Understanding the Nano- and Macroscale Processes Impacting Arsenic Mobilization during Managed Aquifer Recharge using Reclaimed Wastewater

Chelsea Wren Neil
Washington University in St. Louis

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WASHINGTON UNIVERSITY IN ST. LOUIS

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Understanding the Nano- and Macroscale Processes Impacting Arsenic Mobilization during Managed Aquifer Recharge using Reclaimed Wastewater
by
Chelsea W. Neil

A doctoral dissertation presented to the Graduate School of Arts & Sciences of Washington University in partial fulfillment of the requirements for the degree of Doctor of Philosophy

December 2015
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Managed aquifer recharge (MAR) utilizing reclaimed wastewater is a vital means of replenishing natural freshwater supplies in order to meet growing demands. Unfortunately, this process has been found to induce unfavorable geochemical reactions which mobilize arsenic from aquifer sediments. This process is further complicated by the simultaneous formation of iron(III) (hydr)oxide secondary minerals, which can sorb aqueous arsenic. It is crucial to fully elucidate these physico-chemical processes in order to establish safe MAR operations which minimize arsenic release. Thus, the mechanisms controlling arsenic release from arsenopyrite during MAR were investigated from the nano- to macroscale.
First, nanoscale iron(III) (hydr)oxide nucleation and growth was investigated *in situ* for aqueous systems relevant to MAR, including systems with arsenate, phosphate, and natural organic matter (NOM) present. It was found that oxyanions increased the growth of precipitates, while NOM induced large fractal aggregate formation. When arsenate and NOM existed together in solution with precipitating iron(III) (hydr)oxides, smaller aggregates and larger-sized particles both formed. We observed *in situ* that iron(III) (hydr)oxides formed in the presence of these constituents will have altered sizes and aggregation states. These changes will significantly affect their reactive surface area, subsequently impacting their capacity for arsenic attenuation in natural and engineered aquatic systems.

Next, arsenopyrite dissolution and secondary mineral precipitation and phase transformation were investigated at the microscale for wastewater and model wastewater systems. The effects of chloride, NOM, and Fe$^{3+}$ ions were tested for model wastewaters. For the chloride system, faster aging of secondary mineral precipitates and higher arsenic mobility under aerobic conditions were observed. For NOM-containing systems, precipitation was inhibited. For Fe$^{3+}$ systems, arsenic mobilization, secondary precipitation extent, and phase transformation were all accelerated. Newly reported information on secondary mineral phase transformation in the presence of different wastewater constituents gives important insight into how these minerals will interact with arsenic, potentially mitigating the risk of arsenic contamination.

Finally, arsenic mobilization from arsenopyrite at the macroscale was studied over a longer time frame in soil column reactors. After reaction, arsenic and iron solid phase speciation were determined using sequential extraction. Empirical dissolution rates were incorporated into CrunchFlow, a reactive transport simulator, to model arsenic mobilization and secondary mineral precipitation. Model calculations for aqueous arsenic concentrations and secondary mineral
phase formation quantities were compared with experimental results, and recommendations were made to improve the model. Through this study, we demonstrated the importance of using quantitative arsenopyrite dissolution rates measured under MAR conditions in order to accurately predict arsenic mobilization. The development of better reactive transport models for arsenic mobilization will help to predict how site-specific mineralogy and MAR operating parameters can influence the degree of arsenic mobilization and transport in groundwater.

Outcomes from this study address critical knowledge gaps in our understanding of the geochemical conditions which mobilize naturally-occurring arsenic from sediments. Results are applicable not just to MAR operation, but also to acid mine drainage sites and locations with pervasive arsenic contamination of groundwater resources.
Chapter 1: Introduction

Fresh, clean drinking water is a vital resource that is taken for granted in some parts of the world. In January 2015, the World Economic Forum announced that the global water crisis is the number one risk to the human population with regard to its impact on society.\textsuperscript{1} Currently, the World Health Organization estimates that 750 million people lack access to safe water worldwide.\textsuperscript{2} Furthermore, access to safe water disproportionately affects lower income and rural areas, with an estimated 842,000 people dying each year of waterborne diseases.\textsuperscript{3}

Increased global population, rapid socioeconomic development, and climate change have affected clean water supplies in many regions. Of all accessible freshwater sources, 98\% is stored in groundwater aquifers.\textsuperscript{4} As our freshwater needs continue to increase, we are utilizing this freshwater resource at rates greatly exceeding those of natural recharge, which can take from a few hours to tens of thousands of years.\textsuperscript{5} This imbalance in our groundwater use has many detrimental environmental consequences, including the drying of wetlands, destructive settling of the surrounding land, and contamination of groundwater by saltwater intrusion.\textsuperscript{6-8}

In order to meet growing global water demands, locations around the world have been assessing the potential for artificially recharging groundwater with secondary water sources. Managed aquifer recharge (MAR) has been used as a blanket term to describe the variety of techniques and secondary water sources utilized for this engineered process. However, many unpredicted and unwanted geochemical processes can occur when secondary water is introduced into delicate groundwater systems. We need better characterization of these systems in order to establish safe and sustainable MAR practices.
1.1. Background

1.1.1. Managed Aquifer Recharge (MAR)

Managed aquifer recharge is a vital component in decentralized water supply frameworks and integrated water resources management to meet water needs, particularly in areas where water supplies are low. Figure 1.1 shows a schematic of MAR operation using different recharge strategies. The history of MAR within the United States dates back to the early 1900s, when drainage wells were installed to promote recharge from wetlands, storm runoff, and even sewage into groundwater aquifers. In the 1930s, the development of air conditioning increased groundwater pumping exponentially, and subsequently legislation was passed which required this water to be recharged to aquifers. Recharge was often accomplished through the use of injection wells or spreading basins. The prevalence of these groundwater recharge operations sparked scientific curiosity about the impact of artificial recharge on groundwater quality, and studies were carried out on the resulting changes in aquifer hydrology and temperature.

As municipal water and sewage systems became more widespread, interest grew in the use of treated wastewater for MAR operations. Using wastewater for groundwater recharge has been considered since 1980. Tertiary treated (e.g., “reclaimed”) wastewater has many advantages for use in groundwater recharge operations, including low cost.

Figure 1.1. Schematic showing various methods of MAR of confined and unconfined groundwater aquifers (from BGS, 2005)
and prevalence. In addition, natural filtration and attenuation processes occurring during reclaimed water transport through the vadose zone and in the groundwater aquifer can help to further cleanse the water, resulting in recovered water with a composition no different from groundwater.\textsuperscript{15-18} Soil treatment combined with groundwater recharge using secondary water has been termed aquifer storage, transfer and recovery (ASTR).\textsuperscript{19}

Examples of MAR using treated wastewater can be found all over the globe, including in Israel, Australia, Mexico, South Africa, Thailand, Peru, and the U.S. (e.g., Texas, Arizona, California, Florida, and Hawaii).\textsuperscript{20-25} As MAR is being utilized on a larger scale, the environmental sustainability of these operations has come into question. Studies at MAR field site have found that, in addition to the persistence of some organic compounds and microbes found in wastewater, MAR can induce unfavorable soil-water interactions, releasing arsenic, a toxic metalloid, from aquifer formation minerals. Jones and Pichler\textsuperscript{22} reported that while injection waters to a MAR site in South Central Florida contained 3 \( \mu \text{g/L} \) of arsenic, recovered levels ranged from 10-130 \( \mu \text{g/L} \). Increased arsenic mobilization has also been observed at many other recharge sites using a variety of different recharge techniques and secondary water sources, as well as having different sediment types. A summary of these sites is in Table 1.1.\textsuperscript{26}

Studies on aquifer mineralogy at some affected MAR sites have revealed the source of this mobilized arsenic to be arsenopyrite (FeAsS).\textsuperscript{22} Arsenopyrite is the most commonly occurring As-bearing mineral in the Earth’s crust, and while it is stable under low oxidation/reduction potential (ORP) and circumneutral pH conditions, variations in ORP and aqueous chemistry may mobilize arsenic from arsenopyrite into the surrounding aqueous environment.\textsuperscript{27,28} During MAR, the water chemistry can be drastically different from resident groundwater chemistry in terms of dissolved oxygen levels, total organic carbon (TOC), and the concentration
<table>
<thead>
<tr>
<th>Site</th>
<th>Recharge Water</th>
<th>Aquifer Type</th>
<th>Site Characteristics</th>
<th>Arsenic Level</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Full-scale ASR trial at Bolivar, South Australia</strong></td>
<td>Reclaimed water from the Bolivar Water Reclamation Plant</td>
<td>Carbonate Aquifer</td>
<td>Injection flow rate: 7.9-11.9 L/s Recovery flow rate: 8.7-15.9 L/s Depth: 100-160 m $K_{\text{average}}$: 3 m/day</td>
<td>Injected: 3.0 ± 2.2 μg/L Ambient: 3.0 ± 2.2 μg/L Recovered: 22.5 ± 12 μg/L</td>
<td>Vanderzalm et al.29</td>
</tr>
<tr>
<td><strong>Southwest-Central Florida Groundwater Basin, USA</strong></td>
<td>Surface water</td>
<td>Highly permeable carbonate rocks, Suwannee Limestone, Ocala Limestone</td>
<td>K: 0.98-30 m/day Pyrite: 276-32,406 mg/kg As wt% pyrite: 0.01-1.12</td>
<td>Injected and storage zone: 3 μg/L Recovered: 10-130 μg/L</td>
<td>Wallis et al.30 Jones and Pichler22</td>
</tr>
<tr>
<td><strong>San Joaquin Valley, California, USA</strong></td>
<td>Surplus water from the Stockton East Water District WTP</td>
<td>Fluvial sediment of the Pleistocene Modesto and Riverbank Formations</td>
<td>Injected flux: 2.5×10^6 m^3/surface area Depth: 60 m</td>
<td>Injected: &lt;5 μg/L Recovered: 7-10 μg/L</td>
<td>McNab et al.23</td>
</tr>
<tr>
<td><strong>Fox River Valley, Green Bay, Wisconsin, USA</strong></td>
<td>Surface water and groundwater from another aquifer</td>
<td>Sandstone and limestone</td>
<td>Transmissivity: 102 m^2/day</td>
<td>Recovered: 3-60 μg/L</td>
<td>Bahr et al.31 Brown et al.32</td>
</tr>
<tr>
<td><strong>Manatee, Florida, USA</strong></td>
<td>Reclaimed water</td>
<td>Carbonate aquifer</td>
<td>Aquifer τ: 0.5 months Salinity: 2000 mg/L T: 26ºC; flow rate: 5.26 m^3/min Storage: 19,000 m^3</td>
<td>Injected: ND Ambient: 8 μg/L Recovered: 24 μg/L</td>
<td>Overacre et al.33</td>
</tr>
<tr>
<td><strong>Ruhr Valley, Western Germany</strong></td>
<td>Bank infiltration</td>
<td>Sandy sediment, anoxic Pleistocene aquifer</td>
<td>V: 0.21-0.82 m/day</td>
<td>Maximum of 13.8 μg/L for V = 0.21 m/day Maximum 25.5 μg/L for V = 0.82 m/day</td>
<td>Schlieker et al.24</td>
</tr>
<tr>
<td><strong>Pumping station Schuwacht (Hydron-ZH), Netherlands</strong></td>
<td>Treated and aerated groundwater.</td>
<td>Coarse, sandy sediments of the Sterksel formation</td>
<td>Water periodically injected, flow rate: 30 m^3/h for 2 days Depth: 20-30 m</td>
<td>Injected: 0 μg/L Recovered: 9-14 μg/L</td>
<td>Appelo and de Vet20</td>
</tr>
<tr>
<td><strong>Western Snake River Plain, Idaho, USA</strong></td>
<td>Crop irrigation with surface water</td>
<td>Alluvial gravels and sands</td>
<td>Recharge rate: &gt; 50 cm/year Average O_2: 4.8 mg/L</td>
<td>Surface irrigation: 7 μg/L Seep water: 38 μg/L</td>
<td>Busbee et al.34</td>
</tr>
<tr>
<td><strong>Hetao basin, Northwest China</strong></td>
<td>Alluvial fan overflow and irrigation channels</td>
<td>Alluvial-pluvial sand, fluvial-lacustrine sandy silt, silty clay and organic matter rich clay</td>
<td>K=10-20 m/day</td>
<td>Moderate flow (recharge) zone: 30.6 μg/L Low flow: 131 μg/L Discharge zone: 34 μg/L</td>
<td>Guo et al.35</td>
</tr>
<tr>
<td><strong>Madison River Valley, Montana, USA</strong></td>
<td>Arsenic-rich river water and irrigation</td>
<td>Quaternary alluvium and tertiary volcano-clastic sediment</td>
<td>Groundwater flow rate: 0.34 m^3/day Transmissivity: 2490 m^2/day</td>
<td>Recharge: 41-74 μg/L Oxic zone: 25-50 μg/L Reduced zone: 60-160 μg/L</td>
<td>Nimick36</td>
</tr>
</tbody>
</table>

K is the hydraulic conductivity, V is the linear velocity of the fluid, and τ is residence time
of chemical constituents such as chloride, nitrate, and iron. Table 1.2 summarizes injection water quality for MAR sites which found high arsenic concentrations in recovered groundwater.

In order to establish MAR practices that minimize arsenic mobilization and protect vital clean water resources, we must define the processes impacting arsenic mobilization and attenuation in groundwater and determine how these processes can be affected by MAR operations.

### Table 1.2: Injection water quality at MAR sites with recharge-influenced arsenic mobilization (adapted from Neil et al., 2012)

<table>
<thead>
<tr>
<th>Site Description</th>
<th>As in sediment</th>
<th>pH</th>
<th>Temp.</th>
<th>DO</th>
<th>Eh</th>
<th>Total Fe</th>
<th>NO₃⁻</th>
<th>TOC</th>
<th>Recovered As</th>
</tr>
</thead>
<tbody>
<tr>
<td>Full-scale ASR trial at Bolivar, South Australia²⁷</td>
<td>n/a</td>
<td>7.1±0.5</td>
<td>19±5°C</td>
<td>0.17±0.11 mmol/L</td>
<td>Injected: 450±290 mV</td>
<td>0.004±0.009 mmol/L</td>
<td>0.20±0.21 mmol/L</td>
<td>1.4±0.4 mmol/L</td>
<td>22.5±12 μg/L</td>
</tr>
<tr>
<td>Southwest-Central Florida Groundwater Basin, USA²³, ³¹</td>
<td>3.5 mg/kg</td>
<td>7.6</td>
<td>25.8°C</td>
<td>15.4 mg/L</td>
<td>0.1 mg/L</td>
<td>n/a</td>
<td>0.97-1.2 mmol/L</td>
<td>10-130 μg/L</td>
<td></td>
</tr>
<tr>
<td>San Joaquin Valley, California, USA²³</td>
<td>8-24 mg/kg</td>
<td>7.1</td>
<td>n/a</td>
<td>n/a</td>
<td>0.1 mg/L</td>
<td>n/a</td>
<td>&lt;0.003 mmol/L</td>
<td>DIC=0.53 mmol/L</td>
<td>7-10 μg/L</td>
</tr>
<tr>
<td>Manatee, Florida, USA²⁴</td>
<td>n/a</td>
<td>n/a</td>
<td>24°C</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>10.6 mg/L</td>
<td>24 μg/L</td>
</tr>
<tr>
<td>Ruhr Valley, Western Germany*²⁴</td>
<td>18.7 mg/kg</td>
<td>7.75</td>
<td>n/a</td>
<td>8 mg/L</td>
<td>430 mV</td>
<td>&lt;0.005 mg/L</td>
<td>16 mg/L</td>
<td>DIC=19.2 mg/L</td>
<td>13.8-25.5 μg/L</td>
</tr>
<tr>
<td>Schuwacht (Hydron-ZH), Netherlands²⁰</td>
<td>n/a</td>
<td>7.4</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>44 mg/L</td>
<td>n/a</td>
<td>9-14 μg/L</td>
<td></td>
</tr>
</tbody>
</table>

Pe = -log₁₀[e⁻], high Pe correlates with an oxidizing environments (i.e., high Eh). *Concentration of artificial solutions created to mimic injection water in laboratory setting.
1.1.2. Arsenopyrite oxidative dissolution

In deeper aquifers with depleted oxygen and low resident ORP, arsenic will frequently exist in association with iron sulfide minerals such as pyrite (FeS$_2$). The substitution of arsenic into the crystalline structure of pyrite can occur under both oxidizing and reducing conditions, and the resulting structure contains AsS dianion groups.$^{37}$ The product, called arsenian pyrite, can contain arsenic in quantities as large as 10 wt% and, in terms of dissolution, is more reactive than pyrite that does not incorporate arsenic. Blanchard et al.$^{37}$ suggest that this is the case for arsenian pyrite because during dissolution, sulfur vacancies preferentially form next to the incorporated arsenic, resulting in faster oxidation. The oxidation of arsenian pyrite can be written as follows.$^{38}$

$$\text{FeAs}_x\text{S}_{2-x} + \left(\frac{x}{2} - 2x\right) \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \left(2 - x\right)\text{SO}_4^{2-} + 2\text{H}^+ + x\text{As}_{aq},$$

(1.1)

Figure 1.2. A) Crystal structure of arsenopyrite created using Crystal Maker V.2.3.1. (adapted from Neil et al., 2012) and B) a natural arsenopyrite ore sample.
where x is the fraction of As present in pyrite. When x = 0, this equation provides the pyrite oxidation reaction, and when x = 1, this equation provides the oxidation reaction for arsenopyrite. Arsenopyrite (FeAsS) contains a 1:1:1 ratio of iron, sulfur, and arsenic, and has a monoclinic structure similar to that of marcasite (Figure 1.2A). Figure 1.2B shows a natural arsenopyrite ore sample sourced from Gold Hill, Tooele County, Utah.

