The interaction between arsenic and struvite during coprecipitation and adsorption processes

Ning Ma
Graduate Center, City University of New York

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The Interaction between Arsenic and Struvite during Coprecipitation and Adsorption Processes

By

Ning Ma

A dissertation submitted to the Graduate Faculty in Earth and Environmental Sciences in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York

2014
This manuscript has been read and accepted for the Graduate Faculty in Earth and Environmental Sciences in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Jacob Mey

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Ashaki A. Rouff

Supervisory Committee

THE CITY UNIVERSITY OF NEW YORK
Abstract

The Interaction between Arsenic and Struvite during Coprecipitation and Adsorption Processes

By Ning Ma

Adviser: Dr. Ashaki A. Rouff

The formation of struvite, MgNH₄PO₄·6H₂O (MAP), from wastes is one of the methods that can be used to recover P from wastes efficiently. However, since there are usually toxic components in the wastes, like arsenic (As), the possibility of having toxic contaminants in MAP is a big concern. So, the interaction between As and MAP during coprecipitation (CPT) and adsorption (ADS) processes were studied at pH 8-11. MAP precipitated without As at pH 8-11 was also characterized.

During CPT process, the MAP was precipitated from a MgCl₂-(NH₄)₂HPO₄-NaCl-H₂O system spiked with As at an initial pH (pHᵢ) of 8-11. The batch experiments showed that more As was found in the solids at higher pH and pentavalent As, As(V), was the favorable As oxidation state in the solids. The results from X-ray absorption fine structure spectroscopy (XAFS) indicated that As(V) was incorporated in the solids; whereas the trivalent As, As(III), was adsorbed on the mineral surface. The solids precipitated at pHᵢ 8-11 without the addition of As were also characterized. The ³¹P nuclear magnetic resonance spectroscopy (NMR) confirmed that over 95% of phosphate was in MAP at pHᵢ 8-10, with newberyite (MgHPO₄·3H₂O) as a minor crystalline phase. At pHᵢ 11, only 60% of the
phosphate was in MAP, with 22% and 18% in an amorphous phase and sodium phosphate, respectively.

The As adsorption using MAP and hydroxylapatite (HAP), Ca$_5$(PO$_4$)$_3$OH, studied in a MgCl$_2$-(NH$_4$)$_2$HPO$_4$-NaCl-H$_2$O system with pH fixed at 8-11. As the pH was increased, more As(V) was removed from the solution for both MAP and HAP; for As(III), the removal by either MAP or HAP were limited for pH 8-11. Using radioactive $^{33}$P, a faster phosphate exchange at the mineral-water interface was found on HAP. The XAFS results showed the adsorbed As(V) formed monodentate mononuclear surface complexes on MAP and, for HAP, As(V) was incorporated near the mineral surface.

The studies in this thesis about the interaction between MAP and As can be helpful in producing low-As MAP with maximum recycle of P from wastes with high As concentration and using MAP as an adsorbent to remove As from phosphate-rich wastes.
Acknowledgements

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In the end, I would like to thank my parents for their love, understanding and support through all my studies in universities from China to the US.
Contents

Abstract ........................................................................................................................................ iv
Acknowledgements .................................................................................................................. vi
List of Tables .......................................................................................................................... ix
List of Figures ........................................................................................................................ xi
Chapter 1. Introduction and Background ................................................................................... 1

Chapter 2. The Influence of pH and Oxidation State on the Interaction of Arsenic with Struvite During Mineral Formation ................................................................. 17

Abstract ........................................................................................................................................ 17
Introduction ..................................................................................................................................... 18
Materials and Methods ............................................................................................................... 20
Results and Discussion ................................................................................................................ 23
Acknowledgements ..................................................................................................................... 33
Supporting Information ................................................................................................................ 40

Chapter 3. A 31P NMR and TG/DSC-FTIR Investigation of the Influence of Initial pH on Phosphorus Recovery as Struvite .................................................................................. 48

Abstract ........................................................................................................................................ 48
Introduction ..................................................................................................................................... 49
Material and Methods .................................................................................................................. 52
Results and Discussion ................................................................................................................ 55
Acknowledgements ..................................................................................................................... 63
Supporting Information ................................................................................................................ 73

Chapter 4. The Adsorption of Arsenic on Struvite and Hydroxylapatite in Phosphate-rich Aqueous Phase ................................................................................................................... 74
List of Tables

Table 1.1. Phosphate rock production and resources for 2012 (USGS, 2012). ................................................................. 10

Table 2.1. Structural parameters derived from EXAFS analysis of As(III) and As(V) standards, pH 10-11 As(III), and pH 8-11 As(V) solids. ................................................................. 35

Table S2.1. Dissociation constants for phosphoric acid, arsenous acid and arsenic acid (Lide, 2005). ................................................................. 40

Table S2.2. Final measured pH values for solutions after 24 hours reaction and prior to filtration. ................................................................. 40

Table S2.3. The fraction of redox species in initial As(III) and As(V) solutions after equilibration as predicted by PHREEQC (Parkhurst and Appelo, 1999). Calculated final pH values are consistent with the measured values reported in Table S2.2. ................................................................. 41

Table S2.4. Final As concentrations of struvite precipitated from solutions with 5-50 µM (0.37-3.75 ppm) As(III) or As(V) at pH 8 only. Samples were prepared as described in the Materials and Methods section, except the As concentration was varied. For solids from As(III) solutions, As was not detected (n.d.). For solids generated from As(V) solutions, the As concentration increased with increasing initial As(V) concentration. EXAFS analysis of As(V) solids with sufficient loadings indicated similarity in the fit parameters to the As-O shell, suggesting consistency in the sorption mechanism regardless of initial As concentration. ................................................................. 42

Table 3.1. Relative integrated intensities of $^{31}$P MAS/NMR peaks observed for solids synthesized at pH 8-11 and estimated uncertainties. n.d. means none detected. ................................................................. 67
Table 3.2. Concentrations of evolved H$_2$O(g) and NH$_3$(g) per gram of solid synthesized at pH 8-11. The error for these measurements is ± 0.11 %. The NH$_3$(g) evolved is reported for temperatures from 40-200 °C (≤ 200 °C), and 200-400 °C (≥ 200 °C). The ratio of H$_2$O(g) to total NH$_3$(g) (40-400 °C) and to NH$_3$(g) evolved at 200-400 °C is determined. …………………… ……………………………………………………………………………………………………………………………………………68

Table 4.1. Molar concentrations of phosphate (P) and As and the molar ratio between phosphate and As (P/As) for pH 8-11 solutions. …………………………………………………………………………………………………………………………………………………………………………………………………………………….. 94

Table 4.2. Molar concentration of As(III) species, based on the total As concentration in Table 1. All results were calculated by PHREEQC using the minteq.v4 database. …………………………………………………………………………………………………………………………………………………………………………………………………………………………………….. 95

Table 4.3. Molar concentration of P and As(V) species, based on the total concentrations of P and As in Table 4.1, and the molar ratio of P and As(V) species with same charge. All results were calculated by PHREEQC using the minteq.v4 database. ……………………………………………………………………………………………………………………………………………………………………………………………………………………………………………….. 96

Table 4.4. Structural parameters derived from EXAFS analysis of MAP and HAP solids reacted with As(V) for seven days at pH 10 and 11. The structural parameters of the model minerals are also listed. ………………………………………………………………………………………………………………………………………………………………………………………………………………………………………………. 97
List of Figures

Figure 1.1. P in everyday life (PHOSAGRO, 2011) ................................................. 11

Figure 1.2. Global sources of phosphorus fertilizers (1800-2000) (Cordell, et al. 2011) .............................................................. 12

Figure 1.3. Anthropogenic P input to the ocean and satellite image of eutrophication caused by excess P in the ocean (Filippelli, 2008) ................................................................. 13

Figure 1.4. World phosphate rock production (USGS, 2010) ........................................ 14

Figure 1.5. Commercial MAP based fertilizer Crystal Green®, Ostara (Ostara, 2014) ... 15

Figure 1.6. Pilot-scale MAP crystallizer reactor process design from sewage water (left) (Britton, et al. 2005) and reactor for the production of MAP from urine (right) (Etter, et al. 2011). ........................................................................................................... 16

Figure 2.1. a) Saturation Index (SI) of struvite and; b) solid yield for blank (As-free), As(III) and As(V) solids as a function of pH. ................................................................. 36

Figure 2.2. Total As concentration of As(III) and As(V) solids as a function of pH reported on a log scale. Inset: As concentrations are reported on a linear scale. .......... 37

Figure 2.3. a) XANES spectra and b) first derivative plots of As(III) and As(V) standards, and pH 10-11 As(III), and pH 8-11 As(V) solids. Dashed lines at 11.869 and 11.872 indicate the positions of the white lines for the standards at ~2eV units greater than the edge energy. ................................................................. 38

Figure 2.4. a) $k^3$ weighted EXAFS $\chi$ functions and b) corresponding Fourier transform amplitudes and curve fitting analysis to the inversely Fourier-filtered $k^3\chi$ function in $k$-
space for As(III) and As(V) standards, and pH 10-11 As(III) and pH 8-11 As(V) solids. Experimental data (solid lines) and fits (dotted lines) are shown.

Figure S2.1. The speciation of a) phosphoric acid, b) arsenic acid and c) arsenous acid with pH (Lide, 2005).

Figure S2.2. The theoretical XRD pattern of struvite based on the reference file JCPDS 15-0762 and consistent with that was reported before (Ferraris, et al. 1986).

Figure S2.3. XRD spectra of blanks (As-free), As(III) and As(V) solids at pH 8-11.

Figure S2.4. FT-IR spectra of blanks (As-free), As(III) and As(V) solids at pH 8-11.

Figure S2.5. Time-dependent XAFS spectra for the As(III) solid at pH 11, demonstrating no change in the collected spectra with time, demonstrating no beam-induced oxidation (Manning, et al. 1998). The oxidation of As(III) likely occurred in solution prior to sorption (Manning and Goldberg, 1997).

Figure 3.1. PO₄-P concentrations in solution during solid precipitation at pH; 8-11 over a 24 hour period. The final pH in solution is indicated in brackets.

Figure 3.2. SEM images of solids precipitated at pH; 8-11.

Figure 3.3. XRD patterns of a) solids precipitated at pH; 8-11; b) the solid precipitated at pH; 11. The letters ‘S’ and ‘N’ represent the peaks related to struvite and sodium phosphate, respectively.

Figure 3.4. Quantitative ³¹P MAS/NMR spectra of solids precipitated at the indicated pH; values. Peaks occurring at 8.3, 6, 1.5, and -7 ppm are assigned to kovdorskite, struvite, an
amorphous phase, and newberyite, respectively. Spectra were acquired by direct excitation with 120 s relaxation delays at a spinning rate of 8 kHz and represent 80 acquisitions each.

Figure 3.5. DSC (solid lines) and TG (dashed lines) curves for solids precipitated at pH 8-11. The onset temperature (O.T.) and the peak temperature (P.T.) are represented as open symbols on the DSC curve, with values reported in the legend (± 0.5 °C). The total mass loss (M.L.) as determined from the TG curve at 400 °C is also reported in the legend (± 0.2 %).

Table S3.1. Saturation Index (SI) of P-bearing minerals and pH before and after the precipitation of struvite calculated by PHREEQC using the minteq.v4 database. The initial and final pH were labeled as pH_i and pH_f, respectively.

Figure 4.1. Adsorption of As(III) and As(V) in pH 8-11 solutions using MAP or HAP as absorbent for seven days. All of the As concentrations were relative to the As concentrations in the blanks at the same pH, respectively.

Figure 4.2. Removal of $^{33}$P (a) and phosphate (b) from pH 10 and pH 11 solutions with MAP or HAP after seven-day pre-equilibration. The phosphate concentrations in (b) were relative to the phosphate concentrations in Table 1 for pH 10 and 11 solutions, respectively.

Figure 4.3. (a) $k^3$ weighted EXAFS $\chi$ function and (b) corresponding Fourier amplitudes and curve fitting analysis to the inversely Fourier-filtered $k^3\chi$ function in k-space for MAP and HAP solids reacted with As(V) for seven days in pH 10 and pH 11 solutions. Experimental data (solids lines) and fits (dotted lines) are shown.

Figure S4.1. Adsorption of As(III) and As(V) in pH 8-11 solutions using MAP and HAP normalized by the mineral surface area. The As concentrations of the blanks were considered as 100%.
Figure S4.2. As concentration in MAP and HAP solids reacted with As(V) in pH 10-11 solutions for 7 days.
Chapter 1. Introduction and Background

Phosphorus (P) is an important element in all forms of life. It can be found in RNA, DNA, ATP and all sorts of membranes, etc. For humans, about 1% of human body weight is P and about 0.1% of total P is needed from food to replenish P lost every day. In agriculture, where people get most of their P supply, P is a crucial nutrient for all plants. For wheat, with extra P supply, the yield is 5 ton/ha compared to 1.6 ton/ha without P on the same arable land (EFMA, 2000). The demand for P from agriculture is huge, tens of millions of tons per year, which increases about 2.5% every year as the world population keeps growing (Steen, 1998). Besides agriculture, P is also needed in industrial processes and is manufactured into detergents and other products, which will cost every family hundreds of dollars per year (Figure 1.1) (PHOSAGRO, 2011). Overall, the global demand for P is about 400 million tons/year (Shu, et al. 2006) and increases 1.5%-2.5% every year as the world population keeps growing (Blodget and Wile, 2012).

P has no stable gaseous phase in the natural environment and thus can only exist in the aqueous or solid phases, mainly as phosphate in different compounds. The largest natural P source is phosphate-bearing rock. Due to the low solubility of phosphate-bearing rocks, the P concentration is usually lower than 1 ppm in soil and the ocean (Busman, et al. 2002; Jacobson, et al. 2000). Although a great amount of P is needed by all kinds of organisms, P is usually a limiting nutrient in terrestrial and marine ecosystems.
The leachable P in the soil can be dissolved in water and carried away, which is also called the redistribution of P. In prehistoric times, the weathering of phosphate-bearing rocks and soil was the main source of P in runoff and streams. Under this circumstance, the redistribution of P happens very slowly, and is controlled by the weathering of phosphate-bearing rocks and soil. The runoffs and streams can dissolve part of the leachable P and carry it to the ocean. The rest of the leachable P is used by plants and enters the food chain. Food is then consumed by the animal habitats nearby and became wastes. Since manure and human excreta are the oldest P fertilizer, due to the limitation of food transportation, this food-human/animal-wastes-fertilizer-food cycle can be considered as a closed P cycle.

However, after the industrial revolution, the growth in population increased the demand for food. The mining of phosphate rock seems to be the only way of getting a huge amount of P at low cost as fertilizer (Figure 1.2) (Cordell, et al. 2011). Thus, more phosphate rock was mined and the redistribution of P in natural environments was expedited. Due to the demand of food from cities, the once closed P cycle was broken as more and more food was transported to cities. The excess P in the runoffs from agriculture and human activities will end up in the ocean and is notorious for the increasing eutrophication events in the past few decades. It impairs the water quality and the fishery industry and even the whole global aquatic ecosystem (Figure 1.3) (Filippelli, 2008).

Nowadays, the production of phosphate-bearing rock is increasing and dominated by several countries around the world (Table 1.1; Figure 1.4) (USGS, 2010, 2012). Fifteen countries contribute over 95% of the world’s total phosphate-bearing rock production.
China, Iraq, Morocco and Western Sahara have more than 80% of the world phosphate-bearing rock resource. As it is predicted by the Hubbert linearization method, the world phosphate production will reach its peak in 20-30 years, around 2020 (Blodget and Wile, 2012). The cost of mining phosphate-bearing rock and the price of P-based fertilizer will increase. For countries that do not have enough reserved phosphate-bearing rock, like Canada and most European countries, import would be the only way to solve the P crisis, which would lead to possible national security concerns.

As mining of phosphate-bearing rock mobilizes more P, the broken cycle of P will get worse (Gilbert, 2009), the recycling of P has been proposed to deal with this P crisis. An old type of fertilizer, human excreta and animal wastes, was reconsidered as an approach to amend the broken P cycle. Based on the fact that the world population is about 7 billion, the P in human wastes is about 10% of the total P demand in 2009. Besides human waste, animal manure is also a traditional source of P. In 2005, 335 million tons of dry manure was produced in the U.S. (USDA, 2005). If the P in this manure is 0.5% by weight (Cordell, et al. 1998), it is about 4% of the world P demand in 2009. Considering the world population and the number of livestock around the world, it is definitely a feasible way to fulfill the P demand by using human and animal wastes. However, as we know, most of the manure has been used as a natural fertilizer directly and most of P in manure is soluble and will be easily washed away by rain and irrigation. So, it is important to fix the P in the wastes first during the recycling of P.
Recycling of P from wastes has been studied using different approaches. The main approaches are chemical and/or biological ones. Chemical methods are aimed to precipitate P in the form of phosphate minerals, like FePO₄ (Fytianos, et al. 1998). But these methods produce inert materials with very low solubility and cannot be easily reprocessed for fertilizer and will cost extra to dispose of. The biological methods can remove P when certain bacteria uptakes P to reproduce (Fuhs and Chen, 1975). However, these methods require a high level of biodegradable organic matter and sophisticated designs, which will cost more than the precipitation methods (Parsons and Smith, 2008).

Struvite, MgNH₄PO₄·6H₂O (MAP), is a mineral found in animal habitats first and later in wastewater treatment systems. It can be used as a means to fix the dissolved P in wastes and recycle the P in the form of fertilizer. Around the mid-19th century, MAP was first found in a German church, where cattle manure left on the soil became phosphate minerals, and in the coastal area of Africa, where plenty of guano was also found due to the activity of birds (Griffith, 1978). In the present day, MAP is commonly seen as a mineral formed inside the pipes in the wastewater treatment system. Its formation is due to the high concentration of magnesium, ammonium and phosphate in the effluent of anaerobic digestion chambers. To avoid clogging, removing MAP precipitates is necessary and has become laborious work.

