ppm)</th>
<th>( k_1 )</th>
<th>( r^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO₄³⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.029</td>
<td>0.97</td>
</tr>
<tr>
<td>1000</td>
<td>0.053</td>
<td>0.99</td>
</tr>
<tr>
<td>1500</td>
<td>0.099</td>
<td>0.98</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>0.027</td>
<td>0.98</td>
</tr>
<tr>
<td>1000</td>
<td>0.056</td>
<td>0.99</td>
</tr>
<tr>
<td>1500</td>
<td>0.065</td>
<td>0.97</td>
</tr>
</tbody>
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second-order kinetics, which we reported for struvite formation using MgO.¹⁶ This interesting observation suggests that no complex intermediate is formed in the overall reaction, for example, NH₄⁺ and PO₄³⁻ adsorption on MgCO₃ is facile and not diffusion limited. This is different from PO₄³⁻ adsorption on MgO where a pseudo-second-order kinetics was measured. Pseudo-second-order kinetics are usually associated with chemisorption mechanism being the rate-controlling step.⁴⁴ This is consistent with the previous literature reports where at pH ≈ 7, the rate-controlling step of MgO was a diffusion-limitation process due to protons with the rate proportional to the proton concentration.⁴⁵ At pH > 7, the rate-controlling factors were Mg²⁺ and OH⁻. These processes as a part of the overall dissolution reaction would lead to the increase in pH observed in this work. Mg(OH)₂ forms preferentially at the MgO surface, so that an MgO lattice reaction can be excluded. The increase in pH was rather small, as shown in Figure 1d, in agreement with the absence of the first hydroxylation step leading to a facile pseudo-first-order reaction. From the \( k_1 \) values reported in Table 1, it can be seen that the change in \( k_1 \),

Figure 3. (a) MgCO₃ and (b) Mg(OH)₂ pXRD spectra. The corresponding Raman spectral components derived from TCA are shown in (c,d), whereas the component individual peak x–y plane maps are shown in (e,f).
closely follows the change in the MgCO₃ concentration, where doubling the concentration, roughly doubles the rate of PO₄³⁻ and NH₄⁺ removal, except in the case of 1500 ppm MgCO₃ for NH₄⁺ removal.

**Compositional and Spatial Homogeneity of the Reactant Magnesium Minerals: MgCO₃ and Mg(OH)₂.** In order to better understand spectral patterns of the reaction products, ex situ Raman experiments combined with pXRD measurements were utilized to better understand compositional complexity of MgCO₃ and Mg(OH)₂ solid crystals. These data are shown in Figure 3. Chemical complexity of bulk MgCO₃ is already apparent from the pXRD pattern shown in Figure 3a. It constitutes a complex hydromagnesite, 4MgCO₃·Mg(OH)₂·4H₂O, structure (ICDD-JCPDS PDF#25-0513). Figure 3b shows a well-defined crystalline pattern of Mg(OH)₂. Figure 3c shows spectral components obtained using TCA of MgCO₃ Raman spectra. The blue component spectrum exhibits a major sharp band at 1120 cm⁻¹ and a broad, less intense band with shoulders at 3250, 3370, and 3550 cm⁻¹ that correspond to the ν₁ symmetric vibrations of CO₃²⁻ and vibrations of the surface H₂O, respectively. The blue component spectrum also exhibits a sharp band at 3650 cm⁻¹ which arises from the surface Mg–OH vibrations. On the other hand, the red component spectrum exhibits peaks at 750, 1120, 1453, 3340, 3510, and 3650 cm⁻¹. According to the literature, all of the red component peaks match those of dypingite, which is another complex hydroxycarbonate species (Mg₅(CO₃)₄(OH)₂·5H₂O). Specifically, 750, 1120, and 1453 cm⁻¹ bands are attributed to the ν₂ in-plane bending, the ν₁ symmetric stretching mode, and the ν₃ antisymmetric stretching vibrations of CO₃²⁻ in dypingite, respectively. The overlapping broad bands from 3200 to 3600 cm⁻¹ arise from the surface H₂O vibrations, whereas the very sharp band at 3650 cm⁻¹ arises from the Mg–OH vibration. Hydro-magnesite peaks are sharper showing higher degree of crystalline order in agreement with Figure 3a pXRD pattern, where separate dypingite component is not immediately apparent. The corresponding spectral images of the unique...
peaks of each component are shown in Figure 3e. Although the optical image appears homogeneous, spatial inhomogeneity becomes apparent in the combined image. Figure 3d shows the only spectral component obtained using TCA of Mg(OH)₂ Raman scan. The 280, 440, and 3650 cm⁻¹ bands agree well with the literature and are attributed to lattice vibrations that are perpendicular (E₂g(T)) or parallel (A₁g(T)) to the crystal c-axis and symmetric OH stretching vibrations, respectively.²⁹ The 3650 cm⁻¹ peak assignment in hydromagnesite (Figure 3c) is thus corroborated by the Mg(OH)₂ spectrum. Spectral mapping of Mg(OH)₂ shown in Figure 3f confirms the presence of a single spectral component with some discontinuities in the image because of the shallow depth of field.