The solubilities of arsenopyrite and arsenian pyrite are similar (logK_{sp} = 216.73 and 215.50 for arsenopyrite and arsenian pyrite [2.5 wt% As], respectively). However, it is more energetically favorable to form two-phase mixtures of pyrite and arsenopyrite than to form arsenian pyrite, and so frequently arsenic-rich pyrites are found to contain randomly dispersed nano-scale domains of pyrite and arsenopyrite, rather than arsenian pyrite. Thus, although arsenian pyrite can form in nature, it is important to characterize arsenopyrite geochemical reactions because they can still occur as nano-sized grains within arsenic-rich pyrite. While arsenopyrite is more stable than arsenian pyrite, it can react under oxidizing or acidic conditions. The solubility of arsenopyrite is limited under oxidizing conditions by the solubility of scorodite (FeAsO_{4}·2H_{2}O), an oxidation product. Under acidic (pH < 4) and reducing conditions, arsenopyrite can transform into realgar (\(\alpha\)-As_{4}S_{4}) or orpiment (As_{2}S_{3}). Reclaimed water utilized for MAR generally has a higher redox potential and significant concentrations of dissolved oxygen. Thus, the oxidation of these arsenic-bearing sulfide minerals is likely an important source of observed arsenic mobilization. Jones and Pichler found that As-bearing pyrite deposits were correlated with instances of arsenic mobilization during MAR in the Upper Floridan aquifer. As a result of these findings, MAR site selection recommendations have stated that arsenic release should be expected where arsenic is known to be present in the sediment as a reduced mineral (i.e., pyrite) and the source water contains oxidants.
Reclaimed wastewater for MAR can contain a number of potential oxidants, including dissolved oxygen ($O_2$), ferric ions ($Fe^{3+}$) (at pH < 5), and nitrate. These constituents can oxidize arsenopyrite through the following mechanisms: \(^{43,44}\)

\[
FeAsS + 1.5H_2O + 2.75O_2(aq) \leftrightarrow Fe^{2+} + H_3AsO_3 + SO_4^{2-}, \quad (1.2)
\]

\[
FeAsS + 7H_2O + 11Fe^{3+} \leftrightarrow 12Fe^{2+} + H_3AsO_3 + SO_4^{2-} + 11H^+, \text{ and} \quad (1.3)
\]

\[
8Fe(As,S)_2 + 13NO_3^- +25H_2O +10H^+ \leftrightarrow 8Fe^{2+} + 8HAsO_4^{2-} + 8SO_4^{2-} + 13NH_4^+. \quad (1.4)
\]

Continued oxidizing conditions will allow $Fe^{2+}$ released from arsenopyrite oxidative dissolution to be further oxidized to $Fe^{3+}$.

Under the circumneutral or higher pH conditions expected to occur in the subsurface, $Fe^{3+}$ can be easily hydrolyzed in aqueous environments to form iron(III) (hydr)oxide secondary mineral precipitates: \(^{45}\)

\[
Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3 + 3H^+. \quad (1.5)
\]

One site implementing MAR in Bolivar, South Australia, monitored groundwater DO levels before and after secondary water injection. Resident groundwater had DO levels of 0.8 mg/L and an ORP of 29 ± 56 mV. Injected secondary water contained 11.9 mg/L DO and had an ORP of 392 ± 32 mV. Five months following recharge, elevated DO levels of 2.7 mg/L remained at the injection well, and the ORP was 112 mV.\(^{33}\) The persistence of DO as an arsenopyrite oxidant, as well as its pervasiveness in injection waters, makes it an important factor when predicting arsenic mobilization during MAR. In addition, wastewater treatment processes such as ozonation, and transport processes, such as pumping, can increase DO levels in secondary water used for MAR.
When considering overall arsenic mobilization from arsenopyrite in groundwater aquifers, oxidative dissolution is not the only player. The formation of iron(III) (hydr)oxide secondary mineral precipitates through eq. 1.5 will also have significant impacts on mobile arsenic concentrations through sorption and co-precipitation with aqueous arsenic. Furthermore, the formation extent of these minerals and their capacity for attenuating arsenic can be affected by MAR-induced water chemistry changes.

1.1.3. Iron(III) (hydr)oxide secondary mineral precipitation

The association of arsenic with iron(III) (hydr)oxides is well documented throughout the literature.\textsuperscript{46-55} Within arsenic-contaminated soil samples, Cances et al.\textsuperscript{49} found that less than 10% of total arsenic was readily mobilized, 10–37% was sorbed, and more than 65% was associated with iron(III) (hydr)oxides and thus poorly mobilized. Ferrihydrite (Fe(OH)\textsubscript{3}), a naturally forming nanoparticle, is frequently associated with arsenic attenuation. Due to its small size and high reactive surface area, ferrihydrite can be an important variable in predicting the fate and transport of waterborne trace contaminants. Accordingly, the nucleation and growth of ferrihydrite contributes large uncertainties to reactive transport modeling of systems where ferrihydrite precipitation is likely to occur.

During MAR, iron(III) (hydr)oxides such as ferrihydrite are known to form as a product of pyrite oxidation close to the secondary water injection site, where oxygen supplies are not yet depleted. In aqueous environments, these newly formed, nano-sized iron(III) (hydr)oxides can strongly sorb arsenic, and desorption is unlikely to occur until the mineral degrades through dissolution. However, iron(III) (hydr)oxide formation will be strongly affected by local water chemistry. Thus, water chemistry changes induced by MAR can impact the extent and kinetics of iron(III) (hydr)oxide nucleation, as well as alter physicochemical properties such as the size,
crystallinity, composition, surface charge, hydrophilicity, and formation location of these precipitates.\textsuperscript{56,57} These properties will subsequently impact the ability of iron(III) (hydr)oxides to adsorb or co-precipitate with arsenic and can change their reactivity and stability in aqueous environments.

Many studies have been conducted on the ability of different anions to compete with or displace arsenic from sorption sites on the ferrihydrite mineral surface. For example, studies have found that both ferrous iron and carbonate can form surface complexes on ferrihydrite that result in arsenic displacement.\textsuperscript{46} Phosphate and silicate have also been shown to compete with arsenate (As(V)) for surface sorption sites.\textsuperscript{50,58-60} However, the majority of these studies consider only arsenic sorption on preformed iron(III) (hydr)oxides. Very few studies have considered how aqueous contaminants can impact the formation of iron(III) (hydr)oxides. This is of particular importance in the case of arsenopyrite oxidative dissolution because arsenic and iron will be mobilized simultaneously.\textsuperscript{26} Characterizing these secondary mineral precipitates is important because later geochemical reactions, such as the reductive dissolution or phase transformation of iron(III) (hydr)oxides, can impact arsenic fate and transport on larger time scales.

Studies have shown that the recovery of groundwater from MAR sites can reductively dissolve newly-precipitated ferrihydrite, and subsequently mobilize associated arsenic, due to the migration of anoxic native groundwater towards the well\textsuperscript{30}. In addition, the reduction of ferrihydrite can occur due to natural recharge with low DO water. This mechanism is a major source of arsenic contamination of shallow aquifers in Bangladesh.\textsuperscript{61} The reduction of As-bearing ferrihydrite can also result from interactions between this mineral and ammonium, sulfide, and organic matter.\textsuperscript{62-64} Frequently, the kinetics of these interactions will be controlled
by microbial processes. For example, iron(III) (hydr)oxide reduction by organic matter (e.g., acetate) can occur through the following microbially-mediated reaction:\textsuperscript{65}

\begin{equation}
8\text{FeOOH} + \text{CH}_3\text{COO}^- + 15\text{H}_2\text{CO}_3 \rightarrow 8\text{Fe}^{2+} + 17\text{HCO}_3^- + 12\text{H}_2\text{O},
\end{equation}

where acetate is a model for organic matter. McArthur \textit{et al.}\textsuperscript{62} speculated that peat beds within aquifers were a possible source for this organic matter. Their study showed a correlation between areas with high groundwater arsenic levels and their proximity to these peat beds. The role of organic matter in reductive dissolution is important because reclaimed water used for MAR is expected to have elevated total organic carbon (TOC) levels compared to groundwater. A thorough understanding of the reactivity and properties of iron(III) (hydr)oxides formed during MAR is necessary in order evaluate the risk of arsenic-bearing iron(III) (hydr)oxide reduction as a potential source for arsenic.

In addition, although arsenopyrite oxidation can produce ferrihydrite, certain reclaimed water constituents may also prevent this reaction. For example, reclaimed water can contain high levels of chloride ions, which have been shown by Hu \textit{et al.}\textsuperscript{56} to prevent iron (hydr)oxide nucleation by complexing with Fe\textsuperscript{3+} ions. However, the pH for this experimental system (pH = 3.7 ± 0.2) was lower than it would likely be in groundwater. Furthermore, while this pathway is an important consideration, it may not always be a factor in predicting arsenic mobility since ferrihydrite formation during MAR will be site-specific. For example, Jones and Pichler\textsuperscript{22} found that it was not thermodynamically favorable for ferrihydrite to form under the geochemical conditions at their Florida MAR operation site. Therefore, investigations must be carried out both to determine the potential for ferrihydrite formation during MAR and to characterize the effect of ferrihydrite formation on arsenic mobility under MAR-relevant conditions.
While important during the early stages of MAR operation, ferrihydrite is only thermodynamically stable at the nanoscale, and will thus undergo phase changes over time to become one of a number of more stable iron oxide polymorphs. In aqueous systems, dissolution and reprecipitation of ferrihydrite can form goethite or maghemite and, eventually, hematite, the most thermodynamically favorable bulk iron oxide mineral. When this occurs, ferrihydrite will irreversibly immobilize contaminants which are adsorbed during phase transformation. In addition, after ferrihydrite transforms into minerals with more crystalline structures, its adsorptive capability will decrease significantly under circumneutral pH conditions due to the decrease in reactive surface sorption sites. Based on previous literature, it was not well understood how these iron(III) (hydr)oxide phase transformation processes would be changed by secondary water injection during MAR. However, this phase transformation will have a significant effect on the long term fate and transport of arsenic, and it warrants further study.

1.1.4. Groundwater transport considerations

In addition to the systematic investigation of arsenopyrite oxidative dissolution and iron(III) (hydr)oxide secondary mineral precipitation, it is important to consider how these nano- and microscale processes will impact arsenic mobility in larger scale systems, which better model the geochemical environments at MAR sites. In particular, the effects of secondary water transport through arsenic-containing sediment must be considered. In addition to the geochemical processes outlined in the previous sections, arsenic fate and transport in these systems can be impacted by factors such as groundwater flow rates, aquifer mineralogy, and the formation of concentration gradients as secondary water mixes and reacts with groundwater and sediment.
At MAR field sites, the injection of secondary water can lead to local changes in natural groundwater flow, which influences the mixing and reaction of oxygenated injection water with native groundwater. For example, the localized elevation of the water table, known as groundwater mounding, has been observed during artificial recharge as a consequence of lateral permeability restrictions on the dissipation of hydraulic head at injection wells.\textsuperscript{5, 68} The occurrence of groundwater stagnancy in a “bubble” or “bottle brush” of secondary injection water has also been reported (Figure 1.3).\textsuperscript{69-71} MAR bubbles can form due to a lack of mixing between the injected water and groundwater, and they will vary significantly as a result of aquifer heterogeneity, preferential flow pathways, leakage and buoyancy, and soil chemical makeups. Alteration of subsurface aquifer properties due to MAR operation can influence many environmental factors controlling arsenic mobility on local and microscales. These variations also help explain the large spatial and temporal changes often found in groundwater arsenic concentrations.\textsuperscript{72-81}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{MAR bubble formation during secondary water injection (from Neil et al. 2012)}
\end{figure}
The “bubble” or “bottle brush” concept in the MAR process delineates two major types of macroscale physical boundaries and geochemical domains within which the injected water interacts with native groundwater and aquifer formation minerals. Within the bubble, the water chemistry will not differ significantly from the chemistry of the injected water because of limited mixing with and dilution by native groundwater. This generalization agrees with geochemical and hydrological studies showing that zoned flow fields of injected water prevail in the injection “bubble” as it spreads toward the undisturbed aquifer. On the other hand, outside of the bubble, the geochemical conditions can vary significantly depending on the degree of aquifer anisotropicity (e.g., whether the hydraulic conductivity varies in horizontal and vertical directions) and on the convective flow at the periphery of the “bubble” during injection and recovery phases. These factors will affect not only the MAR recovery rate, but also the conditions of soil-water reactions.

Within these bubbles, aquifer formation minerals will interact almost exclusively with secondary water. Unlike native groundwater, this injected water is not in equilibrium with the sediment and can dissolve other minerals in addition to arsenopyrite. In particular, carbonate minerals have been found to dissolve at a rate of $35 \pm 6 \, \text{g/m}^3$ of aquifer during MAR operation in a carbonate aquifer in South Australia. Amorphous silica has also been shown to dissolve during MAR in a limestone aquifer in South Carolina, USA. In addition, aquifer formation minerals provide a variety of different substrates for secondary mineral precipitation, as well as additional potential minerals which can sorb arsenic. For example, carbonate-rich minerals and clay minerals are both potential arsenic sorbents in groundwater aquifers. As the MAR bubble moves away from the injection well and interacts with these minerals, the water
chemistry will change. For instance, dissolved oxygen and other oxidants can be used up through reaction with reduced sulfide minerals, and TOC can be depleted through microbial processes.

When predicting the risk of arsenic contamination of groundwater resources during MAR, the combined effects of reaction and transport must be incorporated into well-developed, rigorous models. These reactive transport models (RTMs) will provide a quantitative basis for arsenic mobilization projections. Current RTMs do not fully incorporate the many geochemical processes which can impact arsenic mobility during aquifer soil–water interactions at MAR sites. To make accurate predictions and prevent groundwater contamination, RTMs need to encompass all known mechanisms of arsenic release and attenuation, and unknown factors must be elucidated. Among many proposed mathematical models and formulations in current literature, Wallis et al.’s model is the most comprehensive. The Wallis et al.\textsuperscript{30} model considers oxidation of arsenic-bearing pyrite by oxygen, competition between arsenic anions and other ions for sorption sites on ferrihydrite, and reduction of ferrihydrite by H\textsubscript{2}S and dissolved organic carbon. The attenuation mechanism modeled is the simultaneous precipitation of ferrihydrite. However, there is still much room for improvement. In particular, more empirical studies are needed to provide quantitative values for use in these models, and more consideration must be given to the impact of reclaimed water constituents on arsenic mobility. Rigorous RTMs, once developed, will provide a basis for the evaluation, design, and implementation of full-scale MAR operations.

1.2. Research objectives and tasks

1.2.1. Current knowledge gaps

The geochemical reactions of arsenopyrite and iron(III) (hydr)oxides have been studied extensively with regard to their impact on groundwater quality.\textsuperscript{42, 44, 48, 54, 93-99} However, the utilization of reclaimed wastewater during MAR is a new application, and brings with it new
safety and sustainability concerns due to interactions between arsenic-bearing pyrite and reclaimed water. The implementation of MAR using reclaimed wastewater can introduce a number of non-native constituents into groundwater aquifers, including dissolved oxygen, ferric ions, salts, and high concentrations of TOC (Table 1.2). The role of these constituents on arsenopyrite oxidation must be delineated.

In addition, arsenopyrite oxidation will produce iron(III) (hydr)oxide secondary mineral phases, which can also impact aqueous arsenic mobility as outlined. In previous literature, arsenopyrite oxidation has been studied under low pH conditions in order to reduce these effects. However, in groundwater aquifers and in the water bubble during MAR operation, the pH generally is circumneutral or higher. Thus, the formation of iron(III) (hydr)oxides cannot be ignored and will provide a significant attenuation pathway for arsenic mobilized during MAR. The extent of formation, phase transformation, and sorption capacity of these secondary minerals can also be impacted by water chemistry changes during MAR. These impacts are largely unknown and need to be systematically investigated on the nano- to microscale.

Lastly, RTMs of arsenic mobilization during MAR need to be given a thorough scientific basis. By empirically determining values, such as activation energies for arsenic mobilization and iron(III) (hydr)oxide nucleation rates under MAR conditions, these models can better reflect the geochemical reactions occurring at MAR field sites.

1.2.2. Specific research objectives

In order to address the current knowledge gaps and to provide a strong scientific basis for improving the safety and sustainability of MAR, the following objectives for this project were outlined.
**Objective 1:** Determine how water chemistry changes during MAR can influence nanoscale iron(III) (hydr)oxide nucleation and growth and subsequently affect arsenic attenuation.

**Hypothesis:** The precipitation of iron(III) (hydr)oxides is expected to be prevalent under conditions relevant to MAR. The formation kinetics and physicochemical properties of these precipitates can be affected by reclaimed water constituents such as dissolved organic matter, and by the co-release of arsenic and iron from arsenopyrite. By providing nucleation kinetics and mechanisms, we will have a better estimation of the reactive surface area of secondary mineral precipitates.

**Objective 2:** Determine the microscale geochemical processes occurring during MAR which influence arsenic mobilization through the oxidative dissolution of arsenopyrite and precipitation of secondary minerals.

**Hypothesis:** Redox chemistry and aqueous chemistry during MAR will control arsenic mobility. Oxidants present in secondary reclaimed water, including dissolved oxygen and ferric ions, can contribute to arsenic mobilization by oxidizing arsenopyrite. In addition, reclaimed water constituents, such as chloride and organic matter, can impact secondary mineral precipitation. In accordance with previous literature, oxygen is expected to be the primary oxidant under circumneutral pH conditions relevant to MAR.

**Objective 3:** Apply scientific findings to larger scale MAR systems and develop RTMs which can accurately simulate arsenic mobilization by incorporating empirically determined values for arsenopyrite dissolution under MAR conditions.

**Hypothesis:** Column experiments can mimic arsenic transport in MAR systems due to the presence of sediment and the development of vertical concentration gradients. Close to the
injection point, the soil column will be oxygen-rich and, therefore, have the most arsenopyrite oxidation. In addition, RTMs can be improved by incorporating empirical rates for arsenopyrite dissolution determined under MAR conditions to better predict the extents of arsenic mobilization.

1.3. Overview of Dissertation

To pursue the three objectives listed above, research directions were divided into three tasks. In Task 1, nanoscale investigations of iron(III) (hydr)oxide precipitation (nucleation and growth) were conducted, and in Task 2, microscale approaches were used to observe simultaneous arsenopyrite oxidative dissolution and secondary mineral precipitation under MAR conditions. These new findings help to better define the dominant geochemical reactions expected to occur during MAR operation and provide a basis for secondary water quality recommendations to minimize arsenic mobilization. Task 3 entailed the application of our nano- and microscale outcomes to the operation and reactive transport modeling of larger scale soil columns (Objective 3), which better mimic MAR operations. This task helped to demonstrate the importance of considering mineral reactivity under MAR conditions when applying currently available models. Figure 1.4 shows a summary of these tasks.

Task 1 is addressed in Chapter 2. Utilizing in situ grazing incidence small angle X-ray scattering (GISAXS), we observed iron(III) (hydr)oxide nucleation and growth in real-time in systems with different water chemistry to mimic situations expected to occur during MAR and in other natural and engineered aquatic systems. These include the presence of arsenate, phosphate, natural organic matter, and a combination of natural organic matter and arsenate. Ex situ characterization of nanoscale precipitates gave insight to in situ nucleation and growth trends.
**Task 2** is addressed in **Chapter 3**. Arsenic mobilization from arsenopyrite was investigated under aerobic and anaerobic conditions for model wastewaters as well as actual reclaimed wastewater samples from a wastewater treatment plan in Cincinnati, OH. Portions of this project were carried out in collaboration with the U.S. Environmental Protection Agency and Chicago Bridge & Iron Company (CB&I). Different water constituents studied included nitrate versus chloride anions, ferric ions, and natural organic matter. Secondary mineral precipitate phases and extents were also investigated under these different conditions. Systematic connections between precipitation and aqueous arsenic concentrations were made.