As more and more people are aware of the coming phosphorus shortage, MAP has been studied and special designs were invented to help precipitate MAP from municipal sewage water to remove P and prevent clogging. Adding magnesium chloride solution and/or
adjusting the pH can be used to precipitate MAP from sewage water. The precipitated MAP is a high quality fertilizer. The low solubility allows it to release nutrients, magnesium (Mg), nitrogen (N), P, for a relatively long time. In the fertilizer market, MAP is labeled as 5-28-0 (nitrogen: phosphate: potash). The N and P gradually released by MAP will meet the demand of most plants. The high Mg content, 10% wt., makes MAP a better fertilizer for plants with green leaves.

The MAP produced from municipal wastewater and human urine has succeeded in removing excess P and has been used as fertilizer in many countries. One of the successful methods to produce MAP is done by the Ostara Nutrient Recovery Technologies Inc. using municipal wastewater. The commercial name of the recovered MAP by Ostara is Crystal Green® (Figure 1.5). It has already been used in agriculture and fishery (Ostara, 2014). Three sets of treatment equipment have been installed in North America to produce Crystal Green® by the year of 2012 and more will be installed in Europe in the near future. Beside municipal wastewater, human urine is also a common waste that has high P concentration, which has been used to generate MAP by the groups from Swiss Federal Institute of Aquatic Science and Technology (EAWAG) in Nepal and South Africa (Figure 1.6) (Etter, et al. 2011). In the rural areas of these countries, human urine was collected from source separated toilets and mixed with magnesium solution to produce MAP. The MAP was later used as fertilizer by the farmers in these countries. Besides the P sources mentioned above, swine wastewater (Jordaan, et al. 2010; Ryu and Lee, 2010), and confined animal feeding operations (Wang, et al. 2005) were also used to precipitate MAP to recover P.
Although the MAP recovered from municipal wastewater, human urine and other sources can be used as a novel fertilizer, whether the application of MAP can contaminate the soil is a real concern. The sources of MAP are usually rich in heavy metal/metalloid elements, like municipal wastewater, and pharmaceuticals, like human urine and animal manure. If recovered MAP was used as slow release fertilizer, trace amounts of heavy metal and pharmaceuticals, if any, would be utilized by the plants through the slow dissolution of MAP. Once the contaminated plant is harvested and manufactured into food, the contaminants will enter the food chain and accumulate in human tissue and possibly cause chronic diseases. At the same time, the soil, where the contaminated MAP was applied, will become non-arable.

Whether heavy metal/metalloid elements and pharmaceuticals can be removed by MAP during its precipitation process, and if so, how could those contaminants affect the MAP structure are still unknown. Several studies have been done to test the heavy metal and pharmaceuticals in recovered MAP (Ronteltap, et al. 2007). But the contaminants from the P source of recovered MAP can vary from place to place. A better way to study the possible interaction between contaminants and MAP is through carefully controlled laboratory experiments.

One of the possible contaminants in MAP is arsenic (As) (Ueno and Fujii, 2001). As a natural occurring and widely used element, As can be found in drinking water and groundwater and is considered a global hazard. Chronic exposure to As can cause skin cancer, lung cancer, bladder cancer and other diseases (Jomova, et al. 2010). In Bangladesh
and West Bengal, India, 35 to 50 million people are suffering As poison due to the elevated concentration in groundwater, with an average of 200 µg/L As in 3534 tubewells (Chakaborti, et al. 2003; Stuben, et al. 2003; Smedley and Kinniburgh, 2002). Being the major water source of irrigation, groundwater is also responsible for the elevated As concentration in the surface soil and the crops in Bangladesh (Harvey, et al. 2002; Abedin, et al. 2002). Worldwide, the current Maximum Contaminant Level (MCL) for As in drinking water is 10 µg/L, established by the World Health Organization (WHO) and the United States Environmental Protection Agency (USEPA) (EPA, 1999). In the United States, about 10% of wells exceed the USEPA MCL for arsenic, which put 13 million people at the risk of chronic As exposure (Welch, et al. 2009).

Another reason to study the interaction between As and MAP is because this toxic metalloid can readily substitute for P in mineral structures (Lee, et al. 2009). This is due to the similarities in configuration, chemical properties, and ionic radii of the AsO$_4^{3-}$ (2.48 Å) and PO$_4^{3-}$ (2.38 Å) oxyanions (Marcus, 1997). In addition, As is known to form the MAP analog arsenstruvite (MgNH$_4$AsO$_4$·6H$_2$O) (Weil, 2008; Mohan and Pittman, 2007). The concentration of As in municipal wastewater, animal manure and even human urine, can range from 100 ppb, to relatively high concentrations of up to ~15 ppm (Calderon, et al. 1999; Cortinas, et al. 2006; Meng, et al. 2001). Thus if present, As may compete with, and substitute for P in the MAP structure by coprecipitation (CPT) during recovery (Meng, et al. 2001). Reduction or oxidation of As may take place, which can change the oxidation states of As and its behavior during the CPT process. It is critical to understand the
interaction between As and MAP as significant association of As with recovered MAP may pose an environmental risk to soils if it is subsequently used as fertilizer.

Besides the CPT process, the adsorption (ADS) process using MAP as a sorbent could help to remove As from aqueous phases. Although different kinds of sorbents have been developed to remove As through ADS processes (Mohan and Pittman, 2007; Mondal, et al. 2006), phosphate mineral based sorbents were barely studied. Due to its capability of removing As from solutions with high phosphate concentration, the study of phosphate minerals, like MAP in this thesis, could benefit the removal of As in certain complex aqueous environments.

The work in this thesis focuses on the interaction between As and MAP during the CPT and ADS processes. For the CPT process, experiments were conducted at pH 8-11 as MAP recovery is maximized within this range (Mondal, et al. 2006). For the ADS process, the interaction between As and MAP was studied at pH 8-11. Hydroxylapatite (HAP), \( \text{Ca}_5(\text{PO}_4)_3\text{OH} \) was also studied as a sorbent in the ADS process to compare the As removal efficiency of MAP. Due to the redox-sensitive behavior of As, in CPT and ADS processes, both trivalent As, As(III), and pentavalent As, As(V), were used separately as the As source. All As-containing solids were subjected to X-ray absorption fine structure spectroscopy (XAFS) to study the coordination environments of As in order to shed light on its sorption mechanisms. Besides XAFS, other methods were used to characterize the solids, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), scanning electron microscopy (SEM) and
thermogravimetric analysis (TG). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to analyze As concentration in the aqueous phase and the acid-digested solids. In the ADS experiments, radioactive $^{33}$P was also used, in order to study the exchange of phosphate at the water-mineral interface and to help understand the ADS of As on MAP and HAP.

The results of this thesis are critical in understanding the interaction between MAP and As in CPT and ADS processes in alkaline solutions. They will ultimately benefit the use of MAP-based fertilizers and promote the sustainable use of P and the conservation of geologic P resources.
Table 1.1. Phosphate rock production and resources for 2012 (USGS, 2012).

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production</th>
<th>Reserves</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2010</td>
<td>2011</td>
</tr>
<tr>
<td>United States</td>
<td>25,800</td>
<td>28,400</td>
</tr>
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<td>1,800</td>
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<td>5,000</td>
</tr>
<tr>
<td>Other countries</td>
<td>6,400</td>
<td>7,400</td>
</tr>
<tr>
<td>World total (rounded)</td>
<td>181,000</td>
<td>191,000</td>
</tr>
</tbody>
</table>
Figure 1.1. P in everyday life (PHOSAGRO, 2011)
Figure 1.2. Historical global sources of phosphorus fertilizers (1800-2000) (Cordell, et al. 2011)
Figure 1.3. Anthropogenic P input to the ocean and satellite image of eutrophication caused by excess P in the ocean (Filippelli, 2008)
Figure 1.4. World phosphate rock production (USGS, 2010).
Figure 1.5. Commercial MAP based fertilizer Crystal Green®, Ostara (Ostara, 2014).
Figure 1.6. Pilot-scale MAP crystallizer reactor process design from sewage water (left) (Britton, et al. 2005) and reactor for the production of MAP from urine (right) (Etter, et al. 2011).
Chapter 2. The Influence of pH and Oxidation State on the Interaction of Arsenic with Struvite During Mineral Formation

Abstract
Struvite (MgNH$_4$PO$_4$·6H$_2$O) precipitated from animal and human wastes may be a sustainable source of fertilizer. However, arsenic, present in some wastes, may be removed with struvite. Here the sorption of As with struvite during mineral formation at pH 8-11 was assessed. The yield of struvite increased with pH, and was highest at pH 10. For recovered struvite, XRD indicated reduced crystallinity and particle size, and FT-IR suggested less distortion of phosphate tetrahedra with increased pH. The As impurity did not affect the crystallinity or particle size, but did contribute to phosphate distortion. Sorption of As(V) was observed at all pH values, and was highest at pH 10. As(III) sorption was consistently lower than that of As(V), but increased with pH. XAFS suggested coprecipitation of As(V), and adsorption of As(III) as the potential sorption mechanisms. Solids derived from As(III) solutions exhibited dual mechanisms due to the partial oxidation of As(III) to As(V) in solution prior to sorption. For struvite recovery in the presence of As, optimizing the pH to improve yields may increase the As content. Adsorbed As(III) could be removed prior to fertilizer application, however coprecipitated As(V) will release upon mineral decomposition, linking its cycling to that of phosphorus.
Introduction

Phosphorus (P) is a vital element to all forms of life. The largest P source on earth is sequestered in minerals, predominantly apatite (Ca$_5$(PO$_4$)$_3$(OH)) in phosphate-bearing rocks (Oelkers and Valsami-Jones, 2008) considered a non-renewable resource. As a limiting nutrient in ecosystems, P is widely used in agriculture, primarily in the form of fertilizers (Suttle, 2010). However, in the past 150 years the demand for P has increased dramatically, and will continue to do so as the global population rises exponentially (Oelkers and Valsami-Jones, 2008). As the production of P fertilizers accounts for 80-90% of phosphate mined from rocks (Childers, et al. 2011), a greater dependence on non-renewable geologic phosphate reserves is anticipated (Elser and Bennett, 2011). This means that alternative sources of P require exploration.

Removal and recovery of P from wastewater by chemical precipitation and microbial activity is receiving attention as a solution to meet the rising P demand (Parsons and Smith, 2008; Gilbert, 2009). Previous research has indicated that P can be recovered from sewage sludge (Doyle and Parsons, 2002; Uysal, et al. 2010), swine wastewater (Jordaan, et al. 2010; Ryu and Lee, 2010), confined animal feeding operations (Wang, et al. 2005) and urine (Prywer and Torzewska, 2009; Ronteltap, et al. 2010; Etter, et al. 2011; Sakthivel, et al. 2012) through induced precipitation as the mineral struvite (MgNH$_4$PO$_4$·6H$_2$O). This involves the crystallization of struvite from a solution oversaturated with respect to its constituent ions, which in turn may be achieved by adjusting parameters such as the pH, and ion content of the waste (Le Corre, et al. 2009). Approximately 60-98% of P can be recovered from targeted wastes as struvite (Le Corre, et al. 2009), which can provide 10-
50% of the P required for fertilizer use. Due to its high P content and slow P release rate, struvite is in turn a suitable substitute for fertilizers derived from phosphate rocks (Manning, 2008).

One concern, that has not been adequately addressed, is that wastes targeted for P recovery may contain elevated concentrations of metals and other contaminants which may associate with struvite during precipitation. One such contaminant is the toxic metalloid arsenic (As), with reported concentrations in urine, manure and sewage sludge ranging from ~100 ppb up to ~15 ppm (Ronteltap, et al. 2007; Calderon, et al. 1999; Cortinas, et al. 2006; Phyllis Database, 2011). Even at low initial concentrations, As was found to be removed with struvite precipitated from urine (Ronteltap, et al. 2007) and a sewage sludge effluent (Uysal, et al. 2010). The sorptive behavior of As with struvite, however has not been previously considered. Various sorption mechanisms may be of relevance, including the coprecipitation of As into the struvite structure during formation, or adsorption to the surface of the precipitated mineral. Of note is that As(V) can readily substitute for P in mineral structures due to the similarity in configuration, chemical properties, and ionic radii of the arsenate, AsO$_4^{3-}$ (2.48 Å) and phosphate, PO$_4^{3-}$ (2.38 Å) oxyanions (Marcus, 1997). This is substantiated by the formation of the struvite analog arsenstruvite (MgNH$_4$AsO$_4$·6H$_2$O) (Ferraris and Franchini-Angela, 1973), which has previously been suggested as a means of removing As from contaminated wastewater (Weil, 2008). This implies that during struvite recovery AsO$_4^{3-}$ may coprecipitate with the mineral by substitution at PO$_4^{3-}$ sites. However, this is complicated by the redox reactivity of As, whereby the presence of As(III) as arsenite AsO$_3^{3-}$, may affect the extent (Dixit and Hering,
2003; Burton, et al. 2009) and mechanism of sorption. Despite the known association of As with struvite, and the likely influence of its oxidation state on this process, there are no previous systematic studies elucidating the sorption mechanisms of As with struvite.

This is a novel study to examine the sorption of As(III) and As(V) with actively precipitating struvite. The goal of this research is to delineate the aqueous conditions under which As sorption with struvite occurs, and to determine the dominant mechanisms dictating this sorption process. This is critical as contingent upon the final As concentration, oxidation state, and binding mechanism, struvite repurposed as fertilizer may pose an environmental risk to soils and organisms. Furthermore, identification of the sorption mechanism can be used to predict the conditions of As release prior to, and once struvite is applied to soils. Ultimately, this research is a first-step in determining the potential environmental impact of struvite fertilizers. This will advance the use of struvite for this purpose, ultimately recouping P otherwise lost in wastes. In turn this will promote the sustainable use of P and the conservation of geologic P resources.

Materials and Methods

Batch experiments

All solutions were prepared with de-ionized water at room temperature (~20-22 °C) in high density polyethylene (HDPE) bottles. Stock solutions of 10 mM As were prepared using NaAsO₂ and Na₂HAsO₄·7H₂O as the sources of As(III) and As(V), respectively. The solutions were freshly prepared before use. Solutions of MgCl₂·6H₂O and (NH₄)₂HPO₄ were prepared such that when mixed in equal volumes their final concentrations would be
17 mM, and the initial saturation index (SI) of struvite would be at least 2. This initial SI value was chosen as it is known to produce a homogeneous struvite precipitate (Bouropoulos and Koutsoukos, 2000). The required solution chemistry was calculated using the software PHREEQC (Parkhurst and Appelo, 1999) with the minteq.v4 database, and the struvite solubility product from the literature (Ohlinger, et al. 1998). The ionic strength of all solutions was adjusted to 0.1 M with NaCl.

For the precipitation experiments, the (NH₄)₂HPO₄ solution was spiked with 50 µM (3.7 ppm) of either As(III) or As(V). This concentration was chosen as it is an intermediate value in the range of As concentrations observed in various wastes (Ronteltap, et al. 2007; Calderon, et al. 1999; Cortinas, et al. 2006; Phyllis Database, 2011), and to provide sufficient solid loadings for the subsequent characterization of sorbed As. The As bearing (NH₄)₂HPO₄ solution was then mixed with an equal volume of the MgCl₂·6H₂O solution in the presence of 0.1 g/L of commercial struvite (Alfa Aesar), added as seed. The seed material is used to overcome the initial energy barrier associated with particle nucleation, and furthermore is known to optimize the crystallization of struvite during the precipitation process (Le Corre, 2006). Titration to adjust the sample pH was initiated within < 10 seconds after mixing. The pH was adjusted to 8, 9, 10 or 11, using a 2N NaOH solution. These values were chosen as struvite recovery is known to be most efficient within this range (Stratful, et al. 2001), which often necessitates adjusting the pH of wastes to facilitate struvite formation (Le Corre, et al. 2009). Precipitation was observed within the first few minutes of mixing however, the suspension was allowed to react for 24 hours to ensure that this process was complete. At the end of the reaction time aqueous samples were recovered.
using 0.45 µm syringe filters. The entire solution volume was then filtered and the recovered solids were allowed to dry at room temperature. These solids are subsequently referred to by the initial As oxidation state in the solution from which they were formed i.e. As(III) and As(V) solids. All samples were prepared in duplicate. Filtered aqueous samples and acid-digested solids were analyzed for total As by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer DV 5300 instrument. Arsenic-free solids were precipitated under identical conditions to those described above at pH 8, 9, 10 and 11 for use as blanks.

**Powder x-ray diffraction (XRD)**

XRD analysis was performed using a Philips X’Pert Pro instrument. In preparation for analysis the solids were pulverized using a mortar and pestle, and mounted on glass slides in an acetone slurry. Spectra were collected using CuKα radiation over the range of 5-50° 2θ, in 0.02° steps with a counting time of 0.6 s per step. The obtained spectra were background corrected and analyzed by the Rietveld method using X’Pert Highscore Plus from PANAnalytical B.V.

**Fourier transform infrared spectroscopy (FT-IR)**

Data were collected in attenuated total reflectance (ATR) mode using a Perkin Elmer Spectrum 100 FT-IR spectrometer and a universal ATR accessory, equipped with a ZnSe crystal. The pulverized solid was mounted directly on the ZnSe crystal and pressure applied with the accessory arm. The FT-IR spectra for all solids were collected from 650-4000 cm⁻¹.
at a resolution of 4 cm\(^{-1}\). A background of ambient atmosphere was subtracted. The resultant spectra were the average of 30 scans.