**Composition and Spatial Homogeneity of Struvite Crystals Formed via NH₄⁺ and PO₄³⁻ Adsorption/Reaction on MgCO₃** Next, the effect of MgCO₃ concentration on the solid product speciation and homogeneity was probed via pXRD and Raman. The starting pH was 5.4 (that of 600 ppm NH₄H₂PO₄) in this round of analysis. Three concentrations of MgCO₃, that is 500, 1000, and 1500 ppm, were utilized, whereas 600 ppm NH₄H₂PO₄ was used in all cases. 500, 1000, and 1500 ppm MgCO₃/600 ppm NH₄H₂PO₄ correspond to molar ratios of [Mg²⁺/NH₄⁺/PO₄³⁻] of [1.1:1:1], [2.2:1:1], and [3.3:1:1], respectively. These ratios were chosen to represent three concentration regimes: Mg-rich, stoichiometric, Mg-excess. pXRD results shown in Figure 4a clearly show that in all three cases the solid product bulk crystalline structure was the same and matched that of struvite.¹⁶,⁵⁵ To analyze the identity and molecular structures present at the solid product surface in a spatially resolved manner, 500/600 ppm MgCO₃/NH₄H₂PO₄ and 1500/600 ppm MgCO₃/NH₄H₂PO₄ were further analyzed with Raman spectroscopy, and major spectral components were identified using TCA. For all spectra in Figure 4b, the data showed three unique spectral components present. Literature data showed that struvite crystals synthesized using aqueous 1:1 NH₄⁺ and PO₄³⁻ solutions and water soluble MgCl₂ exhibited Raman bands at 101, 148, 189, 229, 297, 393, 440, 570, 700, 750, 950, 981, 1020, 1125, 1429, 1469, 1675, 2357, a broad band at 2800–3430, 3498, and 3603 cm⁻¹.⁵⁵ The bands from 101 to 370 cm⁻¹ were attributed to the skeletal vibrations of struvite.³⁵,⁴⁹ A sharp, prominent band at ~950 cm⁻¹ and smaller bands at 981 and 1020 cm⁻¹ were attributed to the symmetric and asymmetric PO₄³⁻ stretches, respectively.³⁵ Two prominent peaks in 1400–1700 cm⁻¹ region were assigned to the deformational vibrations of NH₄⁺ tetrahedra.⁵² Lastly, a broad band corresponding to different N–H and O–H (in H₂O) stretches was observed in the 2200–3600 cm⁻¹ region because of the hydrogen bonding. The red component in Figure 4b was assigned to struvite. The green component with major bands at 1120, 3440, 3510, and 3650 cm⁻¹ and minor shoulders at 560, 704, 947, 993, 2950, and 3153 cm⁻¹ can be interpreted as a magnesium-rich dyeing-like phase.⁴⁷ Any surface OH groups will exhibit a sharp band at ~3650 cm⁻¹ due to the symmetric Mg–OH stretch. Hence, the blue component exhibited major bands at 560, 947, 993, 1120, 3153, 3440, and 3650 cm⁻¹. Based on band assignments in Figure 3c, which shows characterization data of the reactant precursor, it can be concluded that this is an intermediate to struvite with MgCO₃-like chemical environment and few OH groups on the surface. Based on these TCA components shown in Figure 4b, Raman maps for 500/600 ppm MgCO₃/NH₄H₂PO₄ and 1500/600 ppm MgCO₃/NH₄H₂PO₄ were constructed and shown in Figure 4c,d, respectively. Only unique peaks of each component were utilized to analyze localization of different solid phases. In both cases, the red component with bands at 947, 993, and 1050 cm⁻¹ was predominantly present in the highest intensity within the crystalline needles, which is the predominant crystal shape of struvite.³⁵ The solid product surrounding the crystalline needles showed localization of the green component, with Raman bands at 1120 and 3650 cm⁻¹ from CO₃²⁻ and OH⁻ species, respectively. Very little of the blue component was present in the spectral images. It is key to note that in the case of 1500/600 ppm MgCO₃/NH₄H₂PO₄, much less green component was present in Raman maps compared to those of 500/600 ppm MgCO₃/NH₄H₂PO₄, suggesting that a large excess of MgCO₃ is needed to consume this intermediate phase and push the equilibrium toward struvite formation.