**Task 3** is addressed in **Chapter 4**. Large scale soil columns were created and arsenic mobilization during bottom-up flow was monitored over 30 days. After reaction, the iron and arsenic mineralogy of the column was measured using sequential extraction. Arsenic concentrations were modeled using CrunchFlow reactive transport modeling, which was informed by outcomes of **Tasks 1 and 2**.

Finally, major conclusions and environmental implications of this work are outlined in **Chapter 5**, along with recommended future directions.
Portions of this chapter have been published in *Journal of Environmental Monitoring*, 2012, 14(7), 1772-1788 (DOI: 10.1039/C2EM30323J) and are reproduced by permission of The Royal Society of Chemistry.
Chapter 2: Nanoscale: Investigation of nucleation and growth of iron(III) (hydr)oxides under MAR conditions

Portions of this chapter have been published in Environmental Science & Technology, 2014, 48 (20), 11883–11891. Other results have been submitted to a peer-reviewed journal.

2.1. Overview

Iron(III) (hydr)oxides play an important role in controlling the fate and transport of contaminants in aquatic systems. The nucleation kinetics, morphology, and quantity of iron(III) (hydr)oxide nanoparticles is greatly affected by water chemistry, thus directly impacting their reactive surface area and the fate of associated waterborne contaminants. In this chapter, in situ grazing-incidence small angle X-ray scattering (GISAXS) and complementary ex situ characterization techniques were used to investigate heterogeneous iron(III) (hydr)oxide nucleation on quartz in the presence of phosphate, arsenate, natural organic matter (NOM), and NOM together with arsenate.

For the iron(III) only system, the radius of gyration ($R_g$) of heterogeneously formed precipitates grew from 1.5 to 2.5 ($\pm$ 1.0) nm within 1 hour. For the system containing $10^{-5}$ M arsenate, $R_g$ grew from 3.6 to 6.1 ($\pm$ 0.5) nm and for the system containing $10^{-5}$ M phosphate, $R_g$ grew from 2.0 to 4.0 ($\pm$ 0.2) nm. While the systems containing these oxyanions had more growth, the system containing only iron(III) had the most nucleation events on substrates. Ex situ analyses of homogeneously and heterogeneously formed precipitates indicated that precipitates in the arsenate system had the highest water content and that oxyanions may bridge iron(III) hydroxide polymeric embryos to form a structure similar to ferric arsenate or ferric phosphate.
When NOM was present simultaneously with precipitating iron(III) (hydr)oxides, unique fractal aggregation behavior of newly formed particles was observed in situ within the system. Furthermore, the coexistence of arsenic and NOM lead to the formation of two distinct particle size ranges: larger particles dominated by arsenic effects, and smaller particles dominated by NOM effects. These new findings provide important implications for understanding the nucleation, growth, and aggregation of iron(III) (hydr)oxides in aqueous systems where NOM is present, such as natural surface waters and water and wastewater treatment plants, and offer new insight into how these NOM-associated iron(III) (hydr)oxides can interact with aqueous contaminants such as arsenate.

2.2. Introduction

Iron(III) (hydr)oxides play a central role in the geochemical cycling of both natural and anthropogenic aqueous contaminants. Iron(III) (hydr)oxides can form during the oxidative dissolution of Fe(II) minerals, such as pyrite and arsenopyrite, and in acidic systems, such as acid mine drainage, where the dissolution of iron minerals results in supersaturation with respect to iron(III) (hydr)oxides. Initial precipitates can be amorphous and have a high specific surface area, making them powerful sorbents for aqueous trace metal contaminants (e.g., copper (II), chromium (III), and lead (II)) and organic pollutants (e.g., amoxicillin, ampicillin, and fluoroquinolone antibacterial agents).

The ability of iron(III) (hydr)oxides to immobilize these contaminants can be related to whether they are heterogeneously formed precipitates (e.g., formed at mineral surfaces) or homogeneously formed precipitates (e.g., formed in solution). Heterogeneously formed precipitates will be immobilized, while homogeneously formed precipitates can be transported in aqueous systems. The fate and transport of newly-formed nanoparticles can be affected by their
aggregation status as well. In addition, the kinetics, morphology, composition, and formation location of iron(III) (hydr)oxides on mineral surfaces are significantly affected by water chemistry such as pH, ionic strength, and the presence of different aqueous ions. Hence, to better understand immobilization mechanisms of toxic metal and organic contaminants in aquatic environments, we have focused on the heterogeneous nucleation and growth of iron(III) (hydr)oxides in this study.

Among many environmentally important anions, arsenate and phosphate are two oxyanions of interest due to their strong interactions with iron(III) (hydr)oxides. Arsenate is of particular interest due to its chronic toxic effects on humans. The U.S. EPA’s maximum contaminant level (MCL) for arsenic in drinking water is 10 µg/L. Arsenic contamination of drinking water is a problem facing over 137 million people worldwide according to the World Health Organization. The source of this arsenic is frequently naturally occurring minerals such as arsenic-bearing pyrites (e.g., arsenian pyrite or arsenopyrite) present in groundwater aquifers. Arsenic can be mobilized through the oxidation of these minerals, resulting in the simultaneous release of iron (II, III) and arsenate ions and the subsequent precipitation of arsenic-bearing iron(III) (hydr)oxides. This process is frequently the source for arsenic mobilization during MAR, and provides a potential sink for aqueous arsenic. Phosphate is important due to its structural similarity to arsenate, resulting in competitive effects on arsenate sorption and coprecipitation. Furthermore, phosphate can be introduced to natural aquatic systems due to fertilizer runoff and groundwater infiltration of sewage and industrial discharge.

Iron(III) (hydr)oxides, which are generally positively charged, will have strong electrostatic interactions natural organic matter (NOM) in addition to these oxyanions due to the negative
charge of NOM. In regions where arsenic contamination of ground and surface waters is a concern, such as Bangladesh, NOM is also ubiquitously present at concentrations ranging from 0-10 mg C/L in surface water and 0-2 mg C/L in groundwater. Therefore, it is important to fully understand how NOM can interact both with precipitating iron(III) (hydr)oxides and with contaminants such as arsenate. Previous studies have shown that coating of iron(III) (hydr)oxide nanoparticles by NOM can be detrimental to arsenic sorption by inducing unfavorable electrostatic interactions and redox reactions, or by competing for sorption sites on the iron(III) (hydr)oxide surface. With regard to As–Fe–NOM interactions, Liu et al. previously found that As(III) can complex with stable Fe–NOM colloids. Additionally, Chen et al. found that iron(III) (hydr)oxides formed in the presence of NOM contained more organic carbon. However, arsenic was not present for their investigations. Thus, the exact fate of arsenic in the presence of NOM and iron(III) (hydr)oxides is still not clear.

There are decades of studies investigating arsenate removal through sorption and coprecipitation with iron(III) (hydr)oxides, as well as phosphate competition over available sorption sites. However, limited studies exist which systematically investigate in situ the effects of these oxyanions on iron(III) (hydr)oxide precipitation, particularly during the early stages of nucleation and growth. Furthermore, no studies have examined in situ the early stages of iron(III) (hydr)oxide formation in solutions containing both arsenic and NOM, which reflects natural systems more closely than using a sequential approach.

The main objective of our current study was therefore to investigate the in situ nucleation and growth of iron(III) (hydr)oxides in the presence of arsenate or phosphate oxyanions, natural organic matter, and natural organic matter and arsenate together utilizing grazing-incidence small angle X-ray scattering. Nucleation and growth (i.e., precipitation) kinetics of iron(III)
(hydr)oxide were investigated on quartz, an environmentally abundant substrate for natural aquatic systems. The mechanisms behind iron(III) (hydr)oxide precipitation in these systems were then explored by complementary *ex situ* characterization approaches, including atomic force microscopy (AFM), transmission electron microscopy (TEM), high resolution X-ray diffraction (HRXRD), and thermal gravimetric analysis (TGA), to explain observed differences in precipitation kinetics and precipitate morphology (i.e., size, volume, and, therefore, surface area evolution). Our outcomes have important implications not only for arsenic mobilization and attenuation during MAR operation, but for iron(III) (hydr)oxide formation and reactivity in many natural and engineered aquatic systems.

### 2.3. Experimental approach

#### 2.3.1. Materials and chemicals

Substrates used for heterogeneous precipitation studies were high quality single crystal quartz wafers with a surface roughness of less than 5 Å (MTI Corporation, Richmond, CA). Quartz was x-cut, revealing the (110) surface to contact the aqueous solution. Quartz was chosen because it is ubiquitous in groundwater aquifers. Pleistocene sand aquifer material can consist of 70–90% quartz.\(^{138}\) Quartz does not have a distinctive cleavage plane, therefore the abundance of the (110) surface in natural systems would be approximately equal to the abundance of any other surface with a similar surface energy (e.g., \(\bar{1}01\) and 10\(\bar{1}\) surfaces).\(^{139,140}\) Quartz wafers were cut into squares to fit in GISAXS reaction cells and cleaned using Nochromix® and sulfuric acid as outlined in the Supporting Information for this chapter.

Reaction solutions were created using reagent grade Fe(NO\(_3\))\(_3\)·9H\(_2\)O, NaNO\(_3\), Na\(_2\)HAsO\(_4\)·7H\(_2\)O, and Na\(_2\)HPO\(_4\)·7H\(_2\)O and ultrapure water. Fe(III) concentrations were kept at 10\(^{-4}\) M for all systems, while concentrations of 10\(^{-5}\) M arsenate and phosphate were used for *in*
*situ* GISAXS and *ex situ* experiments. Systems testing for arsenate and/or NOM effects also contained $10^{-5}$ M As(V) and 1.5 mg/L non-purgeable organic carbon (NPOC). Suwannee River NOM (SRNOM), purchased from the International Humic Substances Society (IHSS), was used as the NOM source. Interactions between iron(III) (hydr)oxides and NOM occur primarily due to the carboxyl and phenolic acidic functional groups present on the NOM. Suwannee River NOM from the IHSS has been well-characterized. The quantification of carboxyl and phenolic acidic functional groups can be found in Table 2-S1 in this chapter’s Supporting Information, along with details on the preparation of SRNOM stock solutions.

The pH of all systems was 3.6 ± 0.2 and the saturation index (SI) did not vary significantly between the systems. Because the first pKa’s for arsenic and phosphoric acid are 2.3 and 2.2, respectively, both oxyanions will be doubly protonated at the system pH.$^{141, 142}$ Based on thermodynamic calculations, the speciation of arsenate was calculated to be 96.5% $\text{H}_2\text{AsO}_4^-$ and 3.4% $\text{H}_3\text{AsO}_4$ and the speciation for phosphate was calculated to be 97.3% $\text{H}_2\text{PO}_4^-$ and 2.7% $\text{H}_3\text{PO}_4$. Reported saturation indices (SIs in Table 2.3) and aqueous speciation percentages were calculated using the Geochemist's Workbench ® software program (GWB, Release 8.0,

**Table 2.1. Reaction conditions for *in situ* GISAXS experiments**

<table>
<thead>
<tr>
<th>System</th>
<th>[NaNO$_3$]</th>
<th>[Fe(III)]</th>
<th>[H$_2$AsO$_4^-$]</th>
<th>[H$_2$PO$_4^-$]</th>
<th>[NOM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III) only</td>
<td>10 mM</td>
<td>10$^{-4}$ M</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(III) + H$_2$AsO$_4^-$</td>
<td>10 mM</td>
<td>10$^{-4}$ M</td>
<td>10$^{-5}$ M</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(III) + H$_2$PO$_4^-$</td>
<td>10 mM</td>
<td>10$^{-4}$ M</td>
<td></td>
<td>10$^{-5}$ M</td>
<td></td>
</tr>
<tr>
<td>Fe(III) + NOM</td>
<td>10 mM</td>
<td>10$^{-4}$ M</td>
<td></td>
<td></td>
<td>1.5 mg C/L</td>
</tr>
<tr>
<td>Fe(III) + As(V) + NOM</td>
<td>10 mM</td>
<td>10$^{-4}$ M</td>
<td>10$^{-5}$ M</td>
<td></td>
<td>1.5 mg C/L</td>
</tr>
</tbody>
</table>
RockWare, Inc., Urbana, IL) using thermo.dat database file. 10 mM sodium nitrate provided the background ionic strength for all systems due to the abundance of sodium in natural aqueous systems and because nitrate is not expected to interact with iron(III) (hydr)oxides

2.3.2. *In situ* grazing-incidence small angle X-ray scattering

To conduct GISAXS, a clean quartz substrate was first placed in a cleaned, specially designed GISAXS fluid cell. Ultrapure water (resistivity > 18.2 MΩ·cm) was injected into the cell and the surface was aligned with the X-ray beam. The water was then removed and the reaction solution (Table 2.1) was introduced. 1 mL of the solution was immediately injected into the cell and *in situ* GISAXS measurements began. There was an approximately two minute lag time between creating the solution, which started the precipitation reaction, and when the first GISAXS measurement was recorded. The reaction time is defined to start when the solution was created. It is unlikely for precipitates to form in the solution before injection. However, if any did form, these homogeneously formed precipitates would be much larger than those observed to form on the quartz surface over the course of the 1 hour reaction, and thus did not affect our observation of heterogeneous nucleation and growth. The size of these homogeneous particles can range from 4 nm initially to greater than 20 nm after one hour of reaction.56

During the *in situ* reaction period of 1 hour, GISAXS measurements were taken at 1-10 minute intervals. For GISAXS measurements, an incidence angle (αi) of 0.11° was chosen to have 98% reflectivity at the beam energy of 14 keV. Supplementary analysis for iron(III) only, arsenate and phosphate systems using AFM showed that there was not a significant amount of homogeneous particle settling during the 1 hour reaction period (Figure 2-S2 in the Supporting Information). The scattering vector range (e.g. q range) was 0.007–0.300 Å⁻¹. Particle sizing for
heterogeneously formed particles was carried out by fitting the shape of the 1D scattering intensities over the analyzed q range. More details on the GISAXS experimental set-up can be found in the Supporting Information. Experiments were conducted at the Advanced Photon Source (APS), beamline 12-ID-B, at Argonne National Laboratory (ANL) (Argonne, IL).

GISAXS measurements produced a series of time-resolved, 2D scattering images at the mineral surface. The first scattering image was used as a background and subtracted from subsequent images. The 2D images were reduced to 1D by cutting along the Yoneda wing, where the scattering is enhanced by the grazing incidence effect (Vineyard effect). 1D intensities (I) were plotted versus q for different time points to show the evolution in scattering intensities due to iron(III) (hydr)oxide nucleation and growth on quartz substrates. GISAXS data analysis was carried out using the GISAXS-SHOP macro in Igor Pro (v 6.22A, WaveMetrics, Inc., OR) available at APS beamline 12-ID-B. More details on GISAXS analysis can be found in Chapter 2’s Supporting Information and in our group’s publications.56, 143, 144

When a number of particles, N, with the electron density $\rho_p$ and mean individual particle volume V are dispersed in liquid with the electron density $\rho_w$, the integrated Lorentz corrected intensity, called the invariant Q, can be calculated using the following formula:

$$Q = \int_0^\infty I(q) q^2 dq,$$

(2.1)

where q is the scattering vector. The invariant value is proportional to the total nanoparticle volume (N x V) times the square of the contrast, ($\rho_p - \rho_w$). Integrating these curves gives the relative total particle volume and can be used to compare precipitation quantities between the different reaction systems for heterogeneously formed particles. The Lorentz corrected intensities for the arsenate and phosphate systems can be found in Figure 2-S1.
2.3.3. *Ex situ* experimental techniques

**Investigating morphology using Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM).** *Ex situ* AFM measurements of GISAXS samples were conducted to complement *in situ* GISAXS measurements of heterogeneously formed particle sizes. Tapping mode AFM (AFM, Veeco Inc.) was used to measure the height, amplitude, and phase of precipitates on reacted quartz substrates. AFM tapping mode probes were 125 μm long with phosphorus (n) doped silicon tips (nominal tip radius of 10 nm, MPP-11100−10, Bruker probes). A scanning rate of 0.988 Hz and drive frequencies were between 312 and 320 kHz were used during imaging. Images were processed using Nanoscope 7.20 software. For NOM systems, additional AFM experiments were run with arsenic or NOM added first, and the other components added sequentially after 30 minutes for the Fe(III) + As(V) + NOM system in order to deduce the mechanism of NOM effects.

TEM measurement of homogeneous particles was also carried out to observe their aggregation state (FEI Tecnai Spirit, Hillsboro, OR). For TEM samples, a single drop of each reaction solution was placed on 300-mesh Cu Formvar-carbon grids after 1 hour of reaction and dried in a desiccator immediately prior to imaging.

**Zeta Potential (ζ) Measurements.** Zeta potentials were measured using a Zetasizer (Nano ZS, Malvern Instruments Ltd., Westborough, MA). The zeta potentials for homogeneous and heterogeneous precipitates were measured by injecting the reaction solutions with or without suspended quartz powder, respectively. Quartz powder was used due to the technical difficulties in measuring the zeta potential of single crystal quartz. Zeta potentials for the quartz powder alone were also measured in the different phosphate, arsenate, or NOM solutions with the pH adjusted to be 3.6 ± 0.2.
Quantifying Arsenate, Phosphate, and NOM Incorporation in Iron(III) (Hydr)oxides.

Arsenate, phosphate, and NOM incorporation into iron(III) (hydr)oxides was quantified. First, a large batch of the reaction solution (Table 2.1) was created and precipitates were concentrated at 5000 RPM using Millipore Amicon ultra-15 centrifugal filter units (Millipore Corporation, Billerica, MA, USA). The NMWL of this membrane was 100,000. The particle-rich solution was acidified with 2\% nitric acid to dissolve iron(III) (hydr)oxides. The pH of the 2\% nitric acid was <2.0, which is sufficient to dissolve a large portion of newly formed iron(III) hydroxide phases. Although the precipitates were not rinsed, the contribution from the remaining small volume of solution was calculated and found to be negligible compared to the concentration of iron, arsenic, and phosphorus in the acidified filtrate. These calculations can be found in the Supporting Information. The solution was then diluted and measured for arsenic or phosphorus and iron concentrations using inductively-coupled plasma mass spectroscopy (ICP-MS, Agilent 7500 ce, Santa Clara, CA). The NOM content was measured using a TOC Analyzer (Shimadzu Corporation, Kyoto, Japan). For arsenate and phosphate systems, incorporation into heterogeneously formed precipitates was also measured to confirm trends in the homogeneous system. For these measurements, in situ GISAXS batch reactors were scaled up to contain 50 mL of the reaction solution. Quartz powder (103-381 \(\mu\)m) was added to maintain the same solution volume: surface area ratio as in the GISAXS batch reactor cell. The quartz powder was reacted for one hour in the iron only and arsenate or phosphate-containing systems. The reactor contents were filtered and the quartz powder was rinsed using DI water. Iron(III) (hydr)oxide precipitates were dissolved off of the powder using 2\% nitric acid. The solution was filtered using a 0.2 \(\mu\)m syringe filter and analyzed for iron, arsenic, and phosphorus concentrations using ICP-MS.
Identifying Particle Phases. A number of different techniques were implemented to identify the phase of iron(III) (hydr)oxide precipitates, and detailed descriptions of these techniques can be found in the Supporting Information. Successful characterization of aged particles was achieved using high-resolution X-ray diffraction (HRXRD). Homogeneously precipitated particles were first concentrated using Millipore Amicon ultra-15 centrifugal filter units. The concentrated nanoparticle slurry was transferred to a glass slide and dried overnight in a desiccator. Samples were sent to Sector 11-BM of the APS at ANL, where they were analyzed using HRXRD after 8-11 days of particle aging. The caveat of ex situ HRXRD is that the phase identity can be different from the in situ phase due to this particle aging, which can affect the crystalline phase and water content of precipitates.