**X-ray absorption fine structure spectroscopy (XAFS)**

X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure spectroscopy (EXAFS) data were collected for all solids with As concentrations greater than 5 ppm. Standards for As(III) as NaAsO\(_2\) and As(V) as Na\(_2\)HAsO\(_4\)·7H\(_2\)O were also measured. Spectra were recorded on beamline X11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton NY, at the As K-edge, calibrated at 11.868 keV, using a Si(111) monochromator. The beam was detuned by 40% to minimize the harmonic contribution. Spectra were collected at room temperature in fluorescence mode using a Stern-Heald type Lytle detector. Soller slits and a germanium foil were placed between the detector and the sample to reduce elastic scattering. The spectra were analyzed using Feff (Zabinksy, et al. 1995) and WinXAS software (Ressler, 1997).

**Results and Discussion**

**Batch experiments**

Figure 2.1. shows the effect of pH on the SI of struvite and the mass of precipitated solid. Both the SI (Fig. 2.1a) and the solid yield (Fig. 2.1b) increased with pH, and maximized at pH 10. The increase in solid yield is consistent with previous observation of enhanced struvite recovery with pH (Doyle and Parsons, 2008; Wang, et al. 2005). The positive correlation between SI and yield indicated that the pH played a significant role in the
precipitation process by dictating the SI of struvite. The SI can be represented by the following equations:

\[
SI = \log_{10} \left[ \text{IAP}_{\text{struvite}} / K_{sp \text{ struvite}} \right] \quad (1)
\]

\[
\text{IAP}_{\text{struvite}} = a_{Mg^{2+}} \cdot a_{NH_4^+} \cdot a_{PO_4^{3-}} \quad (2)
\]

\[
K_{sp \text{ struvite}} = 10^{-13.26} \quad (3)
\]

where IAP\textsubscript{struvite} is the ion activity product of participating aqueous species, and K\textsubscript{sp struvite} is the solubility product of struvite set at a value of 10\textsuperscript{-13.26} (Ohlinger, et al. 1998). The increase in SI with pH can be attributed to an increase in the activity of PO\textsubscript{4}\textsuperscript{3-}(aq), and thus the IAP\textsubscript{struvite}. This effect however, is counteracted at pH 11 by a decrease in the NH\textsubscript{4}\textsuperscript{+}(aq) activity due to the dominance of NH\textsubscript{3}\textsuperscript{0}(aq) species, and by the hydrolysis of Mg\textsuperscript{2+}(aq) to MgOH\textsuperscript{+}(aq). Thus, the primary effect of pH on struvite precipitation is to change the activity of the aqueous species that control the IAP\textsubscript{struvite}, which in turn dictates the SI, and thus the yield. The presence of As(III) or As(V) in the initial solution did not have a notable effect on the overall yield of struvite at any given pH (Fig. 2.2). For solids derived from both As(III) and As(V) solutions, the As content of struvite increased with pH, reaching a maximum at pH 10 for the As(V) solids. The As concentration of the struvite solids precipitated in the presence of As(V) were consistently higher than those of As(III) by at least 1-2 orders of magnitude, indicating a much higher affinity of As(V) relative to As(III) for struvite.

The high concentrations of the As(V) solids is expected to be the result of As coprecipitation, consistent with the method of sample preparation. This in turn may be facilitated by the substitution of AsO\textsubscript{4}\textsuperscript{3-} for PO\textsubscript{4}\textsuperscript{3-} in mineral structure. Over the pH range
studied the dominant As(V) species, HAsO$_4^{2-}$(aq) and AsO$_4^{3-}$(aq), are similar in charge and size to the HPO$_4^{2-}$(aq) and PO$_4^{3-}$(aq) species (Marcus, 1997; Lide, 2005) (Table S2.1, Fig. S2.1). This facilitates effective competition between As(V) and P species for similar sites in the mineral structure. The correlation in As(V) concentration with the solid yield indicates that the sorption of As(V) is contingent upon the mass of struvite precipitated, also suggestive of coprecipitation with the mineral as it forms. The increase in the As(V) concentration in the solid is indicative of a greater selectivity for As(V) with increasing pH. This may be a result of the slightly lower acid dissociation constant (pK$_a$) values of arsenic acid compared to phosphoric acid (Table S2.1.). This means that the fraction of HAsO$_4^{2-}$(aq)/H$_2$AsO$_4^-$ (aq) and that of AsO$_4^{3-}$(aq)/HAsO$_4^{2-}$(aq) is always greater than that of the equivalent P species at the same pH, and becomes more pronounced as pH is increased (Fig. S2.1). Deprotonation of both P and As(V) aqueous species may facilitate association with the struvite solid. This is alluded to by a final solution pH of 6.4-6.9 for initial pH 8-9 samples in which HAsO$_4^{2-}$(aq) and HPO$_4^{2-}$(aq) species dominate (Table S2.2). Thus, a higher fraction of deprotonated As(V) species may permit As(V) to more effectively displace P with increasing pH.

For As(III) solids, the dominant aqueous species, H$_3$AsO$_3^0$(aq) and H$_2$AsO$_3^-$ (aq) (Table S2.1; Fig. S2.1) cannot compete effectively with P species in solution due to differences in charge and radius. This means that substitution of these ions for PO$_4^{3-}$ in the mineral structure is likely difficult. In addition, the sorption of As(III) continues to increase above the maximum solid yield, suggesting no influence of the absolute mass of the precipitate on the As(III) content. The sorption of As(III) may be a result of a surface interaction with
the precipitated struvite by an adsorption mechanism. The increase in sorption with pH may be partly influenced by the change in As(III) speciation with pH. At pH 8 the dominant H$_3$AsO$_3^0$(aq) species is primarily excluded from the solid. However, the fraction of deprotonated H$_2$AsO$_3^-$ (aq) species increases with pH. This species may in turn compete more effectively with HPO$_4^{2-}$(aq) and PO$_4^{3-}$(aq) for surface sites, compared to H$_3$AsO$_3^0$(aq), increasing the adsorption of As(III).

_Powder x-ray diffraction (XRD)_

The XRD spectra of all solids exhibited peaks characteristic of the main crystal reflections of struvite, confirming the formation of this mineral (Ferraris, et al. 1986) (Fig. S2.2, S2.3). In the standard XRD spectrum, the (111) reflection dominates (Fig. S2.2), however in the current samples, particularly at lower pH, the (020) and (040) reflections are the most prominent (Fig. S2.3). The pattern is consistent with that obtained for electrochemically deposited polycrystalline struvite with preferred orientation (Moussa, et al. 2006). For the major reflections at a single pH, there is some variation in the peak intensity between blanks and As solids, particularly at lower pH. A larger particle size distribution has been observed for struvite precipitated at low pH (Ronteltap, et al. 2010). Slight variations in the intensity of the reflections may be due to a combination of preferred orientations as a result of differences in the arrangement of crystals contingent upon particle size. Over the entire pH range differences may be a result of small inconsistencies in sample mounting, and thus particle orientation relative to the x-ray beam, impacting the intensity of the reflections.
The pH rather than the presence of As has the most notable effect on the XRD spectra, whereby both the peak intensity and resolution decrease with increasing pH. This is indicative of reduced crystallinity and/or a decrease in particle size of struvite with pH. Increased pH and higher SI has been observed to promote the precipitation of struvite crystals with smaller particle sizes due to large negative zeta-potentials which reduce particle agglomeration and thus growth (Le Corre, 2007). The presence of smaller particles can contribute to peak broadening in XRD spectra, and lower the intensity of the peaks. This is demonstrated in the Scherrer equation, which implies that the full width at half peak maximum varies inversely with the apparent particle size (Patterson, 1939). Smaller particle size with increasing pH may also contribute to the increased sorption of As(III), particularly at pH 11, despite the decrease in struvite yield. This is because if As(III) adsorbs to the mineral surface, a smaller particle size and a commensurate increase in surface area will provide additional sorption sites, thus increasing the As(III) uptake.

**Fourier transform infrared spectroscopy (FT-IR)**

The FT-IR spectra for all solids are similar, however, there is some variation in the broad band centered at ~1000 cm\(^{-1}\), assigned to the \( \nu_3 \) antisymmetric stretching vibration of the PO\(_4^{3-}\) molecule (Banks, et al. 1975) (Fig. S2.4). This broad band splits into two components with peaks at ~1020 cm\(^{-1}\) and ~980 cm\(^{-1}\) due to local distortion in the PO\(_4^{3-}\) tetrahedron (Stefov, et al. 2005), reflective of a lowering of the symmetry of the oxyanion, and potentially that of the crystal lattice (Banks, et al. 1975). Splitting in this band is evident for most samples. For As-free blanks, the splitting in the \( \nu_3 \) PO\(_4^{3-}\) band decreases with increasing pH, suggesting less distortion of the PO\(_4^{3-}\) tetrahedron, and thus higher
symmetry at higher pH. Size-induced changes in crystal symmetry have been observed for partially covalent oxides, whereby the crystal lattice symmetry increases with a decrease in particle size (Ayyub, et al. 1995). The decrease in struvite crystal size with increasing pH, as suggested by the XRD results, may therefore result in an increase in the overall crystal symmetry, and that of the $\text{PO}_4^{3-}$ tetrahedron.

For both the As(III) and As(V) samples there is splitting in the $\nu_3\text{PO}_4^{3-}$ band, which is more pronounced relative to the corresponding As-free solid at pH $\geq 9$. This suggests that sorbed As can further lower the symmetry of the $\text{PO}_4^{3-}$ group. This effect is particularly pronounced at pH 11 where the corresponding blank exhibits the highest symmetry. A similar effect of impurities on the $\text{PO}_4^{3-}$ tetrahedron has been observed for hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), where increased splitting in the $\nu_3\text{PO}_4^{3-}$ band, indicating higher distortion, was observed with increasing $\text{VO}_4^{3-}$ (Boechat, et al. 2000), and Ti concentration (Ribeiro, et al. 2006), attributed to substitution of the species into the mineral structure. This is consistent with the observed effect for As(V) solids, for which coprecipitation is the predicted mechanism. Slight differences in the ionic radii of $\text{AsO}_4^{3-}$ and $\text{PO}_4^{3-}$ imply that some structural adjustment is required to accommodate the larger oxyanion, which in turn may have effects on bulk $\text{PO}_4^{3-}$. Though minimal splitting is observed for the pH 8 As(V) sample, the broadness of the band is suggestive of some separation into its components. Though limited coprecipitation of As(III) is expected, there is still evidence of an effect on the $\nu_3\text{PO}_4^{3-}$ band for these samples.

*X-ray absorption near edge structure spectroscopy (XANES)*
The XANES and its first derivative are shown for the pH 8-11 As(V), and the pH 10-11 As(III) solids (Fig. 2.3). The low As concentrations of the pH 8-9 As(III) solids (< 5 ppm), prohibited characterization by this technique. The oxidation state of As can be determined based on the energy of the edge (Izumi, et al. 2005; Voegelin, et al. 2007), assigned here to the inflection point in the edge jump, located at 11.867 keV for the As(III) standard, and at 11.870 keV for the As(V) standard. The XANES spectra for solids precipitated in the presence of As(V) at pH 8-11 indicate an edge energy consistent with that of As(V), and commensurate with the initial oxidation state of As in solution. For solids derived from As(III) solutions, the edge features indicate the presence of both As(III) and As(V) in the solids, indicating partial oxidation of As(III). Examination of consecutive spectra over time for the As(III) samples did not show any indication of beam-induced oxidation (Manning, et al. 1998) (Fig. S2.5).

To get a rough estimate of the extent of oxidation in As(III) samples, a linear combination fit of the XANES spectra was applied using NaAsO$_2$ and Na$_2$HAsO$_4$·7H$_2$O standards as end members. Linear combination results indicated that the fraction of As(V) is 0.47 at pH 10, and 0.54 at pH 11. Most likely, this oxidation occurred in solution prior to sorption. Thermodynamic calculations do predict that for initial As(III) solutions, some oxidation to As(V) does occur upon equilibration, the fraction of which increases with pH (Table S2.3). This has also been demonstrated experimentally, with significant oxidation of aqueous As(III) to As(V) observed at pH > 9.2 (47). Due to the preferential sorption of As(V), compared to As(III), with struvite (Fig. 2.2), results indicate that even when present as a minor species in As(III) solutions, a significant fraction As(V) is sorbed to the solid.
Extended x-ray absorption near edge fine structure spectroscopy (EXAFS)

The $k^2$-weighted $\chi$ function and radial structure functions (RSFs) are displayed for As(III) and As(V) solids and standards (Fig. 2.4). The EXAFS fit results are summarized in Table 1. Only first-shell oxygens were fit. For the As(V) solids, this is because there is no further structure beyond the first-shell as is evident in the RSFs (Fig. 2.4). For the As(III) solids there may be contributions from subsequent shells based on the RSFs (Fig. 2.4). However, due to the low As loadings, and mixed oxidation state of these samples, these shells could not be fit with confidence.

For the As(V) solids, the As-O bond length decreases from 1.72 Å at pH 8 to 1.69 Å at pH 9-11. The shorter As-O distance is the same as that in arsenicrivate at 1.69 Å (Ferraris and Franchini-Angela, 1973) and is also consistent with the 1.68 Å As-O bond length observed for johnbaumite ($\text{Cas}_5(\text{AsO}_4)_3\text{OH}$) (Lee, et al. 2009). These results, combined with the method of sample synthesis, are suggestive of coprecipitation of As(V) into the struvite structure. The absence of additional shells in the RSFs also alludes to coprecipitation. This is because in the struvite structure subsequent shells are comprised of weak backscatterers (Mg, N) which are at distances $> 4$ Å from the core (Ferraris, et al. 1986), and thus will not be detected in the EXAFS. The slightly longer As-O distance at low pH may be due to a higher distribution of As(V) incorporated near the mineral surface, which may exhibit slightly elongated bond lengths due to surface relaxation phenomena, compared to As(V) in the bulk structure. In addition, due to the high concentration of $\text{HAsO}_4^{2-}(\text{aq})$ at this pH,
with an average As-O bond length of 1.73 Å (Myneni, et al. 1998), the incorporation of a fraction of As(V) as this species cannot be discounted.

For the As(III) solids the fit results indicated longer As-O bonds, compared to As(V) samples, at 1.74 Å. These bonds are shorter relative to those observed for adsorbed As(III) on substrates such as goethite (FeOOH), 1.78 Å and lepidocrocite (γ-FeOOH), 1.78-1.79 Å (Manning, et al. 1997; Farquhar, et al. 2002). Based on the results from XANES, these samples contain a mixture of As(III) and As(V). Assuming that the behavior of As(V) in these samples is consistent with that in the As(V) solids at the relevant pH, and also that the coprecipitation of the As(III) species is less favorable, the resultant bond lengths may be indicative of a combination of adsorbed As(III) and coprecipitated As(V). With nearly equal fractions of As(III) and As(V), the As-O bond length at 1.74 Å is the average of the 1.78 Å observed for adsorbed As(III) and 1.69 Å for coprecipitated As(V). The larger Debye-Waller factors obtained for the As-O shells in these samples, compared to those of the As(V) samples, also indicate a greater distribution of As-O distances in these solids, and thus a mixture of species. In addition, in the raw data, the dampening in the $\chi$ functions relative to the other samples and standards is due to destructive interference between these two O shells, present in different ratios in the samples. Thus sorption in As(III) solutions may be facilitated by the partial oxidation of As(III) to As(V) in solution, with subsequent coprecipitation of As(V), and adsorption of As(III) to the struvite surface. In turn, the presence of coprecipitated As(V) in these samples may explain the splitting in the $\nu_3$ PO$_4^{3-}$ band, and thus reduced symmetry as observed in the FT-IR spectra.
**Struvite recovery in the presence of arsenic**

The yield of struvite is increased with pH, improving the efficiency of the P recovery process (Stratful, et al. 2001). However, with increasing pH a notable fraction of As(V) will coprecipitate with struvite, and the adsorption of As(III) will be enhanced. This poses a dilemma as the conditions favorable for most efficient struvite recovery are also conducive to increased association of As with the solid. This can be problematic if recovered struvite is to be subsequently used as a fertilizer product. The maximum acceptable concentration of As in fertilizers is 75 ppm (USEPA, 1999). Starting with an intermediate initial As concentration, feasible in some wastes, the As concentration of struvite precipitated from As(V) solutions exceeds this value over the entire pH range studied. Thus, for struvite recovery in the presence of As, it is first essential to determine the dominant As speciation to assess the affinity of As for the substrate. Subsequently, a suitable pH needs to be selected to either maximize the yield, or minimize the amount of As in the recovered product.

For wastes with lower initial As concentrations than studied here, the final As content of struvite would be reduced, but the mechanism of sorption likely remains unchanged (Table S2.4). In turn, the sorption mechanism becomes critical if As contaminated struvite is applied to soils as fertilizer. Surface-bound species are known to be the most susceptible to desorption (Rouff, et al, 2005; Rouff et al. 2006). Thus, adsorbed As is likely to be readily mobilized and immediately toxic to plants and organisms. Alternatively, it may be possible to pretreat struvite to remove adsorbed species prior to application. Coprecipitated As however, will be remobilized primarily upon the breakdown of struvite, and hence
released simultaneously with the desired nutrients P, and N. The sorbed As may also directly affect the stability of struvite, influencing the decomposition process, and thus the release of nutrients, as previously observed for chromium (Cr) contaminated struvite (Rouff, et al. 2011). The cycling of slower release, coprecipitated As will therefore be linked with, and can directly affect that of P. In addition, as coprecipitated As is likely As(V), it may compete with P not only in subsequent geochemical, but also in biological processes, introducing toxicity to plants and higher organisms. These implications emphasize the importance of determining the mechanisms of As sorption with struvite.