**Effect of Initial pHe on Spatial Distribution and Speciation of the Solid Products.** Surface water pH can range anywhere from 6.0 to 9.0.³⁵ Additionally, pH of certain wastewaters, such as wastewater from the swine industry (or even municipal wastewater) have pH values above 8.³⁸ The equilibrium pH of the aqueous PO₄³⁻ and NH₄⁺ at 600 ppm without any extraneous ions present would yield a pH value of ~5.4, which increased to 8.5 upon reaction because of the release of OH⁻ ions. Higher initial pH of 8.5 was achieved by
adjusting it with NaOH, and the reaction was repeated with 1000 ppm MgCO₃. The results are shown in Figure 5b compared to those with the initial pH of 5.4 (Figure 5a). Adsorption/reaction of PO₄³⁻ and NH₄⁺ proceeded with faster initial kinetics, for example, a steeper decrease in the aqueous ion concentration was observed than in Figure 5a. The corresponding initial decrease rates were found using linear fit and were 2 and 4 ppm/min for NH₄⁺ and 8.4 and 15 ppm/min for PO₄³⁻ for the initial pH of 5.4 and 8.5, respectively. This is consistent with the literature data, where increasing pH facilitated struvite formation. More importantly, virtually no Mg²⁺ ions were detected during the experiments in solution with starting pH of 8.5, as most of Mg²⁺ is transformed into low-solubility compounds, such as Mg(OH)₂ (Kₛₚ = 5.1 × 10⁻¹²) and Mg₃PO₄ (Kₛₚ = 1.0 × 10⁻²⁴). This suggests a pH-specific reaction mechanism, where initial pH can alter the amount of Mg²⁺ available. For example, a significant fraction of Mg²⁺ ions ~80% for 1000 ppm as shown in Figures 5a and 1b, is still present in aqueous solution and needs to diffuse to the surface to achieve super saturation toward struvite formation. However, when initial pH of 8.5 was used at 100 ppm MgCO₃, almost no Mg²⁺ remained in the solution (Figure 5b).

Unique peaks from TCA components shown in Figure 4b were used to construct Raman maps. The resulting spectral map images are shown in Figure 6. In both cases (initial pH 5.4 and 8.5), the major crystalline product was needles of struvite, whereas the amorphous particles exhibited bands present in the green TCA component. Both cases showed similar component distribution with green and red present in comparable amounts. Based on a similar spatial distribution of each component, it can be proposed that struvite synthesis using very low-solubility MgCO₃ precursor does not show a distinct pH dependence on the solid products speciation at the equilibrium in the pH range tested. In contrast, a strong pH effect on solid product distribution was previously shown during struvite synthesis using MgO, where the initial pH of 8.5 led to PO₄³⁻ consumption decreasing significantly and yielded solid Mg₃PO₄·2H₂O and unreacted MgO with virtually no struvite after 120 min of reaction time. On the other hand, when the synthesis solution was buffered at the pH of 9.2, pXRD analysis of the solid products showed a mixture of struvite and Mg₃PO₄·2H₂O. No solid MgO phase was observed after 120 min synthesis. When MgCO₃ was used, no such pH dependence was observed. This is because in the case of MgO precursor, a slow dissolution step to form surface OH species is necessary, which depends not only on temperature, defect density, particle size, but also, on pH of the solution. However, in the case of MgCO₃, the surface already has abundant OH groups present, as shown by the 3650 cm⁻¹ band in Figure 3. Presence of OH⁻-truncated surface implies that the dissolution step in this case is not as slow, but more importantly, its pH dependence is absent in the pH range of 5.4–8.5, which is used in this work.