Investigating Water Incorporation into Iron(III) (Hyd)oxides. The water content of homogeneous and heterogeneous precipitates was also investigated. For thermal gravimetric analysis (TGA), 1 L batches of homogeneous precipitates were created using the same method outlined in the Supporting Information for HRXRD experiments. Concentrated nanoparticles were added to high temperature platinum TGA pans for analysis. During TGA, the temperature of the sample was increased incrementally from room temperature to 950°C. It was assumed that once the temperature exceeded 107°C, the water from the slurry was evaporated and additional mass loss was due to water in the iron(III) hydroxide crystal structure. For arsenate and phosphate systems, the water content of heterogeneous precipitates was also investigated. Ex situ GISAXS samples were created on quartz substrates as outlined previously. Substrates were immediately rinsed with deionized water and dried using high purity nitrogen. These reacted substrates were imaged within 3 hours using AFM to determine the sizes and morphology of newly-formed precipitates. Substrates were then dried in an oven at 100°C for 24 hours and
imaged again using AFM. Changes in size due to drying were attributed to water loss from the newly-formed precipitates.

**Arsenate associations with iron(III) (hydr)oxides and NOM.** Fourier transform infrared spectroscopy (FTIR) and X-ray absorption spectroscopy (XAS) were carried out on samples containing As(V) and NOM to determine whether complexation changes could be a root cause of observed differences in iron(III) (hydr)oxides nucleation, growth and aggregation. However, no differences were observed from FTIR and XAS results as shown in the Supporting Information. Therefore, changes in the hydrophilicity of the NOM solution were investigated using a contact angle analyzer (Phoenix 300, SEO Corporation, Korea). For these experiments, a clean (110) quartz substrate was utilized. The contact angle was measured between the substrate and solutions that contained 10 mM sodium nitrate, 10 mM sodium nitrate + $10^{-5}$ M As(V), 10 mM sodium nitrate + 1.5 mg/L NPOC, and 10 mM sodium nitrate + 1.5 mg/L NPOC + $10^{-5}$ M As(V).

**2.4. Results and Conclusions**

**2.4.1. Oxyanions affect iron(III) (hydr)oxide nucleation and growth**

![Figure 2.1. GISAXS 1D scattering intensity for iron(III) hydroxide precipitation on quartz in the presence of (A) 10 mM sodium nitrate only, (B) 10 mM sodium nitrate with $10^{-5}$ M arsenate, and (C) 10 mM sodium nitrate with $10^{-5}$ M phosphate. Scattering curves were produced by cutting along the Yoneda wing. Experiments were conducted for 1 hour. No significant water evaporation occurred during this period.](image-url)
In Situ Grazing Incidence Small Angle X-ray Scattering for Oxyanion Systems. Figure 2.1A-C shows the scattering intensities for particles on the quartz surface in the iron only (A), iron with $10^{-5}$ M arsenate (B), and with $10^{-5}$ M phosphate (C) systems. The position of the bend in the 1D scattering curves is reciprocally related to the particle size: a bend in the higher q range is indicative of a smaller average radius of gyration ($R_g$), while a bend in the smaller q range is indicative of a larger average $R_g$. By comparing the bend locations and intensities for the three systems, it is clear that the presence of arsenate and phosphate anions lead to increased precipitate growth.

When higher atomic number elements than iron (e.g., arsenic) are included in the experimental system, the electron density of particles may increase, thereby increasing the contrast and scattering intensity. We calculated the contrast increase based on the precipitate compositions determined by ICP-MS and found that the scattering intensity differences for the

Figure 2.2. Evolutions for primary heterogeneously formed particle (A) volume, (B) radius of gyration ($R_g$), and (C) number evolutions in the 10 mM NaNO$_3$ with $10^{-4}$ M Fe(III) only, $10^{-4}$ M Fe(III) and $10^{-5}$ M As(V), and $10^{-4}$ M Fe(III) and $10^{-5}$ M phosphate systems. The error bars indicate the approximate range for values observed in replicate samples.
arsenate and phosphate systems exceeded that which could be accounted for by differences in contrast alone. Therefore, we neglected the difference in electron density contrast in experimental systems, and assumed that changes in intensity were mainly due to differences in precipitate quantities. Detailed discussion on electron densities for the systems can be found in the Supporting Information.

**Evolution of Size and Volume for Heterogeneously Formed Particles.** To calculate *in situ* primary particle sizes, the 1D scattering curves (Figure 2.1A–C) were fit using the polydisperse sphere model with an included structure factor function. The term “primary particle size” is used to differentiate individual particles from aggregates of pre-existing nanoparticles. The primary particle size evolution can be found in Figure 2.2B. For the system which contained iron only, $R_g$ increased over the 1 hour reaction period from 1.5 to 2.5 ($\pm$ 1.0) nm. For the system containing $10^{-5}$ M arsenate, $R_g$ grew from 3.6 to 6.1 ($\pm$ 0.5) nm and for the system containing $10^{-5}$ M phosphate, $R_g$ grew from 2.0 to 4.0 ($\pm$ 0.2) nm. This

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**Figure 2.3.** *Ex situ* AFM height mode images of (A) clean quartz and substrates reacted in the (B) Fe(III) only, (C) arsenate, and (D) phosphate systems. AFM has a vertical resolution on the sub-angstrom scale, while lateral resolution for tapping mode is ~40 nm. Therefore, the vertical dimensions measured by sectioning of height mode images were used to define *ex situ* particle sizes. The height scale for all images is 10 nm and the scan size is 1 $\mu$m $\times$ 1 $\mu$m.
The trend in particle sizes was corroborated by ex situ AFM observations (Figure 2.3), however the observed sizes, compiled in Table 2.2, were slightly smaller when measured using AFM due to the dehydration of heterogeneously formed precipitates. Line cuts for single particles on the quartz background can be found in the Supporting Information.

The evolution of the invariant $Q$ shown in Figure 2.2A reflects that of the total volume of in situ heterogeneously formed precipitates. The final total particle volume was greatest in the $10^{-4}$ M Fe(III)$-10^{-5}$ M arsenate system, followed by the $10^{-4}$ M Fe(III) only system. The $10^{-4}$ M Fe(III)$-10^{-5}$ M phosphate system had the smallest volume after 1 hour. For all three systems, the volume increased at a faster rate during the initial 20 minutes of reaction. This may be due to the initially strong electrostatic forces between the negatively charged quartz surface (Table 2.3) and the positively charged aqueous iron(III) hydroxide polymeric embryos ($\zeta_d$ in Table 2.3 = 39.9 ± 1.9 mV), the precursors to stable, iron(III) hydroxide nuclei.

Although Fe(OH)$_3$ monomers are electrically neutral, the polymeric embryos in solution are expected to be positively charged, as indicated by their zeta potential. With time, the quartz

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Table 2.2. Comparison of particle sizing using GISAXS, DLS, and ex situ AFM. Differences in particle size can be attributed to different measurement techniques and conditions (e.g., wet versus dried particles), however the particle size trends are consistent for all systems.

<table>
<thead>
<tr>
<th>System</th>
<th>NaNO$_3$ (mM)</th>
<th>Fe(NO$_3$)$_3$ (mM)</th>
<th>H$_2$AsO$_4^-$ (mM)</th>
<th>H$_2$PO$_4^-$ (mM)</th>
<th>Techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>GISAXS$^a$ AFM$^{a,b}$</td>
</tr>
<tr>
<td></td>
<td>1.4–2.7 nm</td>
<td>1–2 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.1</td>
<td>0.01</td>
<td>0</td>
<td>4.1–6.3 nm 2–6 nm</td>
</tr>
<tr>
<td></td>
<td>1.9–3.7 nm</td>
<td>2–4 nm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.1</td>
<td>0</td>
<td>0.01</td>
<td>1.4–2.7 nm 4.1–6.3 nm</td>
</tr>
</tbody>
</table>

$^a$ heterogeneously formed primary particle sizes

$^b$ AFM statistics from observing >100 precipitates at different locations on the substrate surfaces
surface becomes covered in heterogeneous precipitates, as evidenced by the AFM images (Figure 2.3) and the positive zeta potentials of the quartz powder after reaction in all aqueous systems ($\zeta^*$ in Table 2.3). Once the substrate surface is positively charged, it is less easy to attract aqueous iron(III) hydroxide monomers and polymeric embryos due to lower electrostatic driving forces, leading to slower growth.

Particle numbers were also calculated ($N = V/R_g^3$) for the three systems (Figure 2.2C). While the systems containing arsenate and phosphate oxyanions had approximately 2 and 1.5 times more growth (based on primary particle size; e.g., larger $R_g$), respectively, compared to the iron(III) only system, the system containing iron(III) only had approximately 7 times more nucleation than the arsenate system and 4 times more nucleation than the phosphate system

Table 2.3. Comparison of measured pHs, zeta potentials with or without quartz powder, and saturation indices ($SI = \log(Q/K)$) for iron(III) (hydr)oxide precipitation experiments.

<table>
<thead>
<tr>
<th>System</th>
<th>$NaNO_3$ (mM)</th>
<th>$Fe(NO_3)_3$ (mM)</th>
<th>$H_2AsO_4^-$ (mM)</th>
<th>$H_2PO_4^-$ (mM)</th>
<th>IS$^a$ (mM)</th>
<th>pH$^b$</th>
<th>SI$^c$</th>
<th>$\zeta^d$ (mV)</th>
<th>$\zeta^{*e}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>10.19</td>
<td>3.6 ± 0.2</td>
<td>0.31</td>
<td>39.9 ± 1.9</td>
<td>51.3 ± 2.1</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>0.1</td>
<td>0.01</td>
<td>0</td>
<td>10.26</td>
<td>3.6 ± 0.2</td>
<td>0.35</td>
<td>25.9 ± 2.3</td>
<td>44.2 ± 2.4</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>0.1</td>
<td>0</td>
<td>0.01</td>
<td>10.18</td>
<td>3.6 ± 0.2</td>
<td>0.33</td>
<td>30.1 ± 4.1</td>
<td>39.3 ± 1.9</td>
</tr>
</tbody>
</table>

$^a$IS = Ionic strength, calculated using GWB.

$^b$pH values measured after solution mixing. They are consistent with GWB calculations for the low concentrations of arsenate/phosphate.

$^c$SI = Saturation Index = $\log(IAP/K_{sp})$, with respect to ferrihydrite (simplified as Fe(OH)$_3$) at 20°C calculated with GWB using thermo.dat database. IAP: Ion activity product and $K_{sp}$: solubility product.

$^d$Zeta potential ($\zeta$) of homogeneously formed precipitates measured without quartz powder. Measurements taken every 1 minute until values stabilized (20 minutes to 1 hour).

$^e$Zeta potential measurements of heterogeneously formed precipitates on suspended quartz powder ($\zeta^*$).
translated into English, as follows:

GISAXS observations show that when phosphate anions coexist with the iron ions, phosphate seems to interfere with heterogeneous iron(III) (hydr)oxide precipitation quantities, as indicated by the small total precipitate volume. On the other hands, the arsenate system presents unique behavior: while the nucleation frequency is significantly suppressed compared to iron(III) only, the growth of the precipitates is greatly enhanced (Figure 2.2). To determine the mechanism behind these observations, we investigated the physico-chemical properties and identities of precipitates as discussed in the following sections.

**Ex situ Zeta Potential, Composition, and Phase Identification of Iron(III) (Hydr)oxides.** To explain the observed trends in heterogeneous precipitation rates for our three experimental systems, *ex situ* characterization approaches were used to determine the composition and phase of both homogeneously and heterogeneously formed precipitates. Regarding compositions of the precipitates, first, zeta potentials were measured for the homogeneous and heterogeneous precipitation systems (Table 2.3). We found decreases in the zeta potential of the homogeneously formed precipitates (without quartz powders), from $39.9 \pm 1.9$ mV in the $10^{-4}$ M Fe(III) only system to $25.9 \pm 2.3$ mV and $30.1 \pm 4.1$ mV in the $10^{-5}$ M arsenate and phosphate systems, respectively. These decreases indicate that there is significant incorporation of the negatively charged oxyanions into the positively charged iron(III) (hydr)oxides, either through co-precipitation or sorption onto the iron(III) (hydr)oxide surface.

Similar trends are seen for the zeta potentials of heterogeneously formed precipitates with quartz powders as substrates. For the $10^{-5}$ M arsenate and phosphate systems containing $10^{-4}$ M Fe(III), zeta potentials decreased to $44.2 \pm 2.4$ mV and $39.3 \pm 1.9$ mV, respectively, compared to
51.3 ± 2.1 mV for the Fe(III) only system. The higher zeta potential in the arsenate system compared with the phosphate system, despite lower charges for the homogeneous particles system, is likely due to enhanced heterogeneous nucleation and growth in the arsenate system compared to homogeneous formation. Differences between zeta potentials of heterogeneously and homogeneously formed iron(III) (hydr)oxides can be due to different signal/noise ratios in the data because much stronger scattering occurred in the systems containing quartz powder. However, there is agreement between both homogeneously and heterogeneously formed precipitates that the incorporation of these oxyanions will significantly decrease the zeta potential of the precipitates.

The lower zeta potential of heterogeneously formed iron(III) (hydr)oxide precipitates in arsenate and phosphate systems can contribute in part to observed trends in particle sizes; Decreased positive charge near the quartz substrate surface will attract more positively charged, aqueous iron(III) (hydr)oxide polymeric embryos relative to the system containing only Fe(III), leading to increased growth. This effect can be further enhanced by the presence of quartz surfaces which have lower zeta potentials (-26.08 ± 2.81 and -19.67 ± 2.25 mV for arsenate and phosphate systems, compared with -16.11 ± 3.09 mV).

Zeta potential results also give insight into the effects of changing saturation index (SI) on this system. Because our system was a stagnant batch system, the SI may change over the course of the reaction if local concentration gradients form near the quartz surface. For example, in accordance with zeta potential measurements, it is likely that the phosphate and arsenate cases will have a higher saturation index due to the weaker repulsive forces between oxyanion-containing precipitates and iron(III) (hydr)oxide monomers in solution.
The arsenate and phosphate content of heterogeneously and homogeneously precipitated particles was then quantified by dissolving concentrated nanoparticles in acid and measuring phosphorus and arsenic concentrations using ICP-MS. For the $10^{-4}$ M Fe(III)$-10^{-5}$ M arsenate system, the oxyanion content was $8.1 \pm 2.3$ mol% for homogeneously formed particles and $6.5 \pm 1.3$ mol% for heterogeneously formed particles. For the $10^{-4}$ M Fe(III)$-10^{-5}$ M phosphate systems, the oxyanion content was $13.1 \pm 1.8$ mol% for homogeneously formed particles and $12.2 \pm 1.1$ mol% for heterogeneously formed particles. The close agreement between homogeneously and heterogeneously formed precipitate compositions indicates that results from analyses carried out on homogenenously formed precipitates, such as phase identification, likely

![HRXRD spectra](image_url)

![Water content of precipitates](image_url)

**Figure 2.4.** Results from (A) HRXRD and (B) TGA showing the effects of oxyanions on iron(III) (hydr)oxides. Broadening of HRXRD peaks in the systems containing oxyanions indicates that the incorporation of arsenate and phosphate result in decreased precipitate crystallinity. TGA results show that the low arsenate system contained the most water.
hold for heterogeneously formed precipitates as well.

Next, samples of homogeneously formed precipitates in the reactions systems were analyzed using HRXRD for *ex situ* phase identification (Figure 2.4A). In the $10^{-4}$ M Fe(III) only system, the observed peaks were characteristic of 6-line ferrihydrite. For systems containing arsenate and phosphate oxyanions, the characteristic peaks were much less defined, indicating that the incorporation of oxyanions during iron(III) (hydr)oxide nucleation and growth resulted in more amorphous precipitates for these systems. Although the spectra resembles that of less crystalline 2-line ferrihydrite, the peak locations are more consistent with literature on the XRD spectra for ferric arsenate\textsuperscript{137, 147} and ferric phosphate,\textsuperscript{148} respectively. Note that the phases identified in HRXRD analysis can be even more crystallized than the *in situ* newly formed phases. Ferric phosphate and ferric arsenate contain corner-linked FeO\textsubscript{6} tetrahedra bridged by PO\textsubscript{4} or AsO\textsubscript{4} tetrahedra, respectively.\textsuperscript{149, 150} This bridging by arsenate and phosphate anions may not only account for larger observed sizes of iron(III) (hydr)oxides but can also explain size differences between the arsenate and phosphate systems because the arsenate anion is larger than phosphate.\textsuperscript{151}

The observed decreased crystallinity is also consistent with previous reports published on the effects of arsenate on the aging of iron(III) (hydr)oxide precipitates. Waychunas *et al.*\textsuperscript{137} found that the incorporation of high quantities of arsenate into iron(III) hydroxide precipitates slowed the transformation of ferrihydrite into hematite by preventing Fe–O–Fe polymerization. Pedersen *et al.*\textsuperscript{67} found that trace amount of arsenate (up to 0.5 mol% As) will have no effect on crystallization rates. It has also been found that for lower arsenate loadings (8416 mg As/ kg iron(III) (hydr)oxide $\approx 1.2$ mol% As), the crystallization of iron(III) (hydr)oxides can lead to stable, irreversible arsenic attenuation.\textsuperscript{152}
ICP-MS results indicated that heterogeneous precipitates in the phosphate system had a higher oxyanion content. Hence, one might expect that more bridging occurred in the phosphate system compared to the arsenate system. However, the nanoparticle sizes were smaller in phosphate system. We therefore hypothesized that differences in the hydrated radii of incorporated oxyanions and water content of precipitates could also contribute to larger precipitates for the arsenate system, as outlined in the following section.