Though wastes are more compositionally complex, and the presence of additional ions may impact the observed processes, these results are the first step in elucidating As sorption processes with struvite. There is a need for similar studies to assess the sorption of other contaminants with struvite, e.g. Cu, Zn, Fe also found in wastes, and in particular, those which may behave similarly to P such as Cr (54). This will ensure the environmental integrity of struvite-based fertilizers, which can in turn diminish the dependence on geologic P resources, and introduce sustainability to the human P cycle.

Acknowledgements

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Tables

Table 2.1. Structural parameters derived from EXAFS analysis of As(III) and As(V) standards, pH 10-11 As(III), and pH 8-11 As(V) solids.

Figures

Figure 2.1. a) Saturation Index (SI) of struvite and; b) solid yield for blank (As-free), As(III) and As(V) solids as a function of pH.

Figure 2.2. Total As concentration of As(III) and As(V) solids as a function of pH reported on a log scale. Inset: As concentrations are reported on a linear scale.

Figure 2.3. a) XANES spectra and b) first derivative plots of As(III) and As(V) standards, and pH 10-11 As(III), and pH 8-11 As(V) solids. Dashed lines at 11.869 and 11.872 indicate the positions of the white lines for the standards at ~2eV units greater than the edge energy.

Figure 2.4. a) k³ weighted EXAFS χ functions and b) corresponding Fourier transform amplitudes and curve fitting analysis to the inversely Fourier-filtered k³χ function in k-space for As(III) and As(V) standards, and pH 10-11 As(III) and pH 8-11 As(V) solids. Experimental data (solid lines) and fits (dotted lines) are shown.
Table 2.1. Structural parameters derived from EXAFS analysis of As(III) (NaAsO$_2$) and As(V) (Na$_2$HAsO$_4$·7H$_2$O) standards, pH 10-11 As(III) and pH 8-11 As(V) solids.

<table>
<thead>
<tr>
<th>Solid</th>
<th>aRadial distance (As-O), Å</th>
<th>bCoordination number, N</th>
<th>cDebye-Waller factor (δ$^2$), Å$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III) standard</td>
<td>1.82</td>
<td>3.0</td>
<td>0.002</td>
</tr>
<tr>
<td>As(V) standard</td>
<td>1.68</td>
<td>4.1</td>
<td>0.002</td>
</tr>
<tr>
<td>As(III) pH 10</td>
<td>1.74</td>
<td>1.7</td>
<td>0.01</td>
</tr>
<tr>
<td>As(III) pH 11</td>
<td>1.74</td>
<td>3.0</td>
<td>0.004</td>
</tr>
<tr>
<td>As(V) pH 8</td>
<td>1.72</td>
<td>3.1</td>
<td>0.002</td>
</tr>
<tr>
<td>As(V) pH 9</td>
<td>1.69</td>
<td>4.2</td>
<td>0.001</td>
</tr>
<tr>
<td>As(V) pH 10</td>
<td>1.69</td>
<td>4.8</td>
<td>0.001</td>
</tr>
<tr>
<td>As(V) pH 11</td>
<td>1.69</td>
<td>4.8</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Estimated error ±: a0.01 Å; b20 %; c0.001 Å$^2$
Figure 2.1. a) Saturation Index (SI) of struvite and; b) solid yield for blank (As-free), As(III) and As(V) solids as a function of pH.
Figure 2.2. Total As concentration of As(III) and As(V) solids as a function of pH reported on a log scale. Inset: As concentrations are reported on a linear scale.
Figure 2.3. a) XANES spectra and b) first derivative plots of As(III) and As(V) standards, and pH 10-11 As(III), and pH 8-11 As(V) solids. Dashed lines at 11.869 and 11.872 indicate the positions of the white lines for the standards at ~2eV units greater than the edge energy.
Figure 2.4. a) $k^3$ weighted EXAFS $\chi$ functions and b) corresponding Fourier transform amplitudes and curve fitting analysis to the inversely Fourier-filtered $k^3\chi$ function in k-space for As(III) and As(V) standards, and pH 10-11 As(III) and pH 8-11 As(V) solids. Experimental data (solid lines) and fits (dotted lines) are shown.
Supporting Information

Table S2.1. Dissociation constants for phosphoric acid, arsenous acid and arsenic acid (Lide, 2005).

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Step</th>
<th>pK$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric Acid</td>
<td>H$_3$PO$_4$</td>
<td>1</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>7.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>12.32</td>
</tr>
<tr>
<td>Arsenous Acid</td>
<td>H$_3$AsO$_3$</td>
<td>1</td>
<td>9.29</td>
</tr>
<tr>
<td>Arsenic Acid</td>
<td>H$_3$AsO$_4$</td>
<td>1</td>
<td>2.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>6.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>11.29</td>
</tr>
</tbody>
</table>

Table S2.2. Final measured pH values for solutions after 24 hours reaction and prior to filtration.

<table>
<thead>
<tr>
<th>Initial pH</th>
<th>Final pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III)</td>
<td>As(V)</td>
</tr>
<tr>
<td>8</td>
<td>6.4</td>
</tr>
<tr>
<td>9</td>
<td>6.9</td>
</tr>
<tr>
<td>10</td>
<td>9.9</td>
</tr>
<tr>
<td>11</td>
<td>11.4</td>
</tr>
</tbody>
</table>
Table S2.3. The fraction of redox species in initial As(III) and As(V) solutions after equilibration as predicted by PHREEQC (Parkhurst and Appelo, 1999). Calculated final pH values are consistent with the measured values reported in Table S2.2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>[As(V)], M</th>
<th>[As(III)], M</th>
<th>Log([As(V)]/[As(III)])</th>
</tr>
</thead>
<tbody>
<tr>
<td>As(III) pH 8</td>
<td>6.5</td>
<td>1.726×10^{-11}</td>
<td>5.000×10^{-5}</td>
<td>-6.5</td>
</tr>
<tr>
<td>As(III) pH 9</td>
<td>6.9</td>
<td>3.747×10^{-11}</td>
<td>4.999×10^{-5}</td>
<td>-6.1</td>
</tr>
<tr>
<td>As(III) pH 10</td>
<td>9.8</td>
<td>1.118×10^{-8}</td>
<td>4.999×10^{-5}</td>
<td>-3.6</td>
</tr>
<tr>
<td>As(III) pH 11</td>
<td>11.8</td>
<td>2.727×10^{-7}</td>
<td>4.973×10^{-5}</td>
<td>-2.3</td>
</tr>
<tr>
<td>As(V) pH 8</td>
<td>6.5</td>
<td>5.000×10^{-5}</td>
<td>4.967×10^{-14}</td>
<td>9.0</td>
</tr>
<tr>
<td>As(V) pH 9</td>
<td>6.9</td>
<td>4.999×10^{-5}</td>
<td>1.558×10^{-14}</td>
<td>9.5</td>
</tr>
<tr>
<td>As(V) pH 10</td>
<td>9.8</td>
<td>5.000×10^{-5}</td>
<td>1.318×10^{-17}</td>
<td>12.6</td>
</tr>
<tr>
<td>As(V) pH 11</td>
<td>11.8</td>
<td>5.000×10^{-5}</td>
<td>9.512×10^{-20}</td>
<td>14.7</td>
</tr>
</tbody>
</table>

^1Calculated Final pH
Table S2.4. Final As concentrations of struvite precipitated from solutions with 5-50 µM (0.37-3.75 ppm) As(III) or As(V) at pH 8 only. Samples were prepared as described in the Materials and Methods section, except the As concentration was varied. For solids from As(III) solutions, As was not detected (n.d.). For solids generated from As(V) solutions, the As concentration increased with increasing initial As(V) concentration. EXAFS analysis of As(V) solids with sufficient loadings indicated similarity in the fit parameters to the As-O shell, suggesting consistency in the sorption mechanism regardless of initial As concentration.

<table>
<thead>
<tr>
<th>Initial [As] µM</th>
<th>As (III) mg/L</th>
<th>As (III) Solid [As] mg/kg</th>
<th>As (V) Solid [As] mg/kg</th>
<th>N</th>
<th>R</th>
<th>DW</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.37</td>
<td>n.d.</td>
<td>4.45</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.75</td>
<td>n.d.</td>
<td>15.12</td>
<td>3.8</td>
<td>1.72</td>
<td>0.006</td>
</tr>
<tr>
<td>20</td>
<td>1.50</td>
<td>n.d.</td>
<td>32.18</td>
<td>3.2</td>
<td>1.73</td>
<td>0.004</td>
</tr>
<tr>
<td>40</td>
<td>3.00</td>
<td>n.d.</td>
<td>72.03</td>
<td>4.3</td>
<td>1.70</td>
<td>0.003</td>
</tr>
<tr>
<td>50</td>
<td>3.75</td>
<td>n.d.</td>
<td>91.60</td>
<td>3.8</td>
<td>1.72</td>
<td>0.002</td>
</tr>
</tbody>
</table>
Figure S2.1. The speciation of a) phosphoric acid, b) arsenic acid and c) arsenous acid with pH (Lide, 2005).
Figure S2.2. The theoretical XRD pattern of struvite based on the reference file JCPDS 15-0762 and consistent with that was reported before (Ferraris, et al. 1986).
Figure S2.3. XRD spectra of blanks (As-free), As(III) and As(V) solids at pH 8-11.
Figure S2.4. FT-IR spectra of blanks (As-free), As(III) and As(V) solids at pH 8-11.
Figure S2.5. Time-dependent XAFS spectra for the As(III) solid at pH 11, demonstrating no change in the collected spectra with time, demonstrating no beam-induced oxidation (Manning, et al. 1998). The oxidation of As(III) likely occurred in solution prior to sorption (Manning and Goldberg, 1997).
Chapter 3. A $^{31}$P NMR and TG/DSC-FTIR Investigation of the Influence of Initial pH on Phosphorus Recovery as Struvite

Abstract

Phosphorus can be reclaimed from nutrient-rich sources as the mineral struvite (MgNH$_4$PO$_4$·6H$_2$O) for re-use as fertilizer. This study determines the impact of initial pH ($pH_i$) from 8-11 on the fraction of precipitated struvite from a MgCl$_2$·(NH$_4$)$_2$HPO$_4$·NaCl-H$_2$O system. The rate of P removal from solution increases with $pH_i$, and maximizes at $pH_i$ 10. Scanning electron microscopy (SEM) of recovered precipitates shows changes in morphology, and decreasing particle size with increasing $pH_i$. $^{31}$P nuclear magnetic resonance spectroscopy (NMR) confirms that struvite constitutes 96-99% of the phosphate at $pH_i$ 8-10, with newberyite (MgHPO$_4$·3H$_2$O) as a minor crystalline phase. At $pH_i$ 11, 60% of the solid is struvite with 22% of the phosphate contained in an amorphous phase, and 18% as sodium phosphate. Thermogravimetric analysis (TG) reveals a correlation in the mass loss from the solids with the percentage of struvite detected. Coupling Fourier transform infrared spectroscopy (FT-IR) with TG indicates that the molar concentration of evolved H$_2$O(g) and NH$_3$(g) is influenced by the adsorption of NH$_4^+$(aq) at $pH_i$ 8-10, and by the low percentage of struvite at $pH_i$ 11. Overall, results indicate that both the amount of P recovered and the fraction of struvite are optimized at $pH_i$ 10. These findings can be used as a starting point in the selection of a suitable $pH_i$ for struvite recovery from nutrient-rich wastes.
Introduction

Geologic phosphorus (P) reserves are currently being depleted, decreasing the supply of P for agricultural purposes, with implications for global food security (Cordell, et al. 2011). The recovery of P from nutrient-rich wastes could simultaneously lessen the burden on geologic P reserves, and provide an additional source of P to address an increasing global demand (de-Bashan and Bashan, 2004). The mineral struvite (MgNH$_4$PO$_4$·6H$_2$O) can be precipitated from urine, animal, plant and municipal wastes (Ronteltap, et al. 2010; Suzuki, et al. 2007; Parsons and Smith, 2008) to recover P from these sources. Struvite may in turn be a viable fertilizer due to the high P and nitrogen (N) content. In addition, the low solubility of struvite means that it can be used as a slow-release fertilizer, providing nutrients to plants and crops over an extended period (Manning, 2008). Struvite-based fertilizers synthesized from different types of nutrient-rich wastes are already being promoted as commercial fertilizers (Ostara, 2014).

The pH$_i$ is the initial pH to which the P-rich waste is adjusted in order to induce P removal. This is of significance as in some cases pH is not controlled or maintained throughout the recovery process (de-Bashan and Bashan, 2004; Suzuki, et al. 2007). Therefore, the pH$_i$ is one of the most important factors that can affect the rate of struvite crystallization, and the chemical and physical properties of the mineral when precipitated from solution. The change in the concentration of total dissolved orthophosphate (PO$_4$-P) can be used to monitor the rate of precipitate (mainly struvite) formation. Using this approach, the nucleation, crystal growth and precipitation of struvite were found to follow a first-order kinetics model with respect to PO$_4$-P concentration (Gunn, 1976; Nelson, et al. 2003; Ben
Moussa, et al. 2011). The crystal growth rate was found to be transport-controlled (Ohlinger, et al. 1999) and dependent on the second order of the concentration of PO₄-P (Harrison, et al. 2011). It has also been proposed that the growth rate may follow a two-step linear model (Bhuiyan, et al. 2008). The pHᵢ of the solution can be used to determine the coefficients in the kinetic equations (Bhuiyan, et al. 2008). The pHᵢ can also dictate the supersaturation (Ma and Rouff, 2012) and the nucleation rate of struvite from solution, but may have a minor effect on the crystal growth rate (Ohlinger, et al. 1999).

The pHᵢ can also affect the morphology, particle size, and thermal properties of struvite. Struvite has an orthorhombic unit cell in space group Pmn2₁ (Abbona, et al. 1984), however the shape and size of crystals can vary with pHᵢ. For example, in the presence of acetate, dendritic, elongated dendritic and needle-shaped crystals were observed to form at pHᵢ 7, 7.5 and 10, respectively (Chauhan, et al. 2008). For struvite crystallized between pHᵢ 7-11, smaller crystals were observed at pHᵢ 9-10 compared to the lower pHᵢ values (Ronteltap, et al. 2010). These physical changes, as well as potential changes in the chemical properties and composition of struvite with pHᵢ could also impact the thermal properties of the mineral. The mineral phase transitions during the thermal decomposition of struvite have been studied extensively (Frost, et al. 2004; Abdelrazig, et al. 1988; Afzal, et al. 1992). It is also known that the presence of impurities can impact these processes (Rouff, 2012). However, the effect of pH of crystallization on the thermal properties of struvite, especially the release of volatile components during the heating process, has not been previously determined. The thermal properties can be used to assess the relative stability of struvite when generated at different pHᵢ. Though these experiments are conducted at above ambient
temperature, this provides an initial assessment of the susceptibility of struvite to decomposition, and thus the release of nutrients when used as a fertilizer.

The purity of struvite with respect to additional mineralogical components and the association of contaminants can also be influenced by pH$_i$. In batch experiments conducted over a pH$_i$ range of 7-10, the pH was found to be the primary factor affecting the production of struvite (Stratful, et al. 2001). At pH$_i$ 6-9 39% hydroxylapatite (Ca$_5$(PO$_4$)$_3$OH), and 5-55% newberyite (MgHPO$_4$·3H$_2$O) were detected separately along with struvite in solids precipitated from wastewater (Barat, et al. 2009; Babic-Ivancic, et al. 2006). Trace components in solution can also associate with struvite during mineral formation, resulting in impurities in the recovered precipitate (Ma and Rouff, 2012; Rouff, 2012). This has been observed for struvite formation in the presence of As, where increasing the pH$_i$ over a range of 8-10 also increased the As content of the recovered solid (Ma and Rouff, 2012).

This study focuses on the impact of pH$_i$ 8-11, a range typical for optimal struvite formation (Nelson, et al. 2003; Stratful, et al. 2001), on the physical and chemical properties of struvite precipitated from a MgCl$_2$-(NH$_4$)$_2$HPO$_4$-NaCl-H$_2$O system. The system was chosen to provide fundamental information concerning the effect of pH on struvite formation, without the influence of additional ions present in more complex solutions. The pH$_i$ was fixed, and the overall pH of the system was allowed to drift with the removal of P until equilibrium was reached. These conditions are similar to those used for struvite recovery from urine and wastewater, where the pH is difficult to control due to economical and/or technical reasons, for example in rural areas of third world countries (Ronteltap, et
The morphology, mineralogy, and thermal behavior of the solids recovered from these solutions were determined. Findings from $^{31}$P nuclear magnetic resonance spectroscopy (NMR) and simultaneous thermal analysis coupled with Fourier transform infrared spectroscopy (TG/DSC-FTIR) provide new insight into the influence of pH$_i$ on struvite formation. In turn, an improved fundamental understanding of the impact of pH$_i$ on the physical properties and chemical composition of precipitates from struvite-saturated solutions is necessary to ultimately improve the recovery of P from nutrient-rich wastes.