Effect of Ca²⁺ from Low-Solubility CaCO₃ on Solid Product Speciation. Numerous studies reported in the literature show inhibitory effect of Ca²⁺ ions during struvite synthesis. In particular, presence of Ca²⁺ ions in solutions containing NH₄⁺, PO₄³⁻ and Mg²⁺ ions leads to competitive reactions between struvite formation using Mg²⁺ ions and calcium phosphate formation using Ca²⁺ ions. As the Ca²⁺/Mg²⁺ ratio in the solution increases, the thermodynamically dominant product becomes calcium phosphate. However, little information is available where NH₄⁺ and PO₄³⁻ solutions are exposed to solid low-solubility Ca²⁺ precursors, such as CaCO₃, as most studies employed soluble MgCl₂ and CaCl₂. This is especially important in the environment where dolomite, a solid solution of CaCO₃ and MgCO₃, is present as a natural mineral.

Solid CaCO₃ particles were first characterized using pXRD and Raman spectroscopy, as shown in Figure 7. pXRD analysis in Figure 7a showed a complete agreement of pXRD peaks with the literature reports of crystalline CaCO₃ phase. The Raman spectrum shown in Figure 7c exhibited major bands at 280, 705, 1086, and 1434 cm⁻¹, which are attributed to the lattice mode, ν₂ in-plane bending, ν₁ symmetric stretch, and ν₃ antisymmetric stretch of the CO₃²⁻, respectively. pXRD and Raman analysis showed only a single spectral component. Spectral maps of the representative peaks shown in Figure 7d clearly showed the spectral component present homogenously throughout the sample, with the three bands (280, 705, and 1086 cm⁻¹) showing intensity at the same locations. Ca(OH)₂, a potential reactive intermediate of CaCO₃ hydration was also analyzed as shown in Figure 7b,d,f. The pXRD pattern agreed well with the literature. Likewise, Raman analysis showed only a single spectral component with major bands at 350 and 684 cm⁻¹ attributed to vibrations of Ca–O and the 3615 cm⁻¹ OH stretch. A small shoulder at 1086 cm⁻¹ was inferred from Figure 7c as CaCO₃ impurity and has been observed in other studies.

Having established spectral properties of CaCO₃ and Ca(OH)₂, two Ca²⁺/Mg²⁺ ratios, namely, 0.2 and 1 were chosen for reactions with aqueous NH₄⁺ and PO₄³⁻, whereas MgCO₃ and NH₄H₂PO₄ concentrations of 1000/600 ppm remained the same. This resulted in precursor concentrations of 1000/600/238 ppm and 1000/600/1190 ppm of MgCO₃/
NH₄H₂PO₄/CaCO₃, respectively. The solid products formed were analyzed using pXRD and Raman spectroscopy, as shown in Figure 8. pXRD analysis in Figure 8a unequivocally showed that at both ratios tested, struvite was the dominant product. However, in the case of Ca²⁺/Mg²⁺ = 1, an unreacted CO₃²⁻ phase was also observed in the product, as seen from the CO₃²⁻ peak in Figure 8a Raman results shown in Figure 8b resulted in three unique spectral components. Based on Raman assignments made above (Figures 3, 4, and 7) and in the literature, the red component bands matched those of struvite, with the exception of 1086 cm⁻¹ which corresponded to solid CaCO₃. The blue component exhibited major bands at 707, 947, 1086, 1430, and 1680 cm⁻¹ that agreed well with those of CaCO₃ except for the 947 cm⁻¹ band, which is attributed to the PO₃³⁻ vibration, also seen in Raman spectra of struvite (red component). Lastly, the green component exhibited bands similar to those of the red component suggesting struvite. However, the green component exhibited both 1086 and 1120 cm⁻¹ bands that correspond to CO₃²⁻ coordinated to both Ca²⁺ and Mg²⁺, respectively. This suggests complex solid reaction products with the green component corresponding to a struvite phase rich in both MgCO₃ and CaCO₃, whereas the red component corresponds to a struvite phase rich in CaCO₃.