**Water Content of Iron(III) (Hyd)roxides.** Although phosphate was incorporated in larger quantities than arsenate, the size of the incorporated oxyanions must also be considered to explain why larger primary particle sizes were observed for the arsenate system. The ionic radius of arsenate as $\text{H}_2\text{AsO}_4^-$, 2.20Å, is slightly larger than that of phosphate, $\text{H}_2\text{PO}_4^-$, which is 2.03Å. This may have a small contribution to the larger particle sizes in the case of arsenate or phosphate oxyanions that form direct inner-sphere bonds with Fe-octahedra. In addition, there may be concurrent formation of outer-sphere complexes between the arsenate or phosphate and the iron(III) (hydr)oxide surface. For this case, the oxyanions will remain solvated by water in aqueous environments. The hydrated ionic radius is then used to describe the radius of both the ion in solution and its tightly-bounded water shell, termed the water of hydration. The hydrated ionic radii of $\text{H}_2\text{AsO}_4^-$ and $\text{H}_2\text{PO}_4^-$ are 5.9Å and 3.02Å, respectively. These outer-sphere complexes may be a source for increased water content for precipitates in the oxyanion-containing system if they remain inside the particles at the early nucleation stage. In addition, the incorporation of arsenate and phosphate anions in the iron(III) (hydr)oxide precipitates will hinder crystallization as evidenced by HRXRD results. The hindered crystallization of these newly formed precipitates can be related to higher water content. Although the volume of water in these precipitates will not be included in calculated invariant values, incorporated water
will impact $R_g$ values. Therefore, water inclusion could also contribute to larger particles sizes for the arsenate system, despite less arsenate incorporation compared with the phosphate system.

To test this hypothesis, investigation of water incorporation into precipitates was carried out using AFM observation on heterogeneously formed particles and TGA for homogeneously formed particles. AFM investigations were carried out on quartz substrates reacted *ex situ*. Substrates were imaged immediately following reaction, after drying with high purity nitrogen gas. Next, samples were dried overnight in an oven to remove any remaining water and reimaged. For heterogeneously formed precipitates, the particle size in the $10^{-4}$ M Fe(III) system and $10^{-4}$ M Fe(III)–$10^{-5}$ M phosphate system remained similar before and after oven drying, with sizes of 1–2 nm in both systems. For the $10^{-4}$ M Fe(III)–$10^{-5}$ M arsenate system, particle size decreased after drying from 1–4 nm to 1–2 nm, which corresponds to volume reduction to 0-12.5%. AFM images of newly-formed and dried samples can be found in Figure 2-S3 in the Supporting Information. TGA further corroborated these observations. For homogeneous nanoparticle slurries, there was significant mass loss between 107°C and 440°C for all systems (Figure 2.4B). The Fe(III) only system contained 14.9% water by mass, while the phosphate and arsenate systems contained 17.1% and 21.6%, respectively. These investigations indicate that the poorly crystalline iron(III) (hydr)oxide precipitates formed in the presence of oxyanions contain more water and that this effect is strongest for the arsenate system. In addition, the greater degree of hydration for oxyanion-containing nanoparticles can in turn help to explain the observed stability of larger and less crystalline precipitates in arsenate and phosphate systems, because more hydrated particles will have a lower surface energy and higher thermodynamic stability.

From our investigation of arsenic and phosphate effects on iron(III) (hydr)oxide precipitation, we observed and quantified the heterogeneous nucleation and growth of iron(III)
Natural organic matter impacts the aggregation state of iron(III) (hydr)oxides

Due to the abundance of natural organic matter in the environment, we further investigated NOM effects on nanoscale iron(III) (hydr)oxide precipitation. In particular, we focused on the coexistence of NOM and arsenate to provide direct implications for MAR systems, along with other ground and surface waters at risk for arsenic contamination.
The systems containing Fe(III) only, Fe(III) + 10^{-5} M arsenate (As(V)), Fe(III) + NOM, and Fe(III) + 10^{-5} M As(V) + NOM were run during multiple beamtime periods. The 1D scattering patterns can be found in Figure 2.5. While there were slight differences in the shape of the scattering curves between these results and previous results for the Fe(III) only and Fe(III) + As(V) system, overall there is strong agreement in particle size trends.

**In situ** GISAXS results show obvious differences in the scattering pattern for systems with and without NOM present, particularly in the low q range (Figure 2.5). The indicated radii show the growth of nanoparticles after 1 h reaction (Figure 2.5F). The particle size is larger for the system with arsenate compare to the Fe(III) only system when NOM is not present (e.g., radius of gyration (R_g) = 5.3 nm in Figure 2.5B (Fe(III) + As(V) system) vs. 2.1 nm in Figure 2.5A (Fe(III) only system), respectively). This is consistent with our previous findings. In the presence of NOM, the size of particles in the Fe(III) + NOM system decreases slightly to 1.8 nm (Figure 2.5C). For the ternary system with Fe(III) + As(V) + NOM, there were differences between the **in situ** GISAXS replicate trials which were categorized into two distinct behaviors. In one case, smaller particles (R_g = 1.6 nm) similar in size to the Fe(III) + NOM system and fractal aggregation were observed on the surface (Figure 2.5D). In another, larger particles (R_g = 8.6) more similar to the Fe(III) + As(V) system were observed (Figure 2.5E). These two distinct trends were observed during multiple trials at different beamtime periods, indicating that for all

<table>
<thead>
<tr>
<th>System</th>
<th>Fractal dimension (d from q^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(III) only</td>
<td>3.31 ± 0.06</td>
</tr>
<tr>
<td>Fe(III) + As(V)</td>
<td>2.19 ± 0.11</td>
</tr>
<tr>
<td>Fe(III) + NOM</td>
<td>1.73 ± 0.09</td>
</tr>
<tr>
<td>Fe(III) + As(V) + NOM</td>
<td>1.87 ± 0.13</td>
</tr>
</tbody>
</table>

Table 2.4. Fractal dimensions for systems with and without NOM present. The fractal dimension is indicative of the density of precipitates or precipitate clusters.
samples reacted under ternary conditions, there were regions where particles were larger and regions where particles were smaller.

The relative total particle volumes were also calculated for these systems after 1 hour reaction, as indicated in Figures 2.5A–E. The volume in the Fe(III) + As(V) system was 1.2 times higher than the Fe(III) only system. The volumes in the Fe(III) + NOM system and Fe(III) + As(V) + NOM system were 0.8 and 0.4 times the volume in the Fe(III) only system, respectively. The volumes for the ternary system replicates were similar despite the difference in particle size. Additional volume evolutions over the one hour reaction period can be found in Figure 2-S9. The primary particles size evolution was also calculated and is shown in Figure 2.5F.

For both NOM-containing systems, there is strong power law scattering in the low q range. This

![Figure 2.6. TEM images of homogeneous precipitation in the (A) Fe(III) only, (B) Fe(III) + As(V), (C) Fe(III) + NOM, and (D) Fe(III) + As(V) + NOM systems after 1 hour of reaction, showing different aggregation behavior in the presence of different aqueous constituents. While some sodium nitrate crystallizes during the drying process, the particles imaged are iron(III) (hydr)oxides rather than salt crystals: They have a small size and exhibit weak diffraction, while sodium nitrate salts from drying have a much bigger size and a strong diffraction pattern.](image)
scattering is due to fractal aggregation of iron(III) (hydr)oxide precipitates, which can be characterized using the fractal dimension \( d \), where \( q^{-d} \) represents the scattering from aggregates. This value is equal to the negative slope of the scattering in the low \( q \) region, e.g., the power law exponent. The fractal dimension gives insight into the density of the fractal aggregates forming in our experimental systems and can be used to distinguish between surface fractals and mass fractals. To compare the four systems (Figures 2.5A–D), the \( d \) values were calculated (Table 2.4). In both NOM systems, smaller values \( (d < 3) \) were observed, indicating mass fractal formation, i.e., less dense aggregates. On the other hand, for systems without NOM, larger values \( (d > 3) \) occurred, suggesting denser particles with surface fractals, e.g., rough surfaces, rather than fractal aggregates.

Chains of NOM tend to have a strong negative electric charge, and can therefore attract positively charged iron(III) (hydr)oxide particles. Due to its hydrophobicity, NOM chains and associated iron(III) (hydr)oxides will then aggregate. Fractal aggregation of NOM-associated nanoparticles has been observed previously. X-ray scattering for these systems thus reflects both the smallest individual primary particle sizes and the scattering of these particles with clusters of their neighbors along the NOM chains. For the two systems with NOM present, there was no significant difference in the fractal dimension, indicating that the smaller particles in these two systems had similar aggregation behavior around NOM chains. However, the nucleation and growth behavior differed greatly for the larger particles, which were also observed in the Fe(III) + As(V) + NOM system (Figure 2.5E).

Differences in aggregation between the ternary system and Fe(III) + NOM system were observed \textit{ex situ} using TEM (Figures 2.6C and D). While the morphology in the Fe(III) only and Fe(III) + As(V) systems were similar (Figure 2.6A and 2.6B, respectively), the morphology was
dramatically different for systems with added NOM. For the Fe(III) + NOM system, large fractal aggregates were observed which appeared to be coated by NOM (red arrow in Figure 2.6C). In the ternary Fe(III) + NOM + As(V) system, much smaller fractal aggregates (blue arrow in Figure 2.6D) were observed along with individual particles. Furthermore, fewer particles were observed compared to any of the other three systems. This is consistent with calculated particle volumes from the GISAXS data. The caveat for ex situ TEM is that there may be changes in morphology due to drying effects. Drying during TEM sample preparation may also promote particle aggregation; however, the degree of aggregation should be the same in each sample.

### 2.4.3. Ternary Fe(III)–As(V)–NOM systems have unique nucleation and aggregation behavior

The mechanism of Fe–As–NOM interactions was investigated further using AFM and sequential addition of arsenate and NOM. First, all four systems were imaged following one hour
of reaction (Figure 2-S5 in the Supporting Information). Next, in order to determine the sequence of Fe–As–NOM interactions, systems were investigated with Fe(III) + As(V) first added to solution, and then NOM added after 30 minutes, or with Fe(III) + NOM in solution initially, and As(V) added after 30 minutes (Figure 2.7). All experiments were conducted in replicate tests to confirm the observed trends. Substrate morphology in the ternary system (Figure 2.7A) was most similar to that of the system with Fe(III) + NOM initially and As(V) added later (Figure 2.7B). Moreover, additional tests were run where the Fe(III) + NOM only system was run for 30 minutes and imaged. Large aggregates were observed in the Fe(III) + NOM only system at 30 minutes (Figure 2.7D). However, when As(V) was added after 30 minutes and reacted to 1 hour total, these aggregates were not present in the system (Figure 2.7B). This result indicates that in the early stages of iron(III) (hydr)oxide nucleation, precipitates may interact exclusively with NOM. However, further interactions with As(V) prevent aggregation or lead to disaggregation, thus resulting in a morphology which is dramatically different from the large aggregates observed in the Fe(III) + NOM only system at 1 hour.

The composition of ternary precipitates and precipitates in the Fe(III) + NOM systems were investigated further for their NOM, As(V), and water contents. The total organic carbon (i.e., NOM) contents of the ternary system and Fe(III) + NOM system were found to be 2.05 ± 0.05 and 1.96 ± 0.10 mg C/μmol Fe, respectively, and the water content of these precipitates was 49wt% water in the Fe(III) + As(V) + NOM system and 64wt% water in the Fe(III) + NOM system (Figure 2.8). Thus, although the two NOM-containing systems have the same NOM content, the water content of the Fe(III) + As(V) + NOM system is less. This may be because particles which contain Fe(III) + As(V) without NOM have a water content of 22wt% (Figure 2.4B), and so the water content in the ternary system (49wt%) will be in between that of the
The arsenic content of the ternary precipitated was measured to be 14.5 ± 1.5 mol% As, which is higher than the 8.1± 2.3 mol% As observed in the system without NOM. This composition is also reflected in the zeta potential measurements (Table 2.5). The zeta potential of iron(III) (hydr)oxide precipitates on quartz powder was 29.7 ± 3.2 mV for the system with As(V) + NOM, compared with 32.3 ± 3.7 mV for the system with NOM only. Without NOM, the zeta potential was 51.3 ± 2.1 mV for the Fe(III) only system and 44.2 ± 2.4 mV for the Fe(III) + As(V) system. Because NOM and As(V) are both negatively charged, the presence of both of these components together lowered the surface charge further. This lower surface charge may in part explain the observed smaller aggregates in the ternary system, because less positively charged iron(III) (hydr)oxide precipitates which contain As(V) may be less likely to adhere to the negatively charged NOM chains.

Sequential addition tests indicate that As(V) can interact with Fe(III)-NOM aggregates, triggering disaggregation (Figure 2.7D). From TEM images, we can hypothesize that a large number of iron(III) (hydr)oxides in the sequential addition system will be coated with NOM prior to As(V) addition (Figure 2.6C). Thus, As(V) can be interacting with NOM directly in

Figure 2.8. TGA data for NOM-containing systems

Fe(III) + As(V) system and that of the Fe(III) + NOM system (64wt%) if the NOM and As(V) are interacting with different fractions of Fe(III) exclusively.

The arsenic content of the ternary precipitated was measured to be 14.5 ± 1.5 mol% As, which is higher than the 8.1± 2.3 mol% As observed in the system without NOM. This composition is also reflected in the zeta potential measurements (Table 2.5). The zeta potential of iron(III) (hydr)oxide precipitates on quartz powder was 29.7 ± 3.2 mV for the system with As(V) + NOM, compared with 32.3 ± 3.7 mV for the system with NOM only. Without NOM, the zeta potential was 51.3 ± 2.1 mV for the Fe(III) only system and 44.2 ± 2.4 mV for the Fe(III) + As(V) system. Because NOM and As(V) are both negatively charged, the presence of both of these components together lowered the surface charge further. This lower surface charge may in part explain the observed smaller aggregates in the ternary system, because less positively charged iron(III) (hydr)oxide precipitates which contain As(V) may be less likely to adhere to the negatively charged NOM chains.

Sequential addition tests indicate that As(V) can interact with Fe(III)-NOM aggregates, triggering disaggregation (Figure 2.7D). From TEM images, we can hypothesize that a large number of iron(III) (hydr)oxides in the sequential addition system will be coated with NOM prior to As(V) addition (Figure 2.6C). Thus, As(V) can be interacting with NOM directly in
order to trigger disaggregation.

Previous studies have shown that phenolate groups on NOM can bind to the central arsenic atom of arsenate. In addition to arsenic interactions with NOM, FTIR and XAS results show that bonding between iron and arsenic does occur in the ternary system (Figure 2-S6 and 2-S7 in the Supporting Information). This can happen because when arsenic is added simultaneously with NOM, it can interact with nucleating iron(III) (hydr)oxides. This can also happen due to the displacement of NOM on the iron(III) (hydr)oxide surface by arsenate, which is known to occur.

Furthermore, previous research has shown that electrostatic effects play a significant role in NOM adsorption. Thus, the decreasing zeta potential observed for ternary precipitates (Table 2.5) can prevent aggregation by making it less favorable for iron(III) (hydr)oxides to adhere to NOM. Iron(III) (hydr)oxides which remain associated primarily with NOM will act similarly to the particles observed in the Fe(III) + NOM only system, retaining a small particle size and high water content. Iron(III) (hydr)oxides which are associated with arsenate, either through initial

<table>
<thead>
<tr>
<th>System</th>
<th>Quartz present?</th>
<th>Zeta Potential (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-4}$M Fe(III)</td>
<td>No</td>
<td>39.9 ± 1.9</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>51.3 ± 2.1</td>
</tr>
<tr>
<td>$10^{-4}$M Fe(III) + $10^{-5}$M As</td>
<td>No</td>
<td>25.9 ± 2.3</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>44.2 ± 2.4</td>
</tr>
<tr>
<td>$10^{-4}$M Fe(III) + 1.5 mg/L NPOC</td>
<td>No</td>
<td>25.3 ± 7.5</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>32.3 ± 3.7</td>
</tr>
<tr>
<td>$10^{-4}$M Fe(III) + $10^{-5}$M As + 1.5 mg/L NPOC</td>
<td>No</td>
<td>20.4 ± 5.0</td>
</tr>
<tr>
<td></td>
<td>Yes</td>
<td>29.7 ± 3.2</td>
</tr>
<tr>
<td>$10^{-5}$M As only</td>
<td>Yes</td>
<td>-16.1 ± 3.1</td>
</tr>
<tr>
<td>$10^{-5}$M As only</td>
<td>Yes</td>
<td>-26.1 ± 2.8</td>
</tr>
<tr>
<td>1.5 mg/L NPOC only</td>
<td>Yes</td>
<td>-18.1 ± 4.1</td>
</tr>
<tr>
<td>$10^{-5}$M As + 1.5 mg/L NPOC</td>
<td>Yes</td>
<td>-21.1 ± 4.3</td>
</tr>
</tbody>
</table>

Table 2.5. Zeta potential measurements for homogeneous and heterogeneous precipitation and for the quartz surface. All systems contain 10 mM sodium nitrate and are at pH 3.6 ± 0.2.
formation or displacement of NOM, will have a larger size and smaller water content more similar to the Fe(III) + As(V) system. Although FTIR and XAS results indicate that As which is bound to the iron(III) (hydr)oxide surface behaves similarly in the presence and absence of NOM, HRXRD spectra for these systems shows differences (Figure 2.9). There was much less of a shift for the ferrihydrite peak, indicating that there is more ferrihydrite present which does not interact with As(V) and remains associated with NOM instead. While there appears to be less arsenate bound to iron(III) (hydr)oxides from HRXRD results, there was still a high percentage of arsenate associated with precipitates according to ICP-MS results. This can occur if arsenic is interacting with the NOM directly. Therefore we next investigated how As(V) can alter the surface chemistry of NOM molecules.

Figure 2.9. HRXRD spectra for a ferrihydrite references and systems containing Fe(III) only, Fe(III) + As(V), Fe(III) + NOM, and Fe(III) + As(V) + NOM. Spectra indicate that Fe(III) can form more ferrihydrite when NOM is present together with As(V) compared to the Fe(III) + As(V) system, thus indicating exclusive interactions. The broad between 2Theta = 10° and 25° in NOM-containing systems is indicative of NOM presence.
by investigating the change in NOM hydrophilicity in the presence of As(V).

We found that when $10^{-5}$ M As(V) was added, the contact angle of the 1.5 mg/L NOM + 10 mM NaNO₃ solution decreased from $23.9 \pm 0.1^\circ$ to $16.8 \pm 0.1^\circ$ (compared to $12.5 \pm 0.2^\circ$ for 10 mM NaNO₃ only and $10.1 \pm 0.5^\circ$ for 10 mM NaNO₃ + $10^{-5}$ M As(V)). This change indicates that the solution became more hydrophilic (Figure 2.10) and therefore that the hydrophobic–hydrophobic interactions which promote NOM aggregation are weaker in the ternary system. This can make the formation of large fractal aggregates, which were observed in the Fe(III) + NOM only system, less favorable.