**Material and Methods**

*Preparation of Struvite-Saturated Solutions*

Solutions of MgCl$_2$·6H$_2$O and (NH$_4$)$_2$HPO$_4$ were prepared in deionized water at room temperature (~20-22 °C) in HDPE bottles. A NaCl electrolyte was used to maintain the ionic strength of the solutions at 0.1 M. Commercial struvite (Alfa Aesar) was added to the (NH$_4$)$_2$HPO$_4$ solution at a loading of 0.1 g/L to overcome the initial energy barrier decreasing the induction time associated with nucleation, and to optimize the crystallization of struvite during precipitation (Le Corre, 2006; Liu, et al. 2011). An equimolar concentration of MgCl$_2$·6H$_2$O was mixed with the (NH$_4$)$_2$HPO$_4$ solution so that the concentration of reagents was 17 mM. The pH$_i$ was adjusted to 8, 9, 10, or 11, using a 2 N NaOH solution.
The initial saturation index of struvite (SI\textsubscript{struvite}), prior to pH adjustment, was calculated to be ~2 using the program PHREEQC (Parkhurst and Appelo, 1999) with the minteq.v4 database, and the struvite solubility product (K\textsubscript{sp \ struvite}) from the literature at 10\textsuperscript{-13.26} (Ohlinger, et al. 1998). The SI\textsubscript{struvite} can be described by the following equations:

\begin{align*}
SI_{\text{struvite}} &= \log_{10} \left[ \frac{\text{IAP}_{\text{struvite}}}{K_{\text{sp \ struvite}}} \right] \quad (1) \\
\text{IAP}_{\text{struvite}} &= a_{\text{Mg}} \cdot a_{\text{NH}_4} \cdot a_{\text{PO}_4^{3-}} \quad (2) \\
K_{\text{sp \ struvite}} &= 10^{-13.26} \quad (3)
\end{align*}

where IAP\textsubscript{struvite} is the ion activity product of participating aqueous species (Ma and Rouff, 2012). For pH\textsubscript{i} 8-11, the SI\textsubscript{struvite} was calculated to be 2.18, 3.05, 3.42, 3.11, respectively. The decrease of SI\textsubscript{struvite} at pH\textsubscript{i} 11 was due to the decrease in the activity of Mg\textsuperscript{2+}(aq), PO\textsubscript{4}\textsuperscript{3-}(aq) and NH\textsubscript{4}\textsuperscript{+}(aq). The SI of other P-bearing minerals was also calculated by PHREEQC for each pH\textsubscript{i} (Table S3.1).

**Phosphorus Removal from Solution**

Solutions with an initial PO\textsubscript{4}-P concentration of 17 mM were prepared as described above at pH\textsubscript{i} 8-11. Immediately after mixing the MgCl\textsubscript{2}·6H\textsubscript{2}O and (NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4} solutions the pH was adjusted and a small volume of solution was retrieved and filtered using 0.45 µm syringe filters. Filtered aqueous samples were retrieved intermittently over a 24-hour reaction time. All aqueous samples were acidified with 6 M HCl immediately after sampling and analyzed for total dissolved orthophosphate (PO\textsubscript{4}-P) by a Lachat QuikChem 8000 nutrient analyzer using ascorbic acid method 31-115-01-1 for orthophosphate. The
detection limit for this technique is 0.01 mg P/L, and major interferents such as iron and silica were not present in solution.

Synthesis and Characterization of Solids

Struvite solids were synthesized at pH 8-11 using the approach described above. After a 24 hour reaction period, the solids were recovered by filtering the entire solution volume using 0.22 µm filters. Recovered solids were allowed to dry at room temperature prior to subsequent analysis.

The morphology of the solids was determined by scanning electron microscopy (SEM) of carbon coated solids using a Hitachi S-2600N instrument. Powder X-ray diffraction (XRD) patterns of the solids were collected using a Philips X’Pert Pro instrument. Data were collected using CuKα radiation over a range of 10-40 degrees 2θ, with a counting time of 1 s for every 0.01°. The diffraction patterns were background corrected and analyzed using X’Pert Highscore from PANalytical B.V. Where necessary, unanticipated phases detected by XRD were further investigated. In this case, the solids were digested in 5% HNO₃ and analyzed for major cations by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer DV 5300.

Nuclear magnetic resonance (NMR) spectroscopy was used to determine the identity of P-bearing phases in the precipitates. The ³¹P MAS/NMR spectra were acquired with a 500 MHz Varian Infinity-plus spectrometer operating at 202.3 MHz for ³¹P. Samples were contained in 4 mm rotors (o.d.) spinning at 8 kHz. Quantitative spectra were acquired by
direct excitation with 4 µs pulses (π/2) and 120 s relaxation delays to allow complete relaxation, with high-power \(^1\)H decoupling during acquisition. The \(^{31}\)P chemical shifts are reported relative to 85% \(\text{H}_3\text{PO}_4(\text{aq})\), using hydroxylapatite as a secondary standard set to 2.65 ppm.

The thermal properties of the solids were determined by simultaneous thermal analysis using thermogravimetry (TG) and differential scanning calorimetry (DSC). Fourier transform infrared spectroscopy (FT-IR) was used to identify and quantify the \(\text{H}_2\text{O}(\text{g})\) and \(\text{NH}_3(\text{g})\) released from the solids during thermal decomposition. For these analyses a Perkin Elmer STA 6000 simultaneous thermal analyzer was connected to a Spectrum 100 FT-IR spectrometer by a gas transfer line and a dedicated FT-IR cell. About 20 mg of solid was placed in a ceramic crucible and heated at a rate of 10 °C/min over a range of 35-500 °C. Dry \(\text{N}_2\) gas was used to purge the sample at a flow rate of 20 mL/min. Evolved gases were transported through the transfer line, into the FT-IR cell, both of which were heated to 250 °C to prevent gas condensation. The FT-IR was programmed to collect background-corrected spectra continuously over a range of 650-4000 cm\(^{-1}\) wavenumbers for the duration of the heating program. The areas of the peaks assigned to \(\text{H}_2\text{O}(\text{g})\) and \(\text{NH}_3(\text{g})\) in the FT-IR spectra were calculated. This was combined with the mass loss from the TG curve to quantify the molar concentrations of \(\text{H}_2\text{O}(\text{g})\) and \(\text{NH}_3(\text{g})\) evolved.

**Results and Discussion**

*Phosphorus Removal from Solution*
At all pH\textsubscript{i} values the concentration of PO\textsubscript{4}-P in solution decreased dramatically in the first 2 hours and gradually leveled off over the 24 hour period (Figure 3.1). The final measured pH values (pH\textsubscript{f}) are consistent with those predicted by thermodynamic calculations using PHREEQC (Table S3.1), and are indicative of equilibrium. Starting with an initial concentration of 17 mM PO\textsubscript{4}-P, the final concentrations at pH\textsubscript{i} 8-11 are 10.5, 5.2, 0.01 and 0.89 mM PO\textsubscript{4}-P, respectively. This result indicates enhanced removal of P from solution as pH\textsubscript{i} is increased, with maximum removal at pH\textsubscript{i} 10. This trend correlates well with the SI\textsubscript{struvite} at the onset of precipitation, which indicates the impact of SI\textsubscript{struvite} and pH\textsubscript{i} on the efficiency of P removal. Besides the influence of SI\textsubscript{struvite} on the final PO\textsubscript{4}-P concentration, this parameter also affects the rate of PO\textsubscript{4}-P removal. As seed material is added to overcome the nucleation energy, significantly reducing the induction time, the primary effect of high SI\textsubscript{struvite} values is to impact the rate of precipitation, and thus P removal from solution. Because of this, a more pronounced reduction in the concentration of PO\textsubscript{4}-P occurs at the beginning of the reaction, within 1-2 hours of the onset of precipitation, at higher pH\textsubscript{i} as seen in Figure 3.1. At pH\textsubscript{i} 10, where SI\textsubscript{struvite} is the highest, the rate of removal, but also the concentration of PO\textsubscript{4}-P removed from the aqueous phase is maximized. This is consistent with previous results which indicated that the mass of recovered solid was highest at pH\textsubscript{i} 10, with a yield of 4.1 g/L compared to 1.0 g/L at pH\textsubscript{i} 8 (Ma and Rouff, 2012).

Scanning Electron Microscopy

The SEM images of single crystals recovered from pH\textsubscript{i} 8-11 solutions show distinct morphologies at different pH\textsubscript{i} values (Figure 3.2a-d). At pH\textsubscript{i} 8, the crystals are well-formed.
blocky crystals indicative of orthorhombic symmetry, and consistent with struvite synthesized from pHi 5-8 in previous studies (Boistelle, et al. 1983; Kamnev, et al. 1999). At pHi 9, the crystals are elongated and bar-shaped, whereas at pHi 10 and 11, the crystals are thinner and flatter. At pHi 11, these thinner crystals were susceptible to curling due to surface tension of water while drying. As stated above, the rate of PO4-P removal from solution is contingent upon pHi. Therefore, the increased rate of precipitation at higher pHi would decrease the PO4-P concentration dramatically. At the same time, since the growth rate of the crystals is controlled by diffusion and/or physical mixing (Nelson, et al. 2003), this rapid reduction in PO4-P would subsequently limit the growth of crystals. Therefore, it is likely that the rapid precipitation at higher pHi reduced the PO4-P concentration limiting subsequent crystal growth and, producing the thin, flat tablet-shaped crystals observed in the SEM.

**X-ray Diffraction**

The XRD patterns indicate that struvite is the dominant phase precipitated from solutions with initial pHi 8-11 (Figure 3.3a). For the solids formed at pHi 8-10, the peaks from the XRD patterns show characteristic reflections of struvite. However, due to variations in the preferred orientation and particle size, the intensity of peaks varied, and not all of the reflections associated with struvite are evident in the XRD patterns. For precipitates formed at pHi 11, characteristic reflections of both struvite and a hydrated sodium phosphate (Na3PO4·0.5H2O), are identified (Figure 3.3b). The presence of Na in solids precipitated at pHi 11, but not at pHi 8-10, was confirmed by ICP-OES analysis of acid-digested solids.
Nuclear Magnetic Resonance Spectroscopy

Results from $^{31}$P-NMR confirm that struvite dominates the precipitates at all pH$_i$ values (Table 3.1 and Figure 3.4). The $^{31}$P MAS/NMR spectra of all samples contain a prominent, narrow peak at a chemical shift of +6.0 ppm that can be assigned to struvite (Shand, et al. 2005). In addition, the samples prepared at pH$_i$ 8-10 contain a small, narrow peak at -7.8 ppm, near the position reported previously for newberyite (Scrimgeour, et al. 2005). The low intensity of this peak is consistent with the absence of newberyite in the XRD pattern. A peak occurs at a chemical shift near +8.3 ppm in spectra of the solids precipitated at pH$_i$ 11 that can be assigned to sodium phosphate, based on the position of the chemical shift (Turner, et al. 1986) and the appearance of XRD reflections consistent with this phase. The pH$_i$ 11 precipitates also yield a broader peak centered near 1.5 ppm that likely arises from an amorphous or poorly crystalline material. On the side of the struvite peak a small shoulder occurs near +5 ppm that can be attributed to kovdorskite (Mg$_2$PO$_4$(OH)·3H$_2$O) based on the similarity in the chemical shift to that of a well-crystallized specimen which gives a narrow peak at +4.7 ppm. Several other small, narrow peaks are also apparent in the spectrum of the pH$_i$ 11 precipitates, but could not be assigned based on data available in the literature. The phase(s) responsible for these smaller peaks are likely present at too low a concentration to be easily identified by XRD.

The P-normalized relative proportions of each phase are determined from the integrated intensities obtained from least-squares fits of the centerband and significant spinning sidebands (not shown in Figure 3.4) to symmetrical peaks. The results are collected in Table 1, with uncertainties estimated from the variation in best-fit parameters with changes
in subjective processing details (e.g., baseline and phase corrections) and fitted peak shapes. (These estimated uncertainties are conservative and far exceed those given by the covariance matrix using observed noise as the uncertainty in spectral intensity values.) At pH\textsubscript{i} 8-10, the fraction of struvite increased from 96\% at pH\textsubscript{i} 8 to \textasciitilde 99\% at pH\textsubscript{i} 9 and 10. At pH\textsubscript{i} 11, 60\% of the P in the solid occurs in struvite. Additional phases are also identified at all pH\textsubscript{i} values. At pH\textsubscript{i} 8-10, newberyite is present as only a minor phase, the fraction of which decreased from 4\% at pH\textsubscript{i} 8, to \textasciitilde 1\% at pH\textsubscript{i} 9 and 10. At pH\textsubscript{i} 11, 22\% of the P is associated with an amorphous phase and 18\% contained in sodium phosphate.

At pH\textsubscript{i} 8-10 the increase in the fraction of struvite in the precipitates is likely influenced by the change in SI\textsubscript{struvite} and the rate of precipitation with pH\textsubscript{i}. Compared to pH\textsubscript{i} 8, at pH\textsubscript{i} 9-10, increased rates of struvite precipitation would limit the amount of ions, Mg\textsuperscript{2+}(aq) and HPO\textsubscript{4}\textsuperscript{2-}(aq), available to form newberyite. The preferential formation of struvite is due to the lower solubility product, $K_{sp\text{ struvite}} = 10^{\text{-13.26}}$ compared to that of newberyite, $K_{sp\text{ newberyite}} = 10^{\text{-5.51}}$ (Abbona, et al. 1982). In addition, it has been reported that in the MgCl\textsubscript{2}-(NH\textsubscript{4})\textsubscript{2}HPO\textsubscript{4}-NaOH-H\textsubscript{2}O system, the difference between the SI of struvite and that of newberyite increases as the pH\textsubscript{i} is increased (Babic-Ivancic, et al. 2006), and is supported by results from thermodynamic calculations using PHREEQC. At pH\textsubscript{i} 11, the high rate of precipitation means that Mg\textsuperscript{2+}(aq), NH\textsubscript{4}\textsuperscript{+}(aq) and PO\textsubscript{4}\textsuperscript{3-}(aq) are also removed from the solution in a short period of time. However, at this pH\textsubscript{i} the reduced activity of NH\textsubscript{4}\textsuperscript{+}(aq) would limit struvite formation, giving way to the precipitation of Mg- and Na-phosphates. Besides, given the decrease in SI\textsubscript{struvite}, the solution chemistry at pH\textsubscript{i} 11 would be quite different from that at pH\textsubscript{i} 8-10, promoting the formation of these additional phases.
Simultaneous Thermal Analysis and Fourier Transform Infrared Spectroscopy

Results from thermal analyses are consistent with pH$_i$-induced changes in the physical properties and chemical composition of the precipitates. The primary peak in the DSC curves represents an endothermic phase transition associated with the decomposition of struvite (Figure 3.5). This peak shifts from 122 °C at pH$_i$ 8 to 110 °C at pH$_i$ 11, indicating that decomposition occurs at lower temperature with increasing pH$_i$. In addition, the onset point also shifts to lower temperature, from 86 °C at pH 8 to 68 °C at pH$_i$ 11 (Figure 3.5). The shifts in the temperatures of the endothermic phase transition and the onset point to lower values may be due to the observed changes in the physical properties of the crystals, notable the crystal shape and size. The morphology of the crystals change from well-formed and blocky crystals to thinner, flatter tablet-shaped crystals as pH$_i$ is increased. In turn, the thinner crystals formed at higher pH$_i$ have a higher surface area due to their shape and size, which make them more susceptible to thermal decomposition.

The total mass loss, as shown on the TG curves (Figure 3.5), is highest at pH$_i$ 9-10 at 53.4-53.2%, with the lowest value of 50.8% recorded at pH$_i$ 11. The mass loss is due to the release of H$_2$O(g) and NH$_3$(g), as confirmed by FT-IR analysis of the evolved gases. The trend coincides well with the fraction of struvite in the solids at pH$_i$ 8-10 (Table 3.1), and indicates the release of more volatile components as the fraction of struvite increases. However, for the solid precipitated at pH$_i$ 11, the mass loss is not proportional to the fraction of struvite due to the presence of other phases with less volatile components relative to struvite.
The relative concentrations of \( \text{H}_2\text{O}(g) \) and \( \text{NH}_3(g) \) released from the solids formed at different \( \text{pH}_i \) (Table 3.2) provide insight into the composition of the solids. The total volatile content of the solids is similar, ranging from 29.7 to 30.0 mmol/g from \( \text{pH}_i \) 8-10, with a slightly lower value of 28.5 mmol/g at \( \text{pH}_i \) 11. The molar ratios of \( \text{H}_2\text{O}(g) \) to \( \text{NH}_3(g) \) range from 1.4-2.5 and are lower than anticipated based on the struvite stoichiometric value, \( \text{H}_2\text{O}(s) : \text{NH}_4^+(s) = 6:1 \), and the ratio in the literature (Rouff, 2012). Since the total volatile content did not change notably, the lower stoichiometric ratio between \( \text{H}_2\text{O}(g) \) and \( \text{NH}_3(g) \) can be interpreted as less \( \text{H}_2\text{O}(s) \) and more \( \text{NH}_4^+(s) \) in the solid compared to that ratio in struvite. This is probably due to the adsorption of \( \text{NH}_4^+(aq) \), which is the dominant N species at \( \text{pH}_i \) 8-10, to the surface of the solids. Since the surface charge of struvite becomes more negative at higher \( \text{pH}_i \) (Le Corre, et al. 2007), and the thinner, smaller crystals are likely to have a higher surface area, more \( \text{NH}_4^+(aq) \) could be adsorbed on the surface as the \( \text{pH}_i \) was increased. The sorption of \( \text{NH}_4^+(aq) \) to struvite can be verified by determining the concentration of \( \text{NH}_3(g) \) released below and above 200 °C (Table 3.2). Based on the study of the decomposition of pure struvite, the release of structural or incorporated \( \text{NH}_4^+(s) \) as \( \text{NH}_3(g) \) is not significant at temperatures lower than approximately 200 °C. Recalculating the ratio of volatiles using only the concentration of \( \text{NH}_3(g) \) released above 200 °C yields values more consistent with that expected for struvite for the \( \text{pH}_i \) 8-10 solids (Table 3.2). Therefore, the release of \( \text{NH}_3(g) \) at lower temperature is suggestive of the evolution of adsorbed \( \text{NH}_4^+(aq) \) associated with the solids. The sorption of \( \text{NH}_4^+(aq) \) would in turn alter the surface charge, potentially disrupting the growth of crystals, resulting in a smaller particle size at higher \( \text{pH}_i \). At \( \text{pH}_i \) 11, less \( \text{NH}_4^+(aq) \) would be available for crystal growth.
due to increased formation of the neutral species, $\text{NH}_3^0(\text{aq})$ due to hydrolysis. Also, the fraction of struvite in these solids is reduced, and additional phases are detected. So although the rate of precipitation at pH$_i$ 11 is still high, the decrease in $\text{NH}_4^+(\text{aq})$ concentration and the formation of additional phases results in a higher ratio of $\text{H}_2\text{O}(\text{g})$ to $\text{NH}_3(\text{g})$ at this pH$_i$.