The TCA maps based on the unique bands of each component shown in Figure 8b for Ca²⁺/Mg²⁺ ratios 0.2 and 1 are shown in Figure 8c,d, respectively. These maps were acquired on a single crystal, as shown in the optical image, in the x-z direction parallel to the laser beam. Effectively, they resulted in the information obtained from the cross-section of a single crystal. In both cases, it can be clearly seen that the red component with notable bands at 947, 993, and 1050 cm⁻¹

Figure 7. (a) CaCO₃ and (b) Ca(OH)₂ pXRD spectra. The corresponding Raman spectral components derived from TCA are shown in (c,d), whereas the component individual peak x–y plane maps are shown in (e,f).
due to struvite is localized in the crystalline product homogeneously. The blue component with the main peak at 1086 cm\(^{-1}\) due to CaCO\(_3\) is localized outside the crystalline product in the particles, which is likely due to the intermediate reactive species. Lastly, in the Ca\(^{2+}\)/Mg\(^{2+}\) ratio of 0.2, the green component with unique peaks at 1120 and 3650 cm\(^{-1}\) due to MgCO\(_3\) is dominantly present outside the crystalline product as part of the particles. For Ca\(^{2+}\)/Mg\(^{2+}\) ratio of 1, the green component was present within the crystals, especially at their edges. Although a dramatic inhibitory effect of Ca\(^{2+}\) on struvite formation was not observed in the current experiments, the presence of unreacted MgCO\(_3\) phase (green component) within the crystalline product can tentatively be interpreted as a result of slight retardation of struvite formation with higher Ca\(^{2+}\) content present in the solution. The absence of a strong inhibitory effect of Ca\(^{2+}\) from CaCO\(_3\) was most likely not observed due to slower dissolution of CaCO\(_3\) compared to MgCO\(_3\), which has been reported in the literature.\(^{73}\) Slower CaCO\(_3\) dissolution led to the excess Mg\(^{2+}\) present in the solution facilitating struvite formation.

Spatial resolution of Raman spectroscopy is dependent upon laser wavelength, as well as numerical aperture-limited and is within \(\sim 1\ \mu m\).\(^{73}\) Complementary electron microscopy analysis was conducted to attain greater resolution to investigate if calcium ions were indeed incorporated into the struvite crystal structure, as shown in Figure 9. For both Ca\(^{2+}\)/Mg\(^{2+}\) ratios of 0.2 and 1, it can clearly be seen that green (Mg), teal (O), and orange (P) components exhibit strong intensities and are colocalized, corroborating homogenous struvite structure of the product. Interestingly, red (Ca) was shown to be present in both the samples in island-like formations, as seen in Figure 9b. By using low-solubility CaCO\(_3\) as the Ca\(^{2+}\) source during struvite formation, Ca\(^{2+}\) was incorporated into the struvite structure to effectively form Ca-incorporated struvite.