In conclusion, the unique iron(III) (hydr)oxide nucleation and aggregation behaviors in the ternary systems results from a combination of physicochemical effects. Iron(III) (hydr)oxides can interact exclusively with As(V) and NOM, resulting in some particles with characteristics (e.g., size and water content) similar to that of the Fe(III) + As(V) system and some particles’ characteristics similar to those of the Fe(III) + NOM systems. This alteration in aggregation behavior can be closely associated with less favorable electrostatic interactions and

![Figure 2.10. Contact angle measurement of solutions with NOM and As(V) on quartz demonstrating changes in NOM hydrophilicity](Image)
weaker hydrophobic–hydrophobic interactions, because As(V) interactions with NOM increased their hydrophilicity.

2.5. Environmental implications

Previously, much of the research related to arsenate, phosphate, and NOM interactions with iron(III) (hydr)oxides has focused on adsorption onto preformed or more crystallized iron(III) (hydr)oxide particles as a means of contaminant remediation. There have also been extensive studies on the competitive effects of phosphate and arsenate on sorption by iron(III) (hydr)oxides and studies on how NOM coating affects this sorption. However, no previous studies have accomplished in situ, time-resolved observation of iron(III) (hydr)oxide nucleation and growth on quartz substrates in the presence of these water constituents.

The current study provides valuable new insights into arsenate and phosphate effects on early stage iron(III) (hydr)oxide precipitation. NOM effects on iron(III) (hydr)oxide precipitation and aggregation were also investigated in the presence and absence of arsenate. Gilbert et al.\textsuperscript{168} has previously reported that aggregate structure can significantly influence the sorption properties of iron(III) (hydr)oxides. Changes in aggregation and disaggregation behavior can also have significant impacts on the fate of contaminants by influencing aggregate transport distances and times in natural and engineered aqueous environments. Furthermore, not all of the products formed in natural systems will be pure iron(III) (hydr)oxides. For example, ferric arsenate-like nanoparticles formed in the Fe(III) + As(V) system. It is important to consider other phases, such as ferric arsenate, when characterizing iron(III) (hydr)oxide formation because these phases can form in addition to or in place of iron(III) (hydr)oxides, affecting their reactivity in aqueous environments.
New quantitative information such as heterogeneous particle sizes and arsenate and phosphate incorporation percentages provided by this study can be used to develop more rigorous reactive transport models of contaminant fate and transport in relevant natural and engineering aquatic systems, including MAR operation, arsenic-contaminated groundwater aquifers, and acid mine drainage sites. Because these observations were made in situ and in real time using our GISAXS fluid cell setup, these findings give a clearer picture of the complex interactions which can occur when dissolved Fe(III) species precipitate to form iron(III) (hydr)oxide or ferric arsenate-like nanoparticles in real aquatic systems. Using this advanced technique, the current study was able to capture iron(III) (hydr)oxide nucleation at its starting point, rather than after an elapsed time, as seen in previous literature. Furthermore, in situ studies allow us to observe nanoparticle nucleation and growth in a fully hydrated environment, allowing for more accurate particle size measurement.

Nanoparticle size is an important consideration because the sizes of these particles can greatly impact their electronic structure. When the particle size is small enough, the band gap increases compared to bigger particles, affecting their redox potential and allowing these nanoparticles to act as semiconductors in environmental systems. The larger band gap can facilitate redox reactions or photo-redox reactions which would not be possible for bulk minerals. A better understanding of mineral reactivity changes is necessary in order to accurately predict the fate and transport of these nanoparticles and associated contaminants. For example, the incorporation of contaminants, such as arsenic, into iron(III) (hydr)oxides can alter reaction rates and pathways by adding defects to the nanoparticles, impacting their photochemical behavior and phase stability.
In addition, the current study gives insight into arsenic fate and transport in systems where NOM coexists with precipitating iron(III) (hydr)oxides, a scenario directly relevant to the geochemical reactions occurring during MAR, where ferrihydrite is frequently incorporated into reactive transport models as a sink for arsenic mobilized during arsenopyrite oxidative dissolution. For instance, although precipitates in the ternary system contained significant quantities of As(V), there was a smaller volume of precipitates in this system. Therefore, in terms of total removal of As(V) by the same aqueous ferric ion concentrations, the ternary system may attenuate less arsenic. These new results advance our knowledge of early stage iron(III) (hydr)oxide formation mechanisms in natural and engineered aquatic systems and can help us to better evaluate the risk of arsenic contamination in complex aqueous environments. By continuing to advance our knowledge of this system, we can better model contaminant interactions with iron(III) (hydr)oxides, as well as improve analytical techniques to observe nanoscale interfacial reactions in environmentally relevant systems.

2.6. Acknowledgments

We are grateful for support received from Washington University’s Faculty Startup and the National Science Foundation (EAR-1424927 and CHE-1214090). CWN acknowledges the generous support of the Mr. and Mrs. Spencer T. Olin Fellowship. We wish to thank Environmental NanoChemistry Group members, Dr. Soenke Seifert at APS, and Dr. Christopher Kim for valuable discussion. Use of the Advanced Photon Source (Sector 11-BM for HRXRD, Sector 12 ID-B for GISAXS, and Sector 13-BM-D) at Argonne National Laboratory was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.
2.7. Supporting Information for Chapter 2

Contents: Experimental details

9 figures (Figures 2-S1 – 2-S9), 1 table (Table 2-S1)

Sample and Solution Preparations

Cleaning single crystal quartz substrates. After being cut into square pieces, quartz substrates were sonicated in acetone for 10 minutes to remove organic contaminants. Substrates were then soaked overnight in a mixture of concentrated sulfuric acid and a commercial oxidizing agent, Nochromix®. Quartz substrates were elevated on their sides to ensure both sides contacted the cleaning solution. Finally, the substrates were rinsed with and stored in deionized water (resistivity > 18.2 MΩ·cm) until experiments. Clean surfaces were confirmed using AFM. Substrates were not stored for longer than 1 week. Just before being utilized in GISAXS experiments, substrates were rinsed again using ultrapure deionized water.

Solution preparation. The solutions for the systems outlined in Table 2.1 were created using reagent grade Fe(NO₃)₃·9H₂O, NaNO₃, Na₂HAsO₄·7H₂O, Na₂HPO₄·7H₂O, Suwanee River NOM (SRNOM) and ultrapure water. To create SRNOM stock solutions, 100 mg of NOM was added to 200 mL of DI water and stirred overnight in the dark. The pH of the solution was adjusted to 8.5 before being vacuum-filtered. The SRNOM stock solution was refrigerated prior to experimentation and NPOC concentrations were measured using a TOC Analyzer (Shimadzu Corporation, Kyoto, Japan). The stock solution was diluted with ultrapure water to create a solution with a NPOC concentration of 1.5 mg/L immediately prior to its use in experiments.
Immediately prior to conducting grazing incidence small angle X-ray scattering (GISAXS), dynamic light scattering (DLS), and other ex situ experiments, the salts were weighed (0.0452 g NaNO₃, 0.0202 g Fe(NO₃)₃·9H₂O, 0.0156 or 0.0016 g Na₂HAsO₄·7H₂O, and 0.0134 or 0.0013 g Na₂HPO₄·7H₂O) and stored in 50 mL centrifuge tubes. Ultrapure water was added to the weighed NaNO₃ to a volume of 45 mL for the iron(II) only system, or to 40 mL for the systems containing arsenate or phosphate. The tube was shaken to mix. For the arsenate and phosphate systems, 50 mL ultrapure water was added to the arsenate or phosphate salts to create a 10⁻⁴ M (for 0.0016 g arsenate salt or 0.0013 g phosphate salt) solution and the tube was shaken to mix. 5 mL of the arsenic or phosphate salt solution was then added to the 40 mL NaNO₃ solution, diluting the arsenate or phosphate to 10⁻⁵ M. This tube was shaken to mix. Finally, 50 mL of ultrapure water was added to the tube containing the weighed Fe(NO₃)₃·9H₂O salt and shaken, creating a 10⁻³ M Fe(NO₃)₃ solution. Then 5 mL of this solution was added to the 45 mL NaNO₃ solution (for the iron(III) only system) or the 45 mL NaNO₃ and phosphate or arsenate solution, shaken, and immediately injected into the reaction cell.

The final solutions contained 10 mM NaNO₃, 10⁻⁴ M Fe(NO₃)₃, and 10⁻⁵ M arsenate or phosphate. The reaction was considered to begin the moment when ultrapure water is added to the weighed Fe(NO₃)₃·9H₂O salt. Accounting for this, only approximately two minutes elapsed between the start of the reaction and when the first GISAXS image was taken. For all systems containing NOM, a 1.5 mg/L NPOC solution was used in place of ultrapure water to make the salt solutions.

**Preparing solutions and quartz powders for DLS and zeta potential measurements.** For DLS and zeta potential measurements for homogeneously formed particles, solutions were prepared as outlined above. To measure the zeta potentials for the heterogeneously formed particles and for
quartz in our different reaction systems, a quartz powder was used in place of the substrate. Quartz was ground using a mortar and pestle to create an array of fine particles. This powder was added to solutions created as outlined above, shaken, and allowed to settle for 10 minutes in order to allow the larger quartz particles to be removed from suspension. Then, the small, suspended quartz particles and upper region of solution were injected into the zeta potential cell to measure the zeta potential. In addition, the zeta potential of the quartz powder itself was measured using the same procedure in 10 mM NaNO₃ and in the presence of arsenate, phosphate, NOM, and NOM and arsenate. For these systems, the pH was adjusted to 3.6 ± 0.2 with nitric acid to match the pH of the reaction systems.

*Ex Situ Analyses of Iron(III) (Hydr)oxide Precipitate Nature*

*Measuring arsenate, phosphate, and NOM content of precipitates.* The solutions outlined in Table 2.1 were created following the above procedure, scaled up to a total volume of 500 mL in order to accumulate enough precipitate to achieve detectable iron, oxyanion and NOM levels. Solutions were reacted for 1 hour before beginning filtration in small batches at 5000 RPM utilizing Millipore Amicon ultra-15 centrifugal filter units. After the entire batch was filtered, the precipitates which had accumulated on the filter were dissolved using a 2% nitric acid solution. The resulting solution was diluted and arsenic, phosphorus and iron concentrations were measured using ICP-MS. NOM incorporation was measured using a TOC analyzer.

After filtration, each sample contained 250 µL of the 0.1 mM iron and 0.01 mM arsenic or phosphate solution. The concentrations of iron in the supernatant from the dissolved nanoparticles were ~1.6–3 mM for iron and ~0.2–0.5 mM for phosphorus and ~0.1–0.3 mM for arsenic. These concentrations were obtained from 5 mL of the acidified solution. Therefore, the
original solution contributed 0.000025 moles of iron and 0.0000025 moles of arsenic or phosphorus. These totals account for only 0.17–0.31% of the measured iron, 0.10–0.25% of the measured phosphorus, and 0.17–0.5% of the measured arsenic. Therefore, the residual solution did not contribute significantly to the measured incorporated values.

**Investigation of the effects of homogeneously formed particle settling.** *Ex situ* experiments were conducted to show the effects of particle settling. Inverted (bottom up) *ex situ* batch systems were run in the GISAXS fluid cell for 10 mM NaNO₃, 10⁻⁴ M Fe(NO₃)₃, and 10⁻⁵ M arsenate or phosphate. The morphology of precipitates on the quartz substrates in each system was analyzed using AFM (Figure 2-S2). The inverted experiments demonstrate that the small precipitates observed on the mineral surface are from heterogeneous precipitation and not from the settling of small homogeneous precipitates, while regular experiments demonstrate that there was not significant settling of larger heterogeneous precipitates.

**Determining phase of precipitates using Raman Spectroscopy and TEM.** Raman spectroscopy was conducted on reacted GISAXS substrates using a Raman microscope (Renishaw, U.K.) with a 633 nm excitation wavelength. However, the only observable peaks were those of the quartz background due to the small quantity of precipitation on the substrate surface. In addition, we used high-resolution transmission electron microscopy (HRTEM) (JEOL JEM-2100F field emission, Tokyo, Japan) to observe homogeneously formed precipitates. For this testing, reaction solutions (Table 2.1) were prepared as outlined. After reaction for 1 hour, one drop of the solution was placed on a Formvar/carbon-coated Cu grid. Excess solution was dabbed off using a clean filter paper and the grids were immediately analyzed using HRTEM to prevent sample aging. Precipitates on the grid were measured using electron diffraction, however no diffraction
patterns were observed (Figure 2-S4). Therefore, it is likely that these precipitates are amorphous during the early stages of nucleation and growth surveyed during \textit{in situ} GISAXS measurements.

**Determining \textit{ex situ} precipitate phases using HRXRD.** The solutions outlined in Table 2.1 were created following the above procedure, scaled up to a total volume of 1000 mL in order to accumulate enough precipitation for HRXRD measurements. Solutions were reacted for 1 hour before beginning filtration in small batches at 5000 RPM utilizing Millipore Amicon ultra-15 centrifugal filter units. After the entire batch was filtered, the precipitates which had accumulated on the filter were dried overnight in a desiccator. Samples were packed in Kapton capillary tubes and sent to 11-BM at APS for analysis using HRXRD. The total time of samples aging between when the reaction started and when the HRXRD measurements were conducted was 8-11 days. HRXRD for NOM containing samples can be found in Figure 2.9. Results from HRXRD on these samples showed a broad peak between 2Theta = 10 and 25°, indicative of NOM presence. The ferrihydrite spectra for these systems were also very noisy and the peaks were not well defined, signifying a poorly crystalline structure. However, these results did not show any definitive differences between the Fe(III) + NOM and Fe(III) + As(V) + NOM ternary system.

**Investigation of NOM and As(V) complexation.** FTIR results (Figure 2-S6) give a more detailed picture of what is occurring in these two systems. NOM-containing systems had a double peak around 1600-1700 cm\(^{-1}\). For the NOM reference, the strongest peak at \(\sim 1720\) cm\(^{-1}\) was likely from C=O bonding. This peak shifted to 1610 cm\(^{-1}\) after reaction, indicating that the deprotonation of the carboxylate anion may be necessary in order to bond with iron(III) (hydr)oxides. For the systems containing arsenate, the large peak in the Fe + As system at \(\sim 826\) cm\(^{-1}\) within range of \(\sim 825-839\) cm\(^{-1}\) in references for adsorbed arsenate on iron oxides. The Fe +
As + NOM system also has a single peak at ~829 cm\(^{-1}\) with no visible second peak, indicated monodentate complex formation for both system.

These results were confirmed with X-ray absorption spectroscopy (XAS), which also showed no differences between the two systems (Figure 2-S7). XAS results show the formation of bidentate mono-nuclear (R \(
\sim \)
 2.5Å) and monodentate mononuclear (R \(
\sim \)
 3.7Å) As(V) complexation. These results may be more accurate, since the bidentate peak is hard to observe using FTIR because it is very close to the monodentate peak. XAS experiments were conducted at Beamline 13BM-D at the Advanced Photon Source (APS), Argonne National Laboratory, which utilizes a Si (111) monochromator. The focused X-ray beam size was 10 \(\mu\)m by 30 \(\mu\)m with a resolution of \(1 \times 10^{-4}\) \(\Delta E/E\) and energy flux of \(1 \times 10^9\) at 10 keV. The As XANES K-edge was measured at 11.867 keV

GISAXS Analysis

GISAXS experimental set-up and data analysis. Prior to running any samples, a \(q\) range calibration was done using a silver behenate standard. During GISAXS measurements, incident X-ray beams are passed through the GISAXS reaction cell, where they interact with particles on the substrate surface. The scattered X-ray beams are collected by a 2-D detector, while those which transmit through the solution hit the photodiode, which is constantly monitored to look for beam fluctuations or sample shifting during measurement. The incidence angle \((\alpha_i)\) between the incident X-ray beam and the substrate surface was chosen to be 0.11°. This value was calculated considering the substrate structure (quartz, SiO\(_2\)) and the beam energy (14 keV) to achieve a reflectivity of 98%. At this angle, the X-ray beam mainly probes scattering from nanoparticles on the substrate surface. For GISAXS measurements, X-ray scattering data was processed by cutting along the Yoneda wing. All data reduction was conducted using the GISAXSshop macro,
available at APS beamline 12-ID-B. The data reduction procedure can be found in our previous publication.170

The scattering curves \( I(q) \) for each different time points (Figure 2.1/2.5) were fit using the following relationship:

\[
I(q) = I_0 P_0(q, r_0, \sigma_0) S(q, I_0s, d, R_h, v_f) \tag{2S(1)}
\]

Within this relationship, \( P(q, R, \sigma) \) is the form factor. For our case, a polydisperse sphere model with the Schultz size distribution was used. This model was chosen because the broad distribution in size and lack of form factor oscillations in the scattering curves.

The structure factor appears in this relationship as \( S(q, I_0s, d, R_h, v_f) \). This factor can be broken down into two parts as follows for a large aggregate system composed of small primary particles:

\[
S(q, I_0s, d, R_h, v_f) = I_0s q^d + S(q, R_h, v_f) \tag{2S(2)}
\]

Within this equation, \( I_0s q^d \) models the Porod scattering from the aggregates. \( I_0s \) is a scaling constant and \( d \) is the Porod power-law exponent (i.e. the fractal dimension). The term \( S(q, R_h, v_f) \) is the structure factor for the primary particles comprising of infinitely large aggregates. The hard-sphere Percus-Yevick model was used for the \( S(q, R_h, v_f) \), wherein \( R_h \) is the hard-sphere interaction radius and \( v_f \) is the volume fraction.

**Calculation of precipitate electron densities.** During GISAXS analyses for the relative total particle volume comparison, we also considered the effects of arsenate and phosphate incorporation on the electron density, which can influence the GISAXS intensities. Increases in the electron density due to oxyanion incorporation would increase the electron density of the particles, leading to higher GISAXS scattering intensities. However, this cannot be attributed to differences in precipitate quantities between the systems. Using the measured oxyanion
incorporation quantities for the homogeneous precipitates, the electron densities were calculated to be 1.12 e/Å$^3$ for the Fe(III) only system, 1.20 e/Å$^3$ for the system containing $10^{-5}$ M arsenate, and 1.34 e/Å$^3$ for the system containing $10^{-5}$ M phosphate. The contrast between the precipitates and water is:

$$\text{Contrast} = (\rho_{\text{precipitate}} - \rho_{\text{water}})^2$$  \hspace{1cm} 2S(3)

The contrast for the $10^{-4}$ M Fe(III), $10^{-4}$ M Fe(III)$-10^{-5}$ M arsenate, and $10^{-4}$ M Fe(III)$-10^{-5}$ M phosphate systems were calculated to be 0.6260, 0.7531, and 1.022 respectively. The GISAXS intensity is proportional to both the contrast and the total volume of particles according to the following relationship:

$$\text{Intensity} = \text{contrast} \times \text{no. of particles} \times \text{individual particle volume}$$  \hspace{1cm} 2S(4)

Therefore, the ratios of the intensities and contrast were compared for the $10^{-4}$ M Fe(III) (standard system) and $10^{-4}$ M Fe(III)$-10^{-5}$ M arsenate or $10^{-4}$ M Fe(III)$-10^{-5}$ M phosphate systems. While the contrast for the arsenate system was 1.2 times the intensity for the iron standard system, the scattering intensity was 18 times higher. For the phosphate system, the contrast was 1.6 times higher and the scattering intensity was 5 times higher.