**Impact of pH$_i$ on Struvite Formation**

This study demonstrates the impact of pH$_i$ on the physical and chemical properties of struvite during its precipitation from solution. As the pH$_i$ is increased from 8-11, an increase in both the rate and the amount of P removal from solution were found over a 24 hour period. Simultaneously, a high rate of precipitation and changes in aqueous speciation result in reduced concentrations of $\text{Mg}^{2+}(\text{aq})$, $\text{PO}_4^{3-}(\text{aq})$ and $\text{NH}_4^+(\text{aq})$, limiting crystal growth at higher pH$_i$. This influences the morphology of the crystals, with the formation of thinner, flatter crystals at pH$_i$ 9-11 compared to more equant, blocky crystals at pH$_i$ 8. The fraction of different mineral phases in the solid is also affected by the pH$_i$. Though struvite is the dominant mineralogical phase at pH$_i$ 8-10, a notable fraction of additional phases are detected at pH$_i$ 11. The changes in morphology and mineralogy also affect the thermal properties of the solids, producing a shift in the temperature of decomposition to lower values at higher pH$_i$, and affecting the total volatile content and the ratio of $\text{H}_2\text{O}(\text{s})$ to $\text{NH}_4^+(\text{s})$ in the samples.

The results of this study have implications for the pH$_i$-dependent recovery of P from nutrient-rich sources, including urine and agricultural wastes. Precipitation of struvite at
pH\textsubscript{i} 8 produces large, well-formed crystals which are the most thermally stable. Though the size and morphology of the crystals formed at pH\textsubscript{i} 9-10 reduces the thermal stability, P removal from solution is higher at these pH\textsubscript{i} values. In addition, the percentage of struvite recovered at these pH\textsubscript{i} values is > 99\% of the total P. At pH\textsubscript{i} 11, though P recovery is high, the struvite content is lower at 60\%, which also signifies less efficient removal of N from solution, in addition to which the solids are the most susceptible to thermal decomposition. Hence, the optimum pH\textsubscript{i} for P recovery from a nutrient-rich source is dependent on the goals of the process. Higher pH\textsubscript{i} ≥ 10 would be necessary if P removal is the priority. However, if maximizing the struvite content is the objective, a pH\textsubscript{i} of 9-10 is ideal. The thermal stability is indicative of the susceptibility of the solid to decomposition, which may be useful in predicting the release of nutrients. If this property is the major concern, then a pH\textsubscript{i} in the lower range should be considered. These observations may be complicated by additional ions in more complex waste solutions. However, these results do provide new fundamental information that can be used as a starting point in the selection of a suitable pH\textsubscript{i} for P recovery based on the desired solid properties. In addition, this research showcases the utility of more advanced techniques such as \textsuperscript{31}P NMR and TG/DSC-FT-IR in confirming the composition of the P-bearing solids, and can be useful for identifying precipitates recovered from nutrient-rich wastes.

\textbf{Acknowledgements} Support for this research was provided by the National Science Foundation under Grant No. EAR-1251732. Thanks to Dr. Patrick Brock for assistance with the SEM. We also thank Dr. Robert Downs and the RRUFF project for the loan of the kovdorskite mineral specimen.
Tables

Table 3.1. Relative integrated intensities of $^{31}$P MAS/NMR peaks observed for solids synthesized at pH$_i$ 8-11 and estimated uncertainties. n.d. means none detected.

Table 3.2. Concentrations of evolved H$_2$O(g) and NH$_3$(g) per gram of solid synthesized at pH$_i$ 8-11. The error for these measurements is ± 0.11 %. The NH$_3$(g) evolved is reported for temperatures from 40-200 °C ($\leq$ 200 °C), and 200-400 °C ($\geq$ 200 °C). The ratio of H$_2$O(g) to total NH$_3$(g) (40-400 °C) and to NH$_3$(g) evolved at 200-400 °C is determined.

Figures

Figure 3.1. PO$_4$-P concentrations in solution during solid precipitation at pH$_i$ 8-11 over a 24 hour period. The final pH in solution is indicated in brackets.

Figure 3.2. SEM images of solids precipitated at pH$_i$ 8-11.

Figure 3.3. XRD patterns of a) solids precipitated at pH$_i$ 8-11; b) the solid precipitated at pH$_i$ 11. The letters ‘S’ and ‘N’ represent the peaks related to struvite and sodium phosphate, respectively.

Figure 3.4. Quantitative $^{31}$P MAS/NMR spectra of solids precipitated at the indicated pH$_i$ values. Peaks occurring at 8.3, 6, 1.5, and -7 ppm are assigned to kovdorskite, struvite, an amorphous phase, and newberyite, respectively. Spectra were acquired by direct excitation with 120 s relaxation delays at a spinning rate of 8 kHz and represent 80 acquisitions each.

Figure 3.5. DSC (solid lines) and TG (dashed lines) curves for solids precipitated at pH$_i$ 8-11. The onset temperature (O.T.) and the peak temperature (P.T.) are represented as
open symbols on the DSC curve, with values reported in the legend (± 0.5 °C). The total mass loss (M.L.) as determined from the TG curve at 400 °C is also reported in the legend (± 0.2 %).
TABLE 3.1. Relative integrated intensities of \( ^{31}P \) MAS/NMR peaks observed for solids synthesized at pH \( i \) 8-11 and estimated uncertainties. n.d. means none detected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>8.3 ppm Na(_3)PO(_4)-0.5H(_2)O</th>
<th>6 ppm struvite</th>
<th>1.5 ppm (broad) amorphous phase</th>
<th>-7 ppm newberyite</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH(_i) 8</td>
<td>n.d.</td>
<td>96(1)</td>
<td>n.d.</td>
<td>4(1)</td>
</tr>
<tr>
<td>pH(_i) 9</td>
<td>n.d.</td>
<td>99.3(3)</td>
<td>n.d.</td>
<td>0.7(3)</td>
</tr>
<tr>
<td>pH(_i) 10</td>
<td>n.d.</td>
<td>99.1(3)</td>
<td>n.d.</td>
<td>0.9(3)</td>
</tr>
<tr>
<td>pH(_i) 11</td>
<td>18(2)</td>
<td>60(2)</td>
<td>22(2)</td>
<td>n.d.</td>
</tr>
</tbody>
</table>
TABLE 3.2. Concentrations of evolved H$_2$O(g) and NH$_3$(g) per gram of solid synthesized at pH$_i$ 8-11. The error for these measurements is ± 0.11%. The NH$_3$(g) evolved is reported for temperatures from 40-200 °C (≤ 200 °C), and 200-400 °C (≥ 200 °C). The ratio of H$_2$O(g) to total NH$_3$(g) (40-400 °C) and to NH$_3$(g) evolved at 200-400 °C is determined.

<table>
<thead>
<tr>
<th>pH$_i$</th>
<th>H$_2$O(g) mmol/g</th>
<th>NH$_3$(g) mmol/g</th>
<th>NH$_3$(g) mmol/g</th>
<th>Total volatiles mmol/g</th>
<th>H$_2$O(g) / total NH$_3$(g)</th>
<th>H$_2$O(g) / NH$_3$(g) ≥ 200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>21.0</td>
<td>5.8</td>
<td>2.9</td>
<td>29.7</td>
<td>2.4</td>
<td>7.3</td>
</tr>
<tr>
<td>9</td>
<td>18.6</td>
<td>9.0</td>
<td>2.6</td>
<td>30.1</td>
<td>1.6</td>
<td>7.2</td>
</tr>
<tr>
<td>10</td>
<td>17.5</td>
<td>10.1</td>
<td>2.5</td>
<td>30.0</td>
<td>1.4</td>
<td>7.0</td>
</tr>
<tr>
<td>11</td>
<td>20.3</td>
<td>6.3</td>
<td>1.9</td>
<td>28.5</td>
<td>2.5</td>
<td>10.6</td>
</tr>
</tbody>
</table>
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Supporting Information

Table S3.1. Saturation Index (SI) of P-bearing minerals and pH before and after the precipitation of struvite calculated by PHREEQC using the minteq.v4 database. The initial and final pH were labeled as pH$_i$ and pH$_f$, respectively.

<table>
<thead>
<tr>
<th></th>
<th>pH$_i$</th>
<th>8.0</th>
<th>9.0</th>
<th>10.0</th>
<th>11.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>1.99</td>
<td>3.98</td>
<td>5.79</td>
<td>6.80</td>
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</tr>
<tr>
<td>MgHPO$_4$·3H$_2$O</td>
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<td>0.74</td>
<td>0.66</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Struvite (MgNH$_4$PO$_4$·6H$_2$O)</td>
<td>2.18</td>
<td>3.05</td>
<td>3.42</td>
<td>3.11</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>pH$_f$</th>
<th>6.5</th>
<th>6.9</th>
<th>9.8</th>
<th>11.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$_3$(PO$_4$)$_2$</td>
<td>-2.34</td>
<td>-2.43</td>
<td>-2.28</td>
<td>1.36</td>
<td></td>
</tr>
<tr>
<td>MgHPO$_4$·3H$_2$O</td>
<td>0.13</td>
<td>-0.19</td>
<td>-2.42</td>
<td>-2.57</td>
<td></td>
</tr>
<tr>
<td>Struvite (MgNH$_4$PO$_4$·6H$_2$O)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Chapter 4. The Adsorption of Arsenic on Struvite and Hydroxylapatite in Phosphate-rich Aqueous Phase

Abstract
During arsenic (As) removal from aqueous phases, the presence of phosphate could cause competition between phosphate and As on the adsorbents and thus decrease the As removal efficiency. Under these conditions, to explore the As removal efficiency by phosphate minerals, struvite, MgNH₄PO₄·6H₂O (MAP), and hydroxylapatite Ca₅(PO₄)₃OH (HAP), were used in alkaline solutions, pH 8-11, with high phosphate concentration. Results from batch experiments showed adsorption of As(V) is more favorable than As(III). For As(V), more As was removed at higher pH and MAP has a higher affinity for As than HAP. Experiments using radioactive $^{33}$P at pH 10-11 to study the phosphate exchange at the water-mineral interface indicated a faster phosphate exchange on HAP than on MAP. The results from X-ray absorption fine structure spectroscopy (XAFS) on MAP and HAP solids reacted with As(V) at pH 10 and 11 indicated the formation of monodentate mononuclear surface complexes on MAP through the formation of a Mg-O-As bond; and incorporation of As near the HAP surface through the formation of a johnbaumite (Ca₅(AsO₄)₃OH)-like structure. This study revealed a new way of As removal through sorption on phosphate mineral surfaces and would benefit the As removal from phosphate-rich alkaline aqueous phases.
Introduction

Among all the heavy metal/metalloid elements that cause water pollution, arsenic (As) is one of the most common ones and As exposure has been a major public health concern for years (WHO, 2010). Point sources, such as mining activities, industrial and agricultural wastes, and non-point sources, such as remobilization of As from As-containing minerals in aquifers, could both contribute to the elevated As concentration in surface water, groundwater and wastewater (Han et al. 2003; Smedley and Kinniburgh, 2002). Especially, for areas using groundwater as their primary drinking water supply, the non-point sources could release As gradually and cause diseases related to chronic As exposure (Berg et al. 2001). Recently, As in baby food containing rice has caused global concern about As contamination in food supplies as a result of the remobilization of As (Meharg, et al. 2008; Jackson, et al. 2012).

Different sorbents were carefully designed to remove As from different As sources (Mohan and Pittman, 2007). Iron based sorbents have been studied extensively with high As removal efficiency (Raven, et al. 1998; Kanel, et al. 2005; Ona-Nguema, et al. 2005). Besides iron based sorbents, aluminum, titanium and carbon based sorbents were also used to remove As from different As sources (Xu, et al. 2002; Bang, et al. 2005; Manju, et al. 1998). In most of the work done on As removal, groundwater and wastewater were the major As sources (Mondal, et al. 2006). However, the variation in the composition of the As sources makes it impossible to find a sorbent for As that can work under all geochemical environments and still have a high efficiency. For example, most of the As removal experiments were done at neutral pH or lower, which leaves a very limited number of
sorbents to use when As removal from alkaline solutions is necessary, such as poultry litter (Mondal, et al. 2006; Mohan and Pittman, 2007; Garbarino, et al. 2003). Another example is the low removal efficiency of As in the presence of phosphate due to the competition between phosphate and As during the sorption process (Liu, et al. 2001). In order to suppress the competition from phosphate, the use of phosphate based minerals/materials, such as hydroxylapatite (HAP), $\text{Ca}_5(\text{PO}_4)_3\text{OH}$, in the removal of As from phosphate-rich aqueous phases has been proposed (Hodson, et al. 2000).

HAP is a common phosphate mineral (Oelkers and Valsami-Jones, 2008). The positively charged sites on the surface of HAP are mainly $\text{Ca}^{2+}(s)$ (Kandori, et al. 2009). There are two types of Ca atoms in the HAP lattice, type I and II Ca atoms, which occupy different sites between phosphate groups and hydroxyl ions (Posner, et al. 1958). HAP has been used alone or with ferrous ion to remove As from the aqueous phase with competition from phosphate (Hodson, et al. 2000; Sneddon, et al. 2005; Ciardelli, et al. 2008). In these studies, the low solubility of johnbaumite, $\text{Ca}_5(\text{AsO}_4)_3\text{OH}$, was considered the main reason for successful As removal. However, the details of the surface complexes formed during the sorption process were not thoroughly studied and whether a johnbaumite-like structure was formed is still unknown.

Besides HAP, struvite, $\text{MgNH}_4\text{PO}_4\cdot6\text{H}_2\text{O}$ (MAP), is also a phosphate mineral that can be used in As removal. MAP is usually found in wastewater treatment plants or precipitated from solutions with high magnesium, ammonium and phosphate concentrations, and has been proposed as a new low-cost high quality fertilizer (Doyle and Parsons, 2002; Ma, et
al. 2014; de-Bashan and Bashan, 2004). On its surface, the positively charged sites are \( \text{Mg(H}_2\text{O)}_6^{2+}(s) \) and \( \text{NH}_4^+(s) \). The sorption of As by MAP during a coprecipitation process could produce an isomorph of MAP, arsenstruvite \((\text{MgNH}_4\text{AsO}_4\cdot6\text{H}_2\text{O})\) (Ma and Rouff, 2012). But, in the adsorption of As using MAP, the structure of the surface complex and whether an arsenstruvite-like structure would form are still unclear. Recently, the studies on the interaction between \( \text{Mg(H}_2\text{O)}_6^{2+}(aq) \) and \( \text{PO}_4^{3-}(aq) \) in RNA folding showed the possibility of forming Mg-O-P bonds between \( \text{Mg(H}_2\text{O)}_6^{2+}(aq) \) and \( \text{PO}_4^{3-}(aq) \) (Misra and Draper, 2002; Gong, et al. 2008; Bowman, et al. 2012). So it is likely that \( \text{PO}_4^{3-}(aq) \) would also interact with \( \text{Mg(H}_2\text{O)}_6^{2+}(s) \) in MAP at the water-mineral interface. Due to the similarity between phosphate and As(V) in charge, size and structure, it is possible that As(V) would form surface complexes with \( \text{Mg(H}_2\text{O)}_6^{2+}(s) \) in MAP through Mg-O-As bonds.

This study focuses on the adsorption of As by MAP and HAP in alkaline solutions, pH 8-11, with relatively high phosphate concentration, 2.5-54 times the As concentration. The adsorption capacity of MAP and HAP were studied using batch experiments. Since the exchange of phosphate at the mineral-water interface could affect the adsorption of anions on positively charged sites, radioactive \(^{33}\text{P}\) was used to explore the exchange of phosphate between the solutions and mineral phases. For both mineral phases, solids with high concentrations of As were subjected to X-ray absorption fine structure spectroscopy (XAFS) study to identify the structure of the As-bearing surface complexes formed during the adsorption process to answer the questions like whether the arsenstruvite-like structure would be formed on MAP and what are the differences between the johnbaumite-like
structure, if formed on HAP, and johnbaumite. This research would explore the possibility of using MAP as a sorbent to remove As through adsorption, which has not been studied yet, and contribute to the study the interaction between As and HAP, both of which would shed light on the use of phosphate-based mineral phases, such as MAP and HAP, to remove As from alkaline wastes with high phosphate concentration, such as sewage sludge and agricultural wastes.

**Material and methods**

All solutions were made at room temperature (20-22 °C) in high density polyethylene (HDPE) bottles using deionized water. The As stock solutions of As(III) and As(V) were freshly made every time using NaAsO$_2$ and NaH$_2$AsO$_4$ salts, respectively. The stock solutions of MgCl$_2$ and (NH$_4$)$_2$HPO$_4$ were mixed so that the pH of the solutions for the adsorption experiment would be 8, 9, 10 or 11, with the initial saturation index (SI) of MAP equal to zero. The amount of MgCl$_2$ and (NH$_4$)$_2$HPO$_4$ stock solutions needed for each pH were calculated using PHREEQC with the minteq.v4 database (Parkhurst and Appelo, 1999), and the solubility product of struvite was set to $10^{-13.26}$ (Ohlinger, et al. 1998). The dissolution of HAP, $6.3\times10^{-4}, 1.2\times10^{-4}, 4.5\times10^{-5}$ and $2.9\times10^{-5}$ of the total mass used for pH 8-11 respectively, at equilibration was also calculated with PHREEQC. The pH of the solution was adjusted using 6 M NH$_4$OH, where necessary. All solutions were prepared in 0.1M NaCl, which was used as a background electrolyte.