**Effect of Ca\(^{2+}\) from High-Solubility CaCl\(_2\) on Solid Product Speciation.** A strong inhibitory effect of Ca\(^{2+}\) on struvite crystal formation was not observed when using low-solubility CaCO\(_3\) precursor, at both Ca\(^{2+}\)/Mg\(^{2+}\) ratios of 0.2 and 1, as shown in Figures 8 and 9. However, inhibitory effect was observed when using soluble CaCl\(_2\), especially in the case of Ca\(^{2+}\)/Mg\(^{2+}\) = 1 (Figure 10). Consistently, two Ca\(^{2+}\)/Mg\(^{2+}\) ratios, namely 0.2 and 1, were used for reactions with aqueous NH\(_4\)\(^{+}\) and PO\(_4\)\(^{3-}\), whereas MgCO\(_3\) and NH\(_4\)H\(_2\)PO\(_4\) concentrations remained the same. This resulted in 1000/600/268...
ppm and 1000/600/1340 ppm of MgCO3/NH4H2PO4/CaCl2, respectively. The solid products were characterized using pXRD and Raman spectroscopy as shown in Figure 10. pXRD analysis showed that at Ca\textsuperscript{2+}/Mg\textsuperscript{2+} ratio of 0.2, struvite was obtained as the major product, whereas in the case of Ca\textsuperscript{2+}/Mg\textsuperscript{2+} ratio of 1, the pXRD pattern did not match that of...
struvite but, instead, matched that of CaCl₂. The latter observation is distinctly different from the data shown in Figure 8, where CaCO₃ was utilized but consistent with the observation is distinctly different. For Ca²⁺/Mg²⁺ of 0.2, the maps show struvite as the dominant solid phase comprised of MgCO₃ according to 1120 and 3650 cm⁻¹. At the time scales used in this study, higher hydromagnesite content (1000–1500 ppm MgCO₃/NH₄H₂PO₄) was needed to form well-defined struvite crystals, whereas lower content—300/600 ppm MgCO₃/NH₄H₂PO₄ corresponding to a substoichiometric [Mg⁺/NH₄⁺/PO₄³⁻] of 0.7:1:1—mostly transformed hydromagnesite into higher crystalline water content species. Moreover, Ca²⁺ source (soluble CaCl₂ vs low-solubility CaCO₃) had a strong effect on the equilibrium solid product speciation. Formation of crystalline carbonate minerals via an amorphous precursor containing Mg²⁺ ions was shown to be kinetically slow, whereas magnesium-substituted amorphous calcite formation was fast. This phenomenon was attributed to the structural water bound to Mg ions hindering dehydration and transformation into the crystalline state. Accordingly, a distinct phase speciation was observed in both pXRD and Raman spectra when CaCO₃ is present, up to Ca²⁺/Mg²⁺ molar ratio of 1, with a maximum reaction time of 120 min. Unique Raman spectral patterns that encompass both PO₄³⁻ and CO₃²⁻ ion vibrations are likely due to the incorporation of isovalent Ca²⁺ and Mg²⁺ carbonate particle inclusions into the struvite crystals. This is a prevalent mode of solid product crystallization at Ca²⁺/Mg²⁺ = 1, whereas at Ca²⁺/Mg²⁺ = 0.2, calcium-containing solid particles are more diffused. Using soluble CaCl₂ at Ca²⁺/Mg²⁺ = 0.2 inhibited the struvite crystal formation to a smaller extent, whereas Ca²⁺/Mg²⁺ = 1 from CaCl₂ exhibited strong struvite formation inhibition, producing an entirely different solid product. Again, in the case of CaCl₂, the maximum reaction time was 120 min. In the case of Ca²⁺/Mg²⁺ = 1 from CaCl₂, calcium hydroxyapatite formation proceeded in parallel to struvite formation, with a unique Raman spectrum that contained CO₃²⁻ ion vibrations. According to the spectral maps, this component was not colocalized with either struvite or hydroxyapatite and can potentially correspond to hydroxylapatite species, where hydroxyl groups are partially substituted by CO₃²⁻ ions.

To summarize, at the time scale studied, the different reaction products observed spectroscopically during reactive transformation of MgCO₃ indicate that struvite crystallization is significantly affected by the composition of the reactive environment, including MgCO₃/NH₄H₂PO₄ ratio, Ca²⁺/Mg²⁺ ratio, and the solubility of the calcium precursor.