### Table 2-S1. SRNOM Characterization provided by the IHSS

<table>
<thead>
<tr>
<th>Carboxyl (meq/g C)</th>
<th>Phenolic (meq/g C)</th>
<th>$Q_1$</th>
<th>$\text{Log}K_1$</th>
<th>$n_1$</th>
<th>$Q_2$</th>
<th>$\text{Log}K_2$</th>
<th>$n_2$</th>
<th>N</th>
<th>RMSE</th>
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<tr>
<td>9.85</td>
<td>3.94</td>
<td>10.57</td>
<td>3.94</td>
<td>3.60</td>
<td>2.61</td>
<td>9.74</td>
<td>1.19</td>
<td>112</td>
<td>0.0725</td>
</tr>
</tbody>
</table>


$Q_1$ and $Q_2$ are the maximum charge densities of the two classes of binding sites

$\text{Log} K_1$ and $\text{Log} K_2$ are the mean log K values for proton binding by the two classes of sites

$n_1$ and $n_2$ are empirical parameters that control the width (in log K) of a class of proton binding sites
Figure 2-S1. Lorentz corrected scattering intensities for heterogeneously formed particles on quartz in the systems containing 10 mM sodium nitrate with (A) $10^{-4}$ M Fe(III), (B) $10^{-4}$ M Fe(III) and $10^{-5}$ M arsenate, and (C) $10^{-4}$ M Fe(III) and $10^{-5}$ M phosphate.
**Fe(III) only**
1 × 1 μm scan size
10 nm height data scale

**Fe(III) + arsenate**
1 × 1 μm scan size
10 nm height data scale

**Fe(III) + phosphate**
1 × 1 μm scan size
10 nm height data scale

**Figure 2-S2.** Comparison of surface morphologies in regular and inverted set-up experiments. AFM has a vertical resolution on the sub-angstrom scale, while lateral resolution for tapping mode is ~40 nm, significantly larger than the precipitate size. Therefore, the vertical dimensions measured by sectioning of height mode images were used to define *ex situ* particle sizes for the various experimental systems.
Fe(III) only
1 × 1 μm scan size
10 nm height data scale

Fe(III) + arsenate
1 × 1 μm scan size
10 nm height data scale

Fe(III) + phosphate
1 × 1 μm scan size
10 nm height data scale

Figure 2-S3. AFM Images and height sections showing the difference in particle size for newly formed heterogeneously formed precipitates and precipitates which have been dried in an oven at 100°C for 24 hours. There was only observable particle shrinking in the system which contained arsenate.
Figure 2-S4. Electron diffraction pattern for homogeneous precipitates in the system containing Fe(III) and arsenate. No diffraction pattern was observed for any system, indicating that precipitates were amorphous in the early stages of nucleation and growth.
Figure 2-S5. AFM images of GISAXS samples reacted for 1 hour

Height scale = 10 nm
Figure 2-S6. FTIR data for homogeneous precipitates in the four reaction systems show no differences in As and NOM binding to iron(III) (hydr)oxides. The red square indicates where peaks from NOM binding occur and the black squares indicate where As(V) is binding.
**Figure 2-S7.** XAS Fourier transform data for As K-edge in reaction systems and sodium arsenate standard samples

**Figure 2-S8.** Tapping mode AFM image of the Fe(III) + NOM sample reacted for 30 minutes
Figure 2-S9. Total particle volume evolutions calculated from GISAXS scattering data. Error bars for size in the Fe(III) only systems are too small to be visible behind the markers.

Chapter 3: Microscale: Determining arsenopyrite
dissolution and secondary mineral precipitation during MAR

Portions of this chapter have been published in *Environmental Science & Technology*, 2014, 48 (8), 4395-4405 and in *Environmental Science & Technology Letters*, 2015, DOI: 10.1021/acs.estlett.5b00311

3.1. Overview

As described in the introduction, managed aquifer recharge (MAR) is one water reuse technique with the potential to meet growing global water demands. However, MAR sites have encountered arsenic mobilization resulting from recharge operations. To combat this challenge, it is imperative to identify the mechanism of arsenic mobilization during MAR. Knowledge gained in Chapter 2 provides a basis for understanding the early stages of iron(III) (hydr)oxide precipitation, which can act as a natural arsenic sink. In this chapter, bench-scale studies were conducted to characterize arsenic mobilization from arsenopyrite (FeAsS) and microscale secondary mineral precipitation for conditions relevant to MAR operations. Experimentally determined activation energies for arsenic mobilization from FeAsS were calculated for different water chemistries for use in reactive transport modeling (Chapter 4).

For the first portion of this study, the effects of anion identity (chloride vs. nitrate) were explored and results were compared with reclaimed water samples. Interestingly, the sodium chloride system showed higher arsenic mobilization under aerobic conditions. In addition, secondary mineral precipitation varied between systems and further affected arsenic
mobilization. For example, the wastewater system inhibited precipitation, while, in the sodium chloride system, faster phase transformation of iron(III) (hydr)oxide precipitates was observed, resulting in hematite formation after 7 days. The phase transformation to hematite would further result in less available surface area for arsenic attenuation.

Next, NOM effects on arsenopyrite dissolution and secondary mineral precipitation were investigated. NOM was found to inhibit secondary mineral precipitation. This effect could contribute to the lack of precipitation in the reclaimed wastewater system, since reclaimed water contains a significant concentration of NPOC.

Finally, the effects of ferric ions on arsenopyrite oxidative dissolution were studied at circumneural pH. Ferric ions can be introduced in secondary water during MAR and are also a product of arsenopyrite oxidative dissolution. Results showed that despite their low solubility, small quantities of additional Fe$^{3+}$ triggered electron transfer between Fe$^{3+}$ and Fe(II) in arsenopyrite, resulting in higher extents of secondary mineral formation and faster phase transformation. In addition, dissolved arsenic concentrations were elevated in these systems due to faster dissolution and faster phase transformation. These findings have significant environmental implications for arsenic transport under dynamic redox conditions, where interactions between Fe$^{3+}$ and arsenopyrite can dominate arsenic-bearing pyrite oxidation as well as iron(III) (hydr)oxide formation and stability.

3.2. Introduction

Increasing groundwater demands have resulted in widespread depletion of aquifers—the underground formations that store 98% of the world’s fresh water resources. In addition to the consequence of drinking and sanitation water shortages, lowered groundwater tables can lead to the drying of wetlands, destructive settling of surrounding land, and contamination of
groundwater by saltwater intrusion.\textsuperscript{172-174} Natural recharge rates will depend on climate, soil composition, and aquifer depth, and can vary significantly in space and time. It is vital to establish a safe and sustainable means of supplementing natural groundwater recharge to avoid undesired detrimental health and environmental impacts.

Managed aquifer recharge (MAR) is considered as one water reuse solution to address water needs in areas where water demand exceeds the natural recharge potential.\textsuperscript{175-177} MAR operations involve the injection and storage of secondary water into subsurface strata, including groundwater aquifers, for future use. Recharge water can be utilized from a variety of natural sources including available surface waters, stormwater runoff, and snowmelt.\textsuperscript{175} In addition, one common source for the secondary water utilized in MAR is “reclaimed” wastewater, which has been treated beyond conventional wastewater treatment.\textsuperscript{178-180} Natural attenuation processes in the vadose zone and underlying aquifer have been shown to remove residual pathogens from the injected reclaimed water.\textsuperscript{181, 182}

Recent studies at MAR field sites have shown that reclaimed water recharge can trigger unfavorable soil–water interactions releasing arsenic, a toxic metalloid, from aquifer materials. For example, Jones and Pichler\textsuperscript{22} reported that while injection waters to a MAR site in South Central Florida contained 3 \(\mu\text{g}/\text{L}\) of arsenic, recovered levels were much higher, ranging from 10–130 \(\mu\text{g}/\text{L}\). Arsenic mobilization as a result of artificial aquifer recharge has also been observed globally at sites in Australia, Germany, China and the Netherlands, as well as in states in the U.S., including Florida, California, Wisconsin, Idaho, and Montana.\textsuperscript{26} Some of these locations, such as Bolivar, South Australia\textsuperscript{180} and Manatee, Florida, USA\textsuperscript{33} reported low ambient arsenic concentrations of 3 \(\mu\text{g}/\text{L}\) and 8 \(\mu\text{g}/\text{L}\), respectively. MAR implementation at these sites lead to recovered levels of 22.5 \(\mu\text{g}/\text{L}\) and 24 \(\mu\text{g}/\text{L}\). Instances of arsenic mobilization from
Suwannee Limestone during MAR in Florida stemmed from arsenian pyrite, containing arsenic at levels of up to 1.12 wt%.\textsuperscript{183} In many cases, recovered arsenic levels have exceeded the Environmental Protection Agency’s maximum concentration level of arsenic (10 µg/L).

The potential for arsenic mobilization during MAR is widespread, and a better understanding of the effects of injected water chemistry on arsenic mobilization is needed. However, despite many observations and intense studies in multiple aquifer systems,\textsuperscript{26, 33, 180, 184} consensus has not been reached on the dominant cause of this observed arsenic mobilization. One proposed mechanism is the oxidation of arsenic-bearing minerals, such as arsenopyrite (FeAsS) or arsenian pyrite (< 0.5–10 wt% As)\textsuperscript{185}, by the electron acceptors such as oxygen, ferric ions and/or nitrate (eq. 1.2–1.4 in the Introduction), which may not otherwise be present in anoxic native groundwater.\textsuperscript{26, 184, 186, 187} Although Fe(III) has a low solubility at higher pHs, previous studies have shown that aqueous Fe(III) is an effective pyrite oxidant at circumneutral pHs.\textsuperscript{188}

The existence of arsenopyrite and arsenic-bearing pyrite in groundwater aquifers has been documented frequently, as have its effects on groundwater arsenic levels.\textsuperscript{183, 189-191} The oxidation of arsenic-bearing pyrite in sandstone drinking water aquifers in Northeastern Wisconsin has led to arsenic levels exceeding 50 µg/L in 86 of 2125 water supply wells.\textsuperscript{189} Arsenopyrite found in bedrock in south-central New Hampshire was responsible for elevated arsenic concentrations in domestic wells of up to 180 µg/L.\textsuperscript{190} Furthermore, MAR will not be not solely utilized to replenish drinking water supplies; groundwater demands must also be met for irrigation and industrial uses, and overdrafting is an issue in many deeper aquifers used for this purpose. High levels of naturally occurring arsenic have also been found in these deeper groundwater aquifers. For example, arsenic concentrations of 1 to 10 mg/L have been observed in groundwater in Fairbanks, Alaska, due to the presence of arsenopyrite-rich sediments.\textsuperscript{191} In addition, recent
surface water replenishment programs and energy-exploration water disposal activities in Colorado, Utah, and further northwest in the U. S., involve bedrock aquifers of metamorphic or igneous origins, which could more likely contain arsenopyrite or arsenian pyrite.\textsuperscript{192, 193}

Arsenic mobilization in groundwater will be governed in part by interactions with iron(III) (hydr)oxide minerals, which have a large capacity for sorbing aqueous arsenic. Iron(III) (hydr)oxides \((\text{Fe(OH)}_3: \text{simplified form of ferrihydrite})\) can form in aqueous environments and as a product of \(\text{Fe}^{3+}\) from arsenopyrite oxidation (eq. 1.5 in the Introduction).\textsuperscript{194, 195} In this chapter, the term “dissolved (or aqueous) \(\text{Fe}^{3+}\) species” is used to describe any reactive hydroxo-\(\text{Fe}^{3+}\) aqueous complexes, such as \(\text{Fe(OH)}_2^+\) or \(\text{Fe(OH)}_3^{aq}\), rather than just free \(\text{Fe}^{3+} (aq)\) cations. The term “\(\text{Fe}^{3+}\)” is used to describe both colloidal \(\text{Fe(III)}\) and hydroxo-\(\text{Fe}^{3+}\) aqueous complexes.

In addition, \(\text{Fe}^{2+}\) from arsenopyrite dissolution can catalyze the phase transformation of iron(III) oxides and hydroxides.\textsuperscript{196-200} During this process, electrons are transferred from aqueous or sorbed \(\text{Fe}^{2+}\) to \(\text{Fe}^{III}\) on the mineral surface. When the sorbed \(\text{Fe}^{2+}\) atom loses its electron, it becomes a new \(\text{Fe}^{III}\) atom on the mineral surface. In turn, the \(\text{Fe}^{III}\) atom which gains the electron from aqueous or sorbed \(\text{Fe}^{2+}\) is reduced to \(\text{Fe}^{2+}\) and becomes solubilized. This electron transfer and atom exchange mechanism leads to the dissolution of the \(\text{Fe}^{III}\) from iron(III) oxides and hydroxides and subsequent recrystallization of \(\text{Fe}^{2+}\) from solution. As a result, phase transformation is catalyzed. Studies have also been carried out on the effect of Fe(II)-catalyzed phase transformation on arsenic associated with Fe(III) mineral precursors.\textsuperscript{201} These studies found that the arsenate became more tightly bound in the crystallized product phases.

Although previous studies have considered the effects of aqueous \(\text{Fe}^{2+}\) on iron(III) (hydr)oxides, there is currently a knowledge gap for more complex redox systems, such as those
occurring during MAR, where Fe(II) minerals may be dissolving while simultaneously precipitating iron(III) (hydr)oxides. In addition, while previous studies have tested the ability of dissolved Fe$^{3+}$ species to oxidize arsenopyrite,\textsuperscript{202, 203} most were conducted under low pH conditions, as dissolved Fe$^{3+}$ species have decreased solubility at higher pHs. However, Moses et al. found that at higher pHs, the oxidation of pyrite, a related iron sulfide mineral, by aqueous Fe$^{3+}$ was an order of magnitude higher than oxidation by dissolved oxygen.\textsuperscript{204} They hypothesized that at these pHs, aqueous Fe$^{3+}$ exists as a hydroxo-Fe$^{3+}$ complex which can still act as an effective oxidant.

The circumneutral oxidation of arsenopyrite by Fe$^{3+}$ is crucial: This pH range is more environmentally relevant than those in previous studies, and these geochemical reactions can trigger the release of toxic arsenic into groundwater resources. While higher or lower pH conditions can occur in specific scenarios such as acid mine drainage, circumneutral pH conditions are more common and can provide a basis for studying other extreme pH scenarios. Furthermore, the Moses et al. study of pyrite oxidation by Fe$^{3+}$ did not consider secondary mineral formation, which can act as a sink for aqueous arsenic in real systems.

While many studies exist on groundwater–arsenic-bearing pyrite interactions\textsuperscript{205, 206} and the subsequent fate and transport of arsenic in groundwater,\textsuperscript{207, 208} no study to date has fully addressed the unique scenario of MAR using reclaimed wastewater. This is in part due to the complicated nature of this scenario, as wastewater not only has many constituents, but also its composition will not be constant during MAR operations or between different MAR sites. We must, therefore, systematically characterize the potential interactions between prevailing reclaimed water components and arsenic-bearing pyrite to establish best practices for MAR and increase its viability as a water reuse option. To achieve this, we start the investigation with
model systems, where water chemistry and solid phase composition is controlled to identify
dominant arsenic mobilization mechanisms, as well as further our understanding of wastewater–
arsenic-bearing pyrite interactions. Arsenopyrite was chosen as the model arsenic-bearing pyrite
for these systems in order to guarantee that samples utilized in different solution and solid-phase
experiments have uniform compositions, allowing us to quantify mobilization and precipitation,
and systematically compare results between different systems. Outcomes from these well-
characterized, model studies will also provide a baseline for future studies utilizing arsenian
pyrite and field site samples, along with more complicated water chemistries.

This bench-scale study, therefore, aims first to examine the kinetics of arsenic mobilization
from arsenopyrite in the presence of reclaimed wastewater and model wastewater solutions of
simplified composition containing either sodium chloride or sodium nitrate at comparable ionic
strengths to reclaimed water. These different anions were chosen to study because of their
presence in reclaimed wastewater and because they are known to impact the formation of
ferrihydrite, a secondary mineral product of arsenopyrite dissolution. Next, additional
potential reclaimed water components (organic carbon from Suwannee River NOM and ferric
ions) were added to the model systems to explore their effects.

Changes in the arsenopyrite solid phase were also examined to determine the extent and
phase of secondary mineral precipitation. This is important because arsenopyrite oxidation
during MAR operations has been reported to form iron(III) (hydr)oxide minerals such as
ferrihydrite, which can impact aqueous arsenic levels by immobilizing arsenic through sorption
and co-precipitation. The new quantitative and qualitative information gained in this study will
improve current reactive transport models for arsenic fate and transport analysis during MAR.
Moreover, the new knowledge acquired can be applied to other systems where arsenic pollution
of groundwater is a concern, such as acid mine drainage sites, uranium mine tailing operations, and locations with pervasive natural arsenic contamination.

### 3.3. Experimental approach

#### 3.3.1. Materials and chemicals

For all experiments, natural arsenopyrite samples were used. Arsenopyrite samples from Gold Hill, Tooele County, Utah, were purchased from the Mineralogical Research Company (San Jose, CA). X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX), and Raman Spectroscopy all confirmed that these samples contained a mixture of quartz and arsenopyrite. X-ray diffraction analysis generated a spectrum showing quartz and arsenopyrite (Figure 3-S1A in the Supplementary Information (SI)). Raman spectroscopy produced two different characteristic spectra depending on whether the beam was focused on quartz or arsenopyrite in the sample powder (Figure 3-S1B in SI). These were compared with the literature and identified as arsenopyrite and quartz.

Arsenopyrite ore samples were ground using a mortar and pestle to produce an array of particle sizes that were separated using sieves. For batch reactor dissolution experiments, 300–500 µm particles were used. The surface area of the 300–500 micron particles was determined using Brunauer–Emmett–Teller (BET) to be 0.116–0.555 m²/g from three measurement trials. Although there is a high variability in surface area measurements, experiments were conducted using the same arsenopyrite mass and particle size range, while the grain purity, texture, and quality was maintained. Therefore, the surface area for each system is expected to be similar. Due to the variability in surface area measurements, surface area was not used to normalize dissolution rates. Because arsenopyrite may be oxidized when being exposed to atmospheric oxygen, altering their reactivity and potentially forming secondary minerals, powdered samples
were cleaned using an acid-washing procedure established by McGuire et al.\(^ {215} \) and stored in an anaerobic chamber prior to reaction.