*Batch adsorption experiment*
In order to maximize As removal, commercial MAP (Alfa Aesar) or HAP (Acros Organics) was added at a loading of 4 g/L to the pH 8-11 solutions. The surface area for MAP and HAP are 119 and 65.8 m$^2$/g, respectively (See Supporting Information for the details of the surface area measurements). The MAP or HAP solids were added to the solution less than five minutes before spiking with As stock solutions to 50 µM for As(III) or As(V). Blank solutions with no MAP or HAP solids were also spiked with As(III) or As(V) to 50 µM for pH 8-11. A small volume of aqueous sample was withdrawn using a 0.45 µm syringe filter every day after the spiking for seven days from all solutions.

Both aqueous samples and acid digested solids were analyzed for total As by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin-Elmer DV 5300 instrument.

To study the adsorption of As on both solids by ICP-OES, the MAP and HAP solids were filtered using 0.22 µm membrane filters after being reacted with As(V) in pH 10 and 11 solutions for seven days. These solids were then allowed to dry at room temperature prior to further analysis.

*Phosphate exchange at the mineral-water interface using radioactive $^{33}$P*

Radioactive $^{33}$P was used to study the adsorption and exchange of phosphate on MAP and HAP. The half-life of $^{33}$P is 25.34 days. Solutions adjusted to pH 10-11 were pre-equilibrated with MAP or HAP, at a loading of 4g/L, for seven days before spiking with $^{33}$P labeled phosphate. Since the ratios of $^{33}$P to $^{31}$P were 1.8×10$^{-8}$ and 5.8×10$^{-8}$ for pH 10
and11 solutions, respectively, the addition of $^{33}$P would have little impact on the ratio between phosphate and the active surface sites of the mineral phases, and therefore the adsorption kinetics. The first aqueous samples were withdrawn within 15 minutes after spiking the solutions with $^{33}$P. Additional aqueous samples were recovered intermittently over a week. All aqueous samples were filtered using a 0.45 µm manifold filter. The recovered aqueous samples were first mixed with liquid scintillation cocktail and then analyzed for radioactivity immediately using a LS6500 Beckman multi-purpose scintillation counter. The experiments were repeated without $^{33}$P. Aqueous samples were withdrawn and filtered with 0.45 µm syringe filters and analyzed for phosphate using a Hach DR 5000 Ultraviolet-Visible spectrophotometer (UV-VIS) right after and seven days after the seven-day pre-equilibration.

**X-ray absorption fine structure spectroscopy (XAFS)**

Extended X-ray absorption fine structure spectroscopy (EXAFS) data were collected for MAP and HAP solids which were reacted with As(V) at pH 10-11 for seven days, and were prepared as described above. Solids reacted with As(III) at pH 8-11 or As(V) at pH 8-9 were not recovered because of limited As removal. Spectra were collected at beamline X11A of the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL), Upton NY, at the As K-edge, calibrated at 11.868 keV, using a Si(111) monochromator. The beam was detuned by 15 % to minimize the harmonic contribution. Spectra were collected at room temperature in fluorescence mode using a Stern–Heald type Lytle detector. Soller slits and a germanium (Ge) foil were placed between the detector and the sample to reduce elastic scattering. The spectra were analyzed using Feff (Zabinksy, et
al. 1995) and WinXAS software (Ressler, 1997). The amplitude reduction factor, $S_0^2$, was set to 0.9 during the analysis. Structural parameters, coordination number (N), distance (R) and debye-waller factor ($\delta^2$), for the first As-O shell, and subsequent As-Mg or As-Ca shells around the central As atom were assessed.

**Results and Discussion**

**Batch experiments**

For As(III), the removal was minimal for both MAP and HAP from pH 8-11 (Figure 4.1a,b); for As(V), as the pH was increased, more As(V) was removed from the aqueous phase for MAP and HAP, especially at pH 10-11 (Figure 4.1c,d). The As(III) and As(V) removal at pH 8-11 normalized by the mineral surface area were also calculated and reported in the supporting information (Figure S4.1), and showed similar trends as in Figure 1 for the adsorption of As(III) or As(V) on the two mineral surfaces. During adsorption, both As(III) and As(V) would need to compete with phosphate in the solution to be adsorbed on the mineral surfaces. Since the phosphate concentration at each pH decreased as the pH was increased (Table 4.1), the competition from phosphate would be lower at higher pH. So, if the competition from phosphate during the adsorption of As(III) and As(V) are similar for both MAP and HAP at pH 8-11, a similar trend of As removal would be expected for both mineral phases.

For MAP and HAP, the removal of As(III) was minimal, less than 10%, for pH 8-11 (Figure 4.1a,b). The limited interaction between As(III) and MAP or HAP would be due to its differences in charge and radius when compared to phosphate. At pH 8-11, the dominant
species of As(III) are H$_3$AsO$_3$(aq) and HAsO$_2^-(aq)$ and more HAsO$_2^-(aq)$ would be formed as the pH was increased (Table 4.2). At pH 8, since the neutral species of As(III), H$_3$AsO$_3^0$(aq), is dominant, little As(III) would be adsorbed in the competition with phosphate through interaction with positively charged Mg(H$_2$O)$_6^{2+}$(s) on the surface of MAP or Ca$^{2+}$(s) on the surface of HAP. Similarly, at higher pH, the -1 charged HAsO$_2^-(aq)$ can hardly compete with HPO$_4^{2-}$(aq), which would be the dominant species of phosphate at higher pH, and form surface complexes with Mg(H$_2$O)$_6^{2+}$(s) and Ca$^{2+}$(s) on MAP and HAP, respectively. In the competition between As(III) and phosphate, charge differences could be the main factor that resulted in the low As(III) removal from both MAP and HAP.

For As(V), unlike As(III), the trend of As removal at pH 8-11 was different between MAP and HAP. As pH was increased from 8 to 11, more As(V) was removed from the solutions for MAP; for HAP, the As removal increased as the pH was increased but peaked at pH 10 (Figure 4.1c-d). For MAP, the As removed from solutions increased from less than 20% at pH 9 to about 70% at pH 11 for MAP (Figure 4.1c). The removal of As(V) could be caused by two main changes as the pH was increased, the weaker competition from phosphate, due to the lower phosphate concentration at higher pH, and more AsO$_4^{3-}$(aq) available for the formation of the Mg-O-As bond. The formation of Mg-O-As bonds during the adsorption process is not only the result of electrostatic interaction but also the polarization and charge transfer between Mg(H$_2$O)$_6^{2+}$(s) and P or As tetrahedra. As the pH was increased, the deprotonation of As(V) tetrahedra would facilitate adsorption by providing more negatively charged As(V), AsO$_4^{3-}$(aq), which could also propel the polarization and charge transfer in the formation of Mg-O-As bond.
For HAP, the removal of As(V) was minimal for pH 8-9. At pH 10-11, the removal of As(V) decreased from about 20% at pH 10 to 15% at pH 11 (Figure 4.1d). Higher removal at pH 10-11 compared to pH 8-9 was also due to the weaker competition from phosphate at higher pH. However, the removal at pH 11 was less than that at pH 10 and was not as predicted based on the decreased phosphate concentration. As calculated by PHREEQC, less HAP was lost to the solution through dissolution at equilibration at pH 11, the decrease of As removal efficiency from pH 10 to 11 could be the result of surface retention at higher pH. At higher pH, the hydrolysis of Ca\(^{2+}\)(s) to Ca(OH)\(^+\)(aq) and the formation of CaPO\(_4\)\(^-\)(aq) could cause a prolonged retention of the HAP surface, which would result in the desorption of As(V) and less As(V) being removed at pH 11 compared with that at pH 10.

**Phosphate exchange at the mineral-water interface using radioactive \(^{33}P\)**

For experiments with \(^{33}P\) labeled phosphate, as time went by, more \(^{33}P\) was removed from pH 10 and 11 solutions by both MAP and HAP (Figure 4.2a). For the experiments without \(^{33}P\), the removal of phosphate was similar for MAP at pH 10-11 and a slight desorption was shown by the end of the experiment for pH 10 and 11; however, for HAP, desorption was only shown at pH 11 (Figure 4.2b). The phosphate concentrations in Table 1 at pH 10 and 11 were referred to as 100% and used to normalize the phosphate concentrations in Figure 2b at pH 10 and 11, respectively.

For the MAP solids pre-equilibrated with pH 10 and 11 solutions, only a small portion of \(^{33}P\) was adsorbed immediately when MAP was in contact with \(^{33}P\) in the beginning. After
seven days, the adsorption of $^{33}$P labeled phosphate decreased the percentage of $^{33}$P in the solution from 95% to 43% for pH 10 and from 82% to 17% for pH 11. Based on the phosphate removal without $^{33}$P for MAP in Figure 2b, it is very likely the formation of Mg-O-$^{33}$P bonds from the substitution of $^{33}$P for $^{31}$P phosphate could be the cause of decreased $^{33}$P activity. For pH 10 solutions, the percentage of removed $^{33}$P after seven days was larger than that of the removed phosphate in Figure 2b by about 19%, which indicated the diffusion and exchange of $^{33}$P with the $^{31}$P phosphate in the MAP lattice. For pH 11 solutions, this number was increased to 32%, even with the noticeable desorption. Compared with the $^{33}$P removal curve at pH 10, the steeper $^{33}$P removal curve at pH 11 could be due to more $^{33}$PO$_4^{3-}$(aq) at higher pH, which would facilitate the nucleophilic attack that would lead to the formation of Mg-O-$^{33}$P bonds. More $^{33}$P lost in the lattice of MAP at higher pH was indicative of more exchangeable phosphate in the lattice with weak electrostatic bonds with Mg(H$_2$O)$_6^{2+}$(s).

For HAP, the majority of the $^{33}$P that was adsorbed by HAP was removed right after spiking. The percentage of $^{33}$P dropped from 100% to 60% and 50% for pH 10 and 11 solutions, respectively, within 15 minutes of spiking (Figure 4.2a). After seven days, 42% and 31% of $^{33}$P were left in pH 10 and 11 solutions. For pH 10, the percentage of $^{33}$P removed right after spiking was the same as the percentage of phosphate removed by HAP after the pre-equilibration at time zero (Figure 4.2b), which indicated a quick equilibration between the two P isotopes adsorbed on the HAP surface in a very short period of time through the substitution of $^{33}$P for $^{31}$P tetrahedra. For pH 11, the phosphate concentration at time 0 was the same, 100%, as the phosphate concentration in the pH 11 solution in Table 1, which
could imply no phosphate adsorption (Figure 4.2b). Meanwhile, since the adsorption of phosphate on the HAP surface is due to the interaction with surface Ca\(^{2+}\)(s), the relative phosphate concentration at time zero should be lower than 100\% due to phosphate removal.

This discrepancy on phosphate concentration at time zero could be the result of surface dissolution, which would compensate the removed phosphate and increase the phosphate concentration, in experiments done without \(^{33}\)P. After seven days, the elevated phosphate concentration, from 100\% to about 110\%, which was much larger than the result given by PHREEQC, was indicative of a prolonged surface dissolution process. As previously discussed, the formation of Ca(OH)\(^+\)(aq) and CaPO\(_4\)\(^-\)(aq) could cause the dissolution at pH 11 due to high OH\(^-\)(aq) and PO\(_4\)\(^3-\)(aq). So at pH 11, the larger \(^{33}\)P removal at the beginning, compared to pH 10, was most likely caused by the increased exchangeable phosphate tetrahedra on the mineral surface due to the Ca\(^{2+}\)(s) deficit, which would cause charge imbalance at the mineral surface and the mobilization of phosphate in the lattice to re-establish a charge balance. The process of re-establishing a charge balanced surface would probably result in disorder to the crystal structure at the surface. The removal curves of \(^{33}\)P were parallel after the first drop of the percentage of \(^{33}\)P, which meant a process that was not quite related to the change of pH was dominating the \(^{33}\)P removal. Based on the slope of the lines, this process could be a slow exchange of \(^{33}\)P with the phosphate in the lattice at the water-mineral interface at pH 10 and 11.

Using \(^{33}\)P to study the exchange of phosphate on MAP and HAP after a pre-equilibration can reveal the properties of the adsorbed phosphate, especially the exchangeable phosphate
on the mineral surface due to surface disorder, as shown on HAP, with minimum disturbance to the equilibration at the water-mineral interface.

Extended X-Ray Absorption Fine Structure Spectroscopy (EXAFS)

The $k^2$-weighted $\chi$ function and radial structure functions (RSFs) are shown for MAP and HAP reacted with As(V) for 7 days in pH 10 and 11 solutions (Figure 4.3). The As concentrations in the MAP are 235 and 372 ppm for solids from the pH 10 and 11 solutions, respectively; for HAP, the concentrations are 70 and 74 ppm for solids from the pH 10 and 11 solutions, respectively (Figure S4.2). The EXAFS fit results are summarized in Table 4. Arsenstruvite, MgNH$_4$AsO$_4\cdot$6H$_2$O, was used as the model mineral to fit the first oxygen (O) for MAP (Ferraris and Franchini-Angela, 1973). In the fitting for the magnesium (Mg) shell, since there are no direct Mg-O-As bonds in arsenstruvite, a mineral, other than arsenstruvite, with Mg-O-As bonds was needed. The mineral with Mg$^{2+}$ and AsO$_4^{3-}$ and no water of crystallization, Mg$_3$(AsO$_4$)$_2$, was chosen as the model mineral for Mg-O-As bonds (Nord and Kierkegaard, 1968). For HAP, johnbaumite, Ca$_5$(AsO$_4$)$_3$OH, was used as the model mineral to fit the first O and type I and type II Ca shells (Lee, et al. 2009).

For MAP, the As-O bond distance is 1.69 Å for both pH 10 and 11 solids, which is the same as the As-O bond distance in arsenstruvite at 1.69 Å. The coordination numbers are very close, 4.2 and 4.1, for pH 10 and 11 to that, 4, in arsenstruvite. The results in bond distance and coordination number indicated that the coordination environment of As is similar to that in arsenstruvite. For the As-Mg shell, the fitting results of coordination number were close for pH 10 and 11, which were 2.1 and 1.8 respectively. However, for
the radial distance, it increased from 3.09 to 3.17 Å from pH 10 to 11, which is longer than
the radial distance, 2.93 Å, in Mg₃(AsO₄)₂, but much shorter than that, 4.44 Å, in
arsenstruvite. The fact that the radial distance of the first As-Mg shell is much closer to
that in Mg₃(AsO₄)₂ than that in arsenstruvite indicated the formation of As-O-Mg bonds,
due to the adsorption of As(V) tetrahedra on MAP. Since the MAP surface will be more
negatively charged at higher pH (Le Corre, et al. 2007), the elongated radial distance of the
As-Mg shell from pH 10 to 11 could be due to the repulsion to the As(V) tetrahedra from
negatively charged surface. Based on the radial distance information of As-O, Mg-O and
O-O bonds from the model minerals, the As-Mg radial distance in the surface complexes
should be between 2.38 Å, which is the As-Mg radial distance in edge-sharing bidentate
surface complexes, and 3.79 Å, which is the As-Mg radial distance in linear monodentate
surface complexes. Besides, since the Mg-Mg radial distance on the same plane in MAP is
between 6.76 Å and 6.94 Å, it is not likely that one As(V) could form Mg-O-As bonds with
two Mg(H₂O)₆²⁺(s). So, it is possible that monodentate mononuclear surface complexes
were formed on the MAP surface with an Mg-O-As angle of 108° and 113° for pH 10 and
11, respectively.

For HAP, the radial distance and the coordination number for the As-O shell for both pH
values are close to those in johnbaumite; however, for the As-Ca shells, only the solid from
the pH 10 solution has similar structural parameters to johnbaumite (Table 4.4). For the
As-O shell, the radial distances, 1.69 Å and 1.70 Å for pH 10 and 11 solutions respectively,
are only slightly longer than that in johnbaumite, 1.68 Å. The minimal increase in the As-
O distance indicated that the distortion of the As(V) tetrahedra were limited. The
coordination numbers for the As-O shell at pH 10 and 11 are 3.2 and 3.0, respectively, which are smaller than the value, 4, in johnbaumite. For the As-Ca shells, the solid reacted with As(V) in the pH 10 solution showed a slightly elongated radial distance for first As-Ca shell, 3.27 Å, and a close radial distance for the second As-Ca shell, 3.60 Å, compared with those in johnbaumite, 3.19 Å and 3.64 Å respectively. However, the low coordination number could be due to the limited Ca\(^{2+}\)(s) on the mineral surface. Combined with the limited distortion in As(V) tetrahedra, it was indicated the As(V) tetrahedron was incorporated in the near-surface of the HAP mineral structure. For the solid recovered from the pH 11 solution, the radial distance and coordination number of As-O were close to those at pH 10. But, both the radial distances and coordination number for the As-Ca shells were very different from those in johnbaumite. Compared to the fitting parameters of the solid in the pH 10 solution, longer radial distances and larger coordination numbers were shown for both As-Ca shells. Considering the surface dissolution at pH 11, the mineral surface could present a stronger disorder due to the Ca\(^{2+}\)(s) deficit from the formation of Ca(OH)\(^{+}\)(aq) than at pH 10. Since the phosphate in the lattice would be mobilized in this strong disorder at the mineral surface, the As(V) would replace the phosphate in the mineral lattice and form a johnbaumite-like structure at the mineral surface. In HAP, the incorporation of anions, such as As(V), could cause larger coordination numbers and elongated radial distances with the Ca shells, especially when structural disorder is presented. For HAP that coprecipitated with As(V), the coordination number of first As-Ca shell was increased from 0.3 in pure johnbaumite to 1.6 for Ca\(_5\)(P\(_{0.89}\)As\(_{0.11}\)O\(_4\))\(_3\)OH (Lee, et al. 2009). Besides, the elongations in both As-Ca shells in solids at pH 11, compared with those in johnbaumite, were about 0.2 Å, which probably caused systematic disorder.
near the HAP surface. So, for HAP at pH 11, the larger coordination number for the first Ca shell, 3.0, and elongated As-Ca radial distances, 3.53 Å and 3.81 Å, for both Ca shells than those in johnbaumite, 0.3, 3.19 Å and 3.64 Å respectively, could be the results of structural disorder.