■ DISCUSSION

A previous work suggested that solid Mg²⁺ precursor above stoichiometric amount is typically needed to form struvite crystals. The fate of the unreacted Mg²⁺ is of major interest because chiefly, pXRD has been utilized to assess the solid reaction product composition, effectively eliminating from consideration any amorphous intermediates or products, such as magnesium hydroxycarbonates that can form via hydro-magnesite reactions with water under ambient conditions. pXRD data in this work showed that for all MgCO₃/NH₄H₂PO₄ ratios, struvite was the only crystalline product, whereas Raman analysis suggested that a dypingite-like phase was also present. Although the exact phase is difficult to assign from Raman spectrum only, the dypingite phase is expected because a dypingite unit cell is more expanded than hydromagnesite because of higher crystalline water content. Similar equilibrium product was observed in parallel with struvite formation using MgO particles with the reaction following pseudo-second-order kinetics. However, adsorption of PO₄³⁻ ions on hydromagnesite followed pseudo-first-order kinetics suggesting no complex kinetics of hydromagnesite hydration to form a reactive intermediate, in contrast to the MgO case, where the rate-controlling step was OH⁻ adsorption followed by Mg²⁺ and OH⁻ desorption. At the time scales used in this study, (maximum reaction time of 120 min), higher hydromagnesite content (1000–1500 ppm MgCO₃/NH₄H₂PO₄) was needed to form well-defined struvite crystals, whereas lower content—300/600 ppm MgCO₃/NH₄H₂PO₄ corresponding to a substoichiometric [Mg⁺/NH₄⁺/PO₄³⁻] of 0.7:1:1—mostly transformed hydromagnesite into higher crystalline water content species.

Our results present spectral evidence of different transformation products of MgCO₃ particles—in the form of hydromagnesite—in NH₄⁺ and PO₄³⁻-containing aqueous
solutions, with and without Ca$^{2+}$ ions present. The formation of the crystalline phase struvite was observed using pXRD in predominant number of solution compositions except when CaCl$_2$ at Ca$^{2+}$/Mg$^{2+} = 1$ was used, with all studies at a maximum reaction time of 120 min. Ex situ Raman spectra, however, provided much deeper understanding of the low crystallinity solid materials not identified via bulk X-ray analysis. For MgCO$_3$ concentrations where significant saturation resulted in significant precipitation of both NH$_4$PO$_4$ and PO$_4^{3-}$ (MgCO$_3 > 500$ ppm; NH$_4$H$_2$PO$_4 = 600$ ppm; [Mg$^{2+}$/NH$_4^+$] = 1.1:1:1), formation of solid struvite was accompanied by a dipydite-like phase formation due to the extra water molecule incorporation into the crystalline structure of the hydromagnesite. Single crystal Raman and STEM/EDXS studies showed complex solid materials formed with Ca$^{2+}$ substituting into the structure of struvite crystals as submicron crystallites. These crystallites possess functional groups of PO$_4^{3-}$ and CO$_3^{2-}$ from both MgCO$_3$ and CaCO$_3$. A distinct difference in solid product speciation was observed when CaCl$_2$ was used as the calcium source. Crystallinity of the struvite product significantly decreased when Ca$^{2+}$/Mg$^{2+} = 0.2$ was used, whereas a distinct shift toward calcium hydroxyapatite was observed for Ca$^{2+}/Mg^{2+} = 1$. These observations clearly highlight the importance of the physicochemical parameters, such as concentration of MgCO$_3$, pH, Ca$^{2+}$ ion concentration, and the solubility of their source on the formation of a distinct crystalline struvite phase. Results presented herein have implications for nutrient (N and P) recovery and recycling from wastewater streams in the form of sustainable, slow-release fertilizers utilizing insoluble and abundant magnesium minerals.

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**Author Contributions**

B.L. and D.K. contributed equally. B.L. performed struvite growth and IC studies, W.T. performed struvite growth at different Ca$^{2+}$/Mg$^{2+}$ precursor ratio, D.B. and D.K. performed Raman analysis, K.H. performed pXRD studies, and L.Z. performed STEM measurements. Lastly, J.B. & D.K. performed experimental design, data analysis, and wrote the manuscript.

**Notes**

The authors declare no competing financial interest.

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