Solutions containing 10 mM sodium nitrate or 10 mM sodium chloride were created using reagent-grade salts. The pH of these solutions was adjusted prior to reaction to 7.0 ± 0.2 using nitric acid for the sodium nitrate solution or hydrochloric acid for the sodium chloride solution. The pH was chosen to match the pH of wastewater samples, which ranged from 6–8, and an ionic strength of 10 mM was chosen to match the conductivity of the wastewater samples (~1100 \( \mu \text{S/cm} \)). Conductivity was measured using an Orion\textsuperscript{TM} DuraProde\textsuperscript{TM} conductivity cell (Thermo Scientific, MA, US) and pH was measured using a pH electrode (Mettler-Toledo, OH, US). Conductivity and pH values did not vary significantly between five reclaimed wastewater samples taken at different times from the Metropolitan Sewer District of Greater Cincinnati (MSDGC) wastewater treatment plant.

Concentrations of nitrate reported in the literature for tertiary effluent range from 0.52–1.16 mM.\(^ {216-219} \)

Although the nitrate concentration used in this study is higher than reported values, 10 mM nitrate was chosen to match the chloride concentration to help delineate the effects of chloride on secondary

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<thead>
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<th>Constituent</th>
<th>Concentration</th>
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<td>Lithium</td>
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</tr>
<tr>
<td>Sodium</td>
<td>188.2 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Magnesium</td>
<td>78.17 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Aluminum</td>
<td>0.074 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Potassium</td>
<td>9.97 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Calcium</td>
<td>67.5 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.180 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Iron</td>
<td>1.31 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.025 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Copper</td>
<td>0.005 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.024 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.003 ( \mu \text{M} )</td>
</tr>
<tr>
<td>Chloride</td>
<td>6.27 ( \text{mM} )</td>
</tr>
<tr>
<td>pH</td>
<td>7.3</td>
</tr>
<tr>
<td>TOC</td>
<td>12.42 mg/L</td>
</tr>
</tbody>
</table>

Table 3.1. Some principle wastewater constituents for samples provided by the Greater Cincinnati Metropolitan Sewer District wastewater treatment plant in November, 2012.
mineral precipitation. Nitrate can provide valuable data for comparison with sodium chloride because nitrate does not complex with aqueous Fe\(^{3+}\) as chloride does. For reaction systems which contained NOM, NPOC was added from an SRNOM stock solution to achieve concentrations of 12.5 mg C/L before the pH was adjusted. This concentration was chosen to match reclaimed wastewater samples. There can be some difference in reactivity between SRNOM and the DOC in our reclaimed water. However, a previous study has found that both SRNOM and WWTP effluent can contain large fractions of fulvic acid (68.4% for SRNOM and 42.5% for treated effluent). For systems containing ferric ions, ferric nitrate was added from a stock solution to achieve a concentration of 1.5 \(\mu\)M Fe\(^{3+}\), which matches concentrations observed in reclaimed water samples. The stock solution was made immediately prior to reaction. At our circumneutral pH and under oxic conditions, Fe\(^{3+}\) is likely to be hydrolyzed rapidly. However, these hydrolyzed compounds can still be reactive and are known to oxidize pyrite. The additional 4.5 \(\mu\)M nitrate added with the ferric ions is assumed to be negligible compare to the 10 mM concentrations of nitrate or chloride from the sodium salts.

The nature of Fe\(^{3+}\) in our system was investigated using MINEQL+ (Ver. 4.6). We found that when the formation of ferrihydrite is considered, only 3.95 \(\times\) 10\(^{-9}\) M Fe(OH)\(_2^+\) is soluble for both the nitrate and chloride systems. Considering only the aqueous phase species, 90% of iron exists as Fe(OH)\(_2^+\) and 10% exists as Fe(OH)\(_3^0\) (aq) for both systems. However, these calculations assume that the system is at equilibrium. Because the real system may have kinetic limitations, dissolved Fe\(^{3+}\) species can exist as aqueous complexes at concentrations higher than equilibrium values. For example, Dousma and Bruyn studied the hydrolysis of ferric nitrate solution and found that, while the formation of smaller polymeric species occurred quickly, larger polymers formed relatively slowly. In addition to dissolved species, Fe\(^{3+}\) can also be present as colloidal
Fe(III) phases. These species can potentially react with arsenopyrite and form iron(III) (hydr)oxide secondary mineral precipitates, as described later in our proposed reaction mechanism for the Fe$^{3+}$-containing systems.

Table 3.1 shows the aqueous composition of the reclaimed wastewater samples used in our experiments. The concentration of metal ions in the wastewater was measured using inductively coupled plasma-mass spectrometry (ICP-MS) (7500ce, Agilent Technologies, CA); the concentration of chloride was measured using a chloride ion selective probe (VWR International Inc., West Chester, PA); and the non-purgeable total organic carbon (TOC) content was determined using a Shimadzu TOC-LCPH Analyzer. Prior to reaction, the pH of the wastewater was adjusted to 7.0 ± 0.2 using nitric acid. For anaerobic systems, pH 7, 10 mM sodium nitrate or sodium chloride solution were made in an anaerobic chamber using deoxygenated water ($P_{O_2} = 0$ atm). NOM or ferric ions were added from stock solutions also created using deoxygenated water in the chamber. Wastewater samples were deoxygenated by stirring them for at least 48 hours in the anaerobic chamber. Anoxic conditions were confirmed using a dissolved oxygen (DO) probe and oxygen gas analyzer in the anaerobic chamber.

### 3.3.2. Batch reactor set up

Batch reactors were used to determine dissolution rates for arsenopyrite under different experimental conditions. Zero-order reaction kinetics in arsenic were confirmed by the linear concentration evolution of arsenic in the reactor (trend lines in Figure 3.1/3.5). Each batch reactor contained 250 mL of the reaction solution and 0.05 g of acid washed FeAsS powder. Reactors were continuously stirred, and temperature was controlled at 5, 22, or $35 \pm 1^\circ\text{C}$ using a hot water or ice bath. Solution samples (2 mL each) were removed at 0, 0.5, 1, 2, 3, 4, 5, and 6 hours, filtered immediately using a 0.2 μm polytetrafluoroethylene (PTFE) membrane syringe
filter and capped to prevent evaporative losses. This time frame was chosen to minimize the effect of secondary mineral precipitation on aqueous arsenic levels. Finally, samples were acidified to 2% v/v acid and arsenic concentrations were measured using ICP-MS. At least three experimental replicates were run to confirm arsenic mobilization trends. It is important to note that the solubility of oxygen varied between these systems due to temperature changes. The calculated oxygen concentrations are 13 mg/L, 9 mg/L, and 7 mg/L for the 5, 22, or 35°C reactors, respectively. However, for all aerobic systems we found that dissolution was higher for systems with higher temperatures, despite having a lower oxygen concentration, so these trends should still be accurate.

During investigation of secondary mineral precipitation on arsenopyrite, batch reactors were run for the longer time frame of 7 days (a detailed description is in Section 3.3.3.). In the 10 mM sodium nitrate and 10 mM sodium chloride model wastewater systems, arsenic speciation in solution samples reacted for 1 and 7 days was carried out using an anion-exchange column packed with Spectra/Gel® Ion exchange resin in its chloride form (Spectrum Laboratories, CA, US). First, 10 mL of filtered batch reactor supernatant was adjusted to pH 3.5. The solution was then passed through the column where the first 5 mL was discarded and the next 5 mL was collected for analysis. Using this method, As(V) was retained in the columns while As(III) passed through the column. Comparison of As levels measured using ICP-MS in the influent and effluent was used to determine quantities of As(III) and As(V).

### 3.3.3. Secondary mineral identification

**Substrate Sample Preparation.** Morphological changes on the arsenopyrite mineral surface were examined using polished arsenopyrite 1-mm thin sections, called “coupons.” Samples were mounted on glass slides using an acetone-soluble epoxy, which was removed before coupons
were used in experiments. A uniformly flat surface was confirmed for unreacted arsenopyrite coupons using atomic force microscopy (AFM) (Figure 3-S2 in the SI) and coupons were stored in the anaerobic chamber. Coupons were cleaned immediately prior to reaction using acetone, ethanol, and isopropynol to remove any organic coating and rinsed with deionized water. Solutions used for solid characterization experiments were created identically to aqueous phase experiments (Section 3.3.1).

**Instrumental Analyses of Precipitates.** To observe the effects of water chemistry on the extent and morphology of secondary mineral precipitation, coupons were reacted under the same conditions used for aqueous-phase experiments. Multiple small coupons were added to batch reactors containing 250 mL of solution and 0.05 g of arsenopyrite at room temperature (22°C). Samples were removed after 6 hours, 1 day, 4 days, and 7 days, rinsed with deionized water and dried with high purity nitrogen gas. The longer time frame allowed better observation of secondary mineral formation and phase transformation, which could potentially occur at MAR sites where groundwater flow is near-stagnant. For systems containing ferric ions, coupons were allowed to react for up to 14 days to observe and quantify secondary mineral precipitates. Reacted coupons were stored in the anaerobic chamber prior to and after analysis using AFM and Raman spectroscopy to prevent further oxidation.

Tapping mode AFM (AFM, Veeco Inc.) was used to characterize secondary mineral precipitates on arsenopyrite coupons by measuring changes in the height, amplitude and phase over the 7 day reaction period. AFM tapping mode probes were 125 μm long with phosphorus (n) doped silicon tips (nominal tip radius of 10 nm, MPP-11100–10, Bruker probes). A scanning rate of 0.988 Hz and drive frequencies between 312 and 320 kHz were used during imaging. To obtain better statistical information and confirm observed precipitation trends, each sample was
measured at multiple locations on the substrate surface using different scan sizes. Images were processed using Nanoscope 7.20 software.

Raman spectroscopy was conducted using an inVia Raman Microscope (Renishaw, UK) on reacted arsenopyrite in order to identify secondary mineral precipitates. Raman measurements were carried out with a 514 nm laser and a grating of 1800 lines/mm. A 20x objective and decreased power were used to limit the energy density of the laser, preventing artificial phase transformation of secondary mineral precipitates.\textsuperscript{225} Tests were also carried out to confirm that Raman settings themselves did not cause any phase transformation of iron(III) (hydr)oxides (Figure 3-S7 in the SI). A detailed description of this testing can be found in the SI. Raman analysis was also conducted using the same instrument on a number of iron oxides standards and unreacted arsenopyrite in order to identify their characteristic peaks for comparison with reacted samples.

\textit{Quantification of total Fe(III) precipitate quantities.} Citrate-bicarbonate-dithionite (CBD) extraction was carried out on arsenopyrite powder reacted in the presence and absence of Fe\textsuperscript{3+} to compare the effects of Fe\textsuperscript{3+} on the total quantity of secondary minerals in these systems.\textsuperscript{226} This procedure selectively dissolves Fe\textsuperscript{III} off the surface of the Fe(II)-containing arsenopyrite, allowing us to quantify the amount of oxidized iron (i.e., iron(III)) that has precipitated on the arsenopyrite surface during reaction. This information provides a valuable basis for comparing the extent of iron oxide precipitation under different aqueous conditions. For this procedure, 0.1 g of reacted arsenopyrite powder was placed in a 50 ml centrifuge tube. Next, 20 ml of 0.3 M sodium citrate and 2.5 ml of 1 M sodium bicarbonate solutions was added to the tube and it was immersed in a water bath and brought to 80°C. Once it reached the proper temperature, 1 g of sodium dithionite powder was added to the tube. The solution was stirred continuously for one
minute, and then periodically for 15 minutes. To stimulate flocculation, 5 ml of saturated NaCl solution and 5 ml of acetone was added to the tube. The suspension was mixed in a warm water bath and centrifuged at 2000 rev/min for 30 minutes. Finally, the supernatant was decanted and iron concentrations in the supernatant were measured using ICP-MS.

*Electrochemical Atomic Force Microscopy (ECAFM).* Preliminary experiments were also conducted examining the effects of an applied potential on the oxidation of pyrite in the presence and absence of arsenate. For these experiments, an electrochemical cell was used with the AFM in order to observe in situ surface morphological changes. For this set-up, the electrochemical cell was fixed with a three-electrode system connected to a potentiostat, which controls the potentiostatic voltage. During reaction, current flowed from the working electrode (i.e., the sample surface) through the liquid to the counter electrode. A reference electrode was also placed in solution through the fluid port to measure and control the absolute potential of the system. For our tests, a flat, polished pyrite substrate was used as the working electrode. The solution contained either 10 mM sodium nitrate or 10 mM sodium nitrate and $10^{-5}$ M arsenate. A potential of 500 mV was applied and the sample was reacted for up to 3 hours. Results can be found in the SI.

### 3.4 Results and Conclusions

#### 3.4.1. Chloride leads to faster mineral aging and higher mobilized arsenic concentrations

First, the geochemical reactions of arsenopyrite were investigated for our simplest model wastewater systems, 10 mM sodium chloride and 10 mM sodium nitrate, and results were compared with true reclaimed water samples. These results provide a basis for the study of more complex model wastewaters in later sections.
Evolution of Aqueous Arsenic Concentration.

Arsenic behavior in the aqueous phase was characterized first. Figure 3.1 shows the arsenic concentration changes with time in the aqueous phase for 10 mM sodium nitrate, 10 mM sodium chloride, and wastewater under aerobic (A1, B1, and C1) and anaerobic (A2, B2, and C2) conditions. Among aerobic systems, the highest arsenic mobility was observed in the 10 mM sodium chloride system. Arsenic concentrations were similar between the wastewater and sodium nitrate systems. The only difference between the two model wastewater systems was the presence of nitrate versus chloride anions, neither of which are expected to interact significantly with arsenopyrite in the presence of dissolved oxygen.
according to the literature. In addition, neither nitrate nor chloride competes with arsenate for Fe(III) adsorption sites. Therefore, differences in the arsenic mobility are not anticipated to result from changes in the oxidative dissolution of arsenopyrite or sorption of arsenic, but, more likely, from effects on secondary mineral formation and phase transformation, which further impact arsenic attenuation.

For the anaerobic systems, the highest arsenic concentration was observed in the sodium nitrate system (up to 0.28 mM), while very low concentrations were observed in the 10 mM sodium chloride and wastewater systems (up to 0.12 mM and 0.08 mM, respectively). For all systems, arsenic mobility was lower under anaerobic conditions (15%, 78%, and 76% reductions for nitrate, chloride, and wastewater systems, respectively, compared to aerobic conditions based on the 6-hour time frame), indicating the role of dissolved oxygen in the oxidative release of arsenic from arsenopyrite through reaction eq. 1.2. The decreased percent reduction in the anaerobic 10 mM sodium nitrate system compared to wastewater and sodium chloride can be due to the oxidation of arsenopyrite by nitrate anions in the absence of dissolved oxygen.

Activation Energy Calculations. For all aqueous systems, the activation energies for arsenic mobilization were calculated using the Arrhenius equation. Because zero-order reaction kinetics were observed in the early stages of dissolution for arsenic, the slope of the concentration evolution at each temperature (e.g., trend lines in Figure 3.1) was assumed to be equal to the rate constant, k, of the reaction. A larger rate constant would therefore correlate with higher arsenic concentrations at the end of the 6-hour reaction period. The rate constant, k, is related to the temperature and activation energy in accordance with the Arrhenius equation:

\[ k = Ae^{-E_a/RT} \]  

(3.1)
Taking the natural logarithm of this equation gives a linear relationship between the rate constant and temperature, $T$:

\[
\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(A).
\]  

(3.2)

The rate constant $k$ for each reaction condition was therefore determined by calculating the slope of the best fit trend line for the concentration evolution at each temperature. The natural log of $k$ was plotted against the inverse of the temperature and the slope of this line was equal to the negative activation energy, $E_a$, divided by the gas constant, $R$.

For the aerobic systems, the calculated activation energies for arsenic mobilization were 40.8 ± 3.5, 36.9 ± 2.3, and 43.6 ± 5.0 kJ/mol for 10 mM sodium nitrate, 10 mM sodium chloride, and wastewater, respectively. For the anaerobic systems, the calculated activation energies for arsenic mobilization were 31.2 ± 3.2, 28.4 ± 3.6, and 44.1 ± 6.3 kJ/mol for 10 mM sodium nitrate, 10 mM sodium chloride, and wastewater, respectively (Table 3.2). The activation energies for iron release were not calculated because aqueous iron levels were below the

<table>
<thead>
<tr>
<th>Aqueous Media</th>
<th>Temperatures (°C)</th>
<th>Activation Energies (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Aerobic</td>
</tr>
<tr>
<td>10 mM Sodium Nitrate</td>
<td>5, 22, and 35</td>
<td>40.8 ± 3.5</td>
</tr>
<tr>
<td>10 mM Sodium Chloride</td>
<td>5, 22, and 35</td>
<td>36.9 ± 2.3</td>
</tr>
<tr>
<td>Wastewater</td>
<td>5, 22, and 35</td>
<td>43.6 ± 5.0</td>
</tr>
</tbody>
</table>

All reactions were carried out at pH 7.0 ± 0.2. The solid-to-liquid ratio was 250 mL:0.05 g FeAsS powder. The surface area of FeAsS coupons added during the experiments outlined in Section 2.2 was calculated and found to be negligible compared to the area of the FeAsS powder. Triplicate reactors were run for all temperatures.

Standard error for $E_a$ values was determined using the equation:

\[
SE = \frac{1}{(n-2)\sum_{i=1}^{n}(y_i - \bar{y})^2} \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{n-1}}
\]

Taking the natural logarithm of this equation gives a linear relationship between the rate constant and temperature, $T$:

\[
\ln(k) = \frac{-E_a}{R} \frac{1}{T} + \ln(A).
\]  

(3.2)
detection limit during the 6-hour reaction period. This may result from the reprecipitation of aqueous iron as iron(III) (hydr)oxides. We expect that this process will further impact aqueous arsenic levels through concurrent arsenic sorption or co-precipitation. Therefore, while activations energies for arsenic mobilization would not be equivalent to that of arsenopyrite oxidation, it provides a better indicator of the overall arsenic mobility in these systems.

The literature provides activation energies for a number of minerals related to this system, including the oxidation of arsenopyrite by dissolved oxygen (57 kJ/mol at pH 5.9), and the reductive dissolution of ferrihydrite (40.7 kJ/mol), hematite (88 kJ/mol), and goethite (94 kJ/mol). The range of observed activation energies indicates that the most likely processes occurring are the oxidation of arsenopyrite by dissolved oxygen or the reduction of ferrihydrite, because all measured activation energies for arsenic mobilization would not be equivalent to that of arsenopyrite oxidation, it provides a better indicator