*Implications for As removal by phosphate minerals*

The results from batch experiments showed that MAP is a better sorbent for As than HAP, even when normalized for available surface area. With weaker competition from phosphate in the aqueous phase, more As(V) was removed by MAP as the pH was increased. For HAP, the removal of As(V) was decreased by surface dissolution at pH 11. During the studies on the exchange of phosphate at the water-mineral interface, a faster $^{33}$P exchange was implied from the quick drop of the $^{33}$P activity in the beginning of the experiment, which indicated the more exchangeable phosphate at the surface of HAP, which could be the result of surface disorder. Based on the results from XAFS, the formation of monodentate mononuclear surface complexes and incorporation through the substitution of phosphate are the mechanisms of As removal for MAP and HAP, respectively. Based on these results, for an alkaline solution with both high phosphate and As concentrations, a better way to remove the As is to oxidize the As to As(V) first, if the dominant As oxidation state is not As(V). Although MAP is a better sorbent to As(V) in terms of removal efficiency, with As incorporated in the near surface structure, As removed by HAP is less susceptible to remobilization than that adsorbed on MAP.
This study reported the As can form monodentate mononuclear surface complexes on MAP for the first time in the study of interaction between As and MAP and also is the first one to provide structural evidence of johnbaumite formation during the incorporation of As near the mineral surface of HAP. So, not only the possibility of forming As analog phase to the phosphate mineral, such as johnbaumite to HAP, but also the possibility of forming new bonds between the positively charged surface group and As should be considered when use of a phosphate-based sorbent to remove As is necessary. Besides, for the MAP precipitated from As-rich solutions, both the As incorporated in the mineral and adsorbed on the surface should be considered, especially when the recovered MAP would be used as fertilizer.

**Acknowledgements** Support for this research was provided by the National Science Foundation under Grant No. EAR-1251732. Thanks to Dr. Patrick Brock for assistance with the SEM. Thanks to K. Pandya of X11A for beamline support, and to Ying Zhu for BET analysis.
Table

Table 4.1. Molar concentrations of phosphate (P) and As and the molar ratio between phosphate and As (P/As) for pH 8-11 solutions.

Table 4.2. Molar concentration of As(III) species, based on the total As concentration in Table 1. All results were calculated by PHREEQC using the minteq.v4 database.

Table 4.3. Molar concentration of P and As(V) species, based on the total concentrations of P and As in Table 4.1, and the molar ratio of P and As(V) species with same charge. All results were calculated by PHREEQC using the minteq.v4 database.

Table 4.4. Structural parameters derived from EXAFS analysis of MAP and HAP solids reacted with As(V) for seven days at pH 10 and 11. The structural parameters of the model minerals are also listed.

Figure

Figure 4.1. Adsorption of As(III) and As(V) in pH 8-11 solutions using MAP or HAP as absorbent for seven days. All of the As concentrations were relative to the As concentrations in the blanks at the same pH, respectively.

Figure 4.2. Removal of $^{33}$P (a) and phosphate (b) from pH 10 and pH 11 solutions with MAP or HAP after seven-day pre-equilibration. The phosphate concentrations in (b) were relative to the phosphate concentrations in Table 1 for pH 10 and 11 solutions, respectively.

Figure 4.3. (a) $k^3$ weighted EXAFS $\chi$ function and (b) corresponding Fourier amplitudes and curve fitting analysis to the inversely Fourier-filtered $k^3\chi$ function in $k$-space for MAP and HAP solids reacted with As(V) for seven days in pH 10 and pH 11 solutions. Experimental data (solids lines) and fits (dotted lines) are shown.
Table 4.1. Molar concentrations of phosphate (P) and As before adsorption on MAP and HAP and the molar ratio between phosphate and As (P/As) for pH 8-11 solutions.

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<td>54</td>
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<td>0.05</td>
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Table 4.2. Molar concentration of As(III) species, based on the total As concentration in Table 1.

All results were calculated by PHREEQC using the minteq.v4 database.

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<tr>
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<td>4.9×10⁻⁵</td>
<td>5.4×10⁻⁷</td>
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</table>
Table 4. Molar concentrations of P and As species, based on the total concentrations of P and As in Table 1, and the molar ratios of P and As species with same charge. All results were calculated by PHREEQC using the minteq.v4 database.

<table>
<thead>
<tr>
<th>P species</th>
<th>As species</th>
<th>P molar conc.</th>
<th>As molar conc.</th>
</tr>
</thead>
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<td>HPO₄²⁻</td>
<td>HASO₄²⁻</td>
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<td>2.0×10⁻⁸</td>
</tr>
<tr>
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<td>9.6×10⁻⁷</td>
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<td>3.2×10⁻⁷</td>
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<tr>
<td>H₃PO₄⁻ / H₂AsO₄⁻</td>
<td>2.0×10⁻¹</td>
<td>3.8×10⁻¹</td>
<td></td>
</tr>
<tr>
<td>H₃AsO₄⁻</td>
<td>3.1×10⁻⁵</td>
<td>5.6×10⁻⁸</td>
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</tr>
</tbody>
</table>
Table 4.4. Structural parameters derived from EXAFS analysis of MAP and HAP solids reacted with As(V) for seven days at pH 10 and 11. The structural parameters of the model minerals are also listed.

<table>
<thead>
<tr>
<th>solid</th>
<th>bond type</th>
<th>coordination number, $N$</th>
<th>radial distance, Å</th>
<th>Debye-Waller factor $(\delta^2)^*$, Å²</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 10 MAP</td>
<td>As-O</td>
<td>4.2</td>
<td>1.69</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>As-Mg</td>
<td>2.1</td>
<td>3.09</td>
<td>0.010</td>
</tr>
<tr>
<td>pH 11 MAP</td>
<td>As-O</td>
<td>4.1</td>
<td>1.69</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>As-Mg</td>
<td>1.8</td>
<td>3.17</td>
<td>0.010</td>
</tr>
<tr>
<td>pH 10 HAP</td>
<td>As-O</td>
<td>3.2</td>
<td>1.69</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>As-Ca</td>
<td>0.5</td>
<td>3.27</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>As-Ca</td>
<td>1.2</td>
<td>3.60</td>
<td>0.010</td>
</tr>
<tr>
<td>pH 11 HAP</td>
<td>As-O</td>
<td>3.0</td>
<td>1.70</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>As-Ca</td>
<td>3.0</td>
<td>3.53</td>
<td>0.010</td>
</tr>
<tr>
<td></td>
<td>As-Ca</td>
<td>2.8</td>
<td>3.81</td>
<td>0.010</td>
</tr>
<tr>
<td>Arsenstruvite</td>
<td>As-O</td>
<td>4.0</td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As-Mg</td>
<td>2.0</td>
<td>4.44</td>
<td></td>
</tr>
<tr>
<td>Mg₃(AsO₄)₂</td>
<td>As-O</td>
<td>4.0</td>
<td>1.69</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As-Mg</td>
<td>1.0</td>
<td>2.93</td>
<td></td>
</tr>
<tr>
<td>Johnbaumite</td>
<td>As-O</td>
<td>4.5</td>
<td>1.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As-Ca</td>
<td>0.3</td>
<td>3.19</td>
<td></td>
</tr>
<tr>
<td></td>
<td>As-Ca</td>
<td>3.3</td>
<td>3.64</td>
<td></td>
</tr>
</tbody>
</table>

* indicates fixed values
Figure 4.1. Adsorption of As(III) and As(V) in pH 8-11 solutions using MAP or HAP as absorbent for seven days. All of the As concentrations were relative to the As concentrations in the blanks at the same pH, respectively.
Figure 4.2. Removal of $^{33}$P (a) and phosphate (b) from pH 10 and pH 11 solutions with MAP or HAP after seven-day pre-equilibration. The phosphate concentrations in (b) were relative to the phosphate concentrations in Table 1 for pH 10 and 11 solutions, respectively.
Figure 4.3. (a) $k^2$ weighted EXAFS $\chi$ function and (b) corresponding Fourier amplitudes and curve fitting analysis to the inversely Fourier-filtered $k^2\chi$ function in $k$-space for MAP and HAP solids reacted with As(V) for seven days in pH 10 and pH 11 solutions. Experimental data (solids lines) and fits (dotted lines) are shown.
Supporting information

Surface area of MAP and HAP

The MAP was degassed for 16 hours at 40 °C; while HAP was degassed for 8 hours at 50 °C. The lower degas temperature of MAP is due to its decomposition at 50 °C during the 8-hour degassing process.

Figure S4.1. Adsorption of As(III) and As(V) in pH 8-11 solutions using MAP and HAP normalized by the mineral surface area. The As concentrations of the blanks were considered as 100%.
Figure S4.2. As concentration in MAP and HAP solids reacted with As(V) in pH 10-11 solutions for 7 days.
Chapter 5. Conclusion and Recommendations for the Future

Conclusion

In this thesis, the interaction between arsenic (As), one of common toxic elements, and struvite, MgNH₄PO₄·6H₂O (MAP), was studied during both coprecipitation (CPT) and adsorption (ADS) processes at pH 8-11. MAP is a mineral that can be used to recover phosphorus (P) from municipal wastes and agricultural wastes through precipitation and being used as high quality fertilizer. However, the interaction between As and MAP is a concern, when MAP was formed from As-rich wastes, such as poultry manure, of soil contamination when MAP was applied as fertilizer. Through the major sorption processes, CPT and ADS, the interaction between As and MAP would be thoroughly studied, which would help to produce low-As fertilizer. Besides, this study could also shed light on the sorption of As using MAP as a sorbent in As-rich aqueous phase.

During the CPT process, the MAP was precipitated from a MgCl₂-(NH₄)₂HPO₄-NaCl-H₂O system spiked with As at an initial pH (pHᵢ) of 8-11. The interaction between MAP and both trivalent As, As(III), and pentavalent As, As(V) was studied. The batch experiments showed that more As was found in the solids at higher pHᵢ and As(V) was the favorable As oxidation state in the precipitated MAP. The X-ray Diffraction (XRD) patterns indicated the decreasing particle size at pHᵢ was increased and the presence of As in the solid did not change the crystallinity of the solids. Unlike the XRD results, the results from the attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FT-IR) showed higher distortion of the phosphate tetrahedra as the pH was increased, which
indicated the impact of As on the phosphate groups in the precipitated MAP. The coordination environment of As was studied using X-ray absorption fine structure spectroscopy (XAFS) showed that As(V) was incorporated in the solids; whereas part of the As(III) was adsorbed on the mineral surface and the rest of the As(III) in the solids, which was oxidized to As(V), was incorporated in the solids.

The solids precipitated from the MgCl₂-(NH₄)₂HPO₄-NaCl-H₂O system at pHᵢ 8-11 without the addition of As was also characterized to study the impact of pHᵢ on the morphology, mineralogy and thermal stability of precipitated MAP and provide future guidance for its application as fertilizer. The P removal through precipitation happened in a very short amount of time, with pHᵢ 10 having the highest P removal efficiency. The images taken using the scanning electron microscopy (SEM) of the solids showed changes in morphology and decreased particle size as the pHᵢ was increased. The ³¹P nuclear magnetic resonance spectroscopy (NMR) confirmed that over 95% of phosphate was in MAP at pHᵢ 8-10, with newberyite (MgHPO₄·3H₂O) as a minor crystalline phase. At pHᵢ 11, only 60% of the phosphate was in MAP, with 22% and 18% in an amorphous phase and sodium phosphate, respectively. The use of thermogravimetric analysis (TG) coupled with Fourier transform infrared spectroscopy (FT-IR) indicated the concentration of the evolved H₂O(g) and NH₃(g) from the precipitates during the thermal decomposition was affected by the adsorption of NH₄⁺(aq) at pHᵢ 8-10 and the percentage of the MAP at pHᵢ 11.
During the ADS process, the possibility of using MAP as a sorbent to As in alkaline solutions was evaluated. MAP and hydroxylapatite (HAP), Ca$_5$(PO$_4$)$_3$OH, were reacted with As(V) or As(III), in a MgCl$_2$-(NH$_4$)$_2$HPO$_4$-NaCl-H$_2$O system with pH fixed at 8-11. For As(III), the removal by either MAP or HAP were limited for pH 8-11. However, as the pH was increased, more As(V) was removed from the solution for both MAP and HAP. For MAP, more As(V) was removed due to weaker competition from phosphate in the solution. For HAP, the removal of As(V) was peaked at pH 10, which indicated that a different sorption process of As(V) on HAP compared to MAP. During the radiotracer experiment with $^{33}$P, the exchange of $^{33}$P for $^{31}$P phosphate at the water-mineral interface happened instantaneously, within 15 minutes, followed by the exchange of $^{33}$P for $^{31}$P phosphate in the mineral lattice on HAP; whereas on MAP, the exchange of the surface, which indicated that the $^{31}$P orthophosphate on MAP were more stable during the exchange with $^{33}$P orthophosphate. The XAFS results showed the adsorbed As(V) formed monodentate mononuclear surface complexes on MAP. For HAP, the presence of the johnbaumite-like structure indicated the incorporation of the As near the mineral surface of HAP.

The study in this thesis about the interaction between MAP and As can be helpful in a few ways. First, during the recycling of P in wastes, the research on the precipitation of MAP and its coprecipitation with As can shed light on how to produce low-As MAP with maximum recycle of P from wastes, especially from wastes with high concentration of As. Through a pre-reduction process, with As(V) being reduced to As(III), the As concentration in the solids could be minimized. Second, the pH$_i$ should be considered
carefully during the precipitation of MAP from wastes that has no As. The small particles, which are more susceptible to thermal decomposition, formed at higher pH, could cause extra time in filtration and then increase the cost. If using the precipitated MAP as a slow-releasing, low-cost fertilizer, larger particle size and higher thermal stability would make lower pH a better choice, even though the recovery rate of P is not as high as that at higher pH. Third, MAP has a higher affinity for As, especially compared with HAP, which makes it possible to use MAP as an adsorbent to remove As from phosphate-rich alkaline wastes and avoid the possible competition from phosphate.

**Recommendations for the Future**

As mentioned in the previous part, there are two major research directions of MAP, using MAP as a means to recover P from wastes and its interaction with As in As-rich alkaline environments through sorption processes, like coprecipitation and adsorption.

For the first part, based on the results from the experiments done in laboratory with synthetic high P solutions, recovering P from wastes, like agricultural wastes, can be explored. Once the wastes is obtained, the chemical composition should be analyzed after thorough filtration. Then, based on the chemical composition, especially the pH of the filtered wastes and the concentrations of magnesium (Mg), ammonia (NH\textsubscript{4}\textsuperscript{+}) and phosphate, Mg and/or phosphate solutions and MAP solid, which is used as seed material, would be added to precipitate MAP from the wastes. Solids characterization, using XRD, SEM, NMR and TG-FT-IR, and the chemical analysis for major and trace elements, using ICP-OES, would be applied on the recovered solids. With this information, a modified method
based on the experiments reported in this thesis can be developed to prevent the toxic components, if any, in the wastes from being incorporated in the precipitates and still have a relatively high efficiency in P recovery. Hopefully, this work can be expanded to a big project to recover P from different kinds of wastes as MAP in a low-cost way and provide a high quality fertilizer for those areas that struggling with food supplies.

Besides being used as a fertilizer, the interaction between As and MAP are also of importance when animal activities are involved as the major source of P. In natural environments, animal excreta can provide P and/or NH$_4^+$ to Mg-rich alkaline environments, such as Mono Lake and other salty lakes, and thus could cause the precipitation of MAP. If As is presented in the lake, the mineralogy and composition of the precipitates due to the interaction between As and MAP could change accordingly due to the variation in the amount of the animal excreta. In this way, changes in animal activities near salty lakes can be documented in the sediments. So, in a salty lake with relatively stable As concentration, the study of MAP in the sediments, if present, could shed light on the animal activities in the past and help to understand the impact of the global warming on the animal habitats and the whole ecosystem if combined with the paleo-climate data in the same area.
Appendix

The precipitation of solids from greenhouse wastewater and monolake water

The two samples were filtered using 0.45 µm membrane filters. The concentrations of magnesium (Mg), phosphorus (P) were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) using a Perkin Elmer DV 5300 instrument; the concentration of NH$_4^+$ was analyzed using a Hach DR 5000 Ultraviolet-Visible spectrophotometer (UV-VIS). Commercial MAP was used as seed with a yield of 0.1 g/L. The stock solutions of (NH$_4$)$_2$HPO$_4$ and MgCl$_2$ were used to spike the filtered aqueous phases, to a final concentration of 17 mM for P and Mg, respectively. Solids were recovered after 24 hours using 0.45 µm membrane filters and let dry at room temperature for further analysis.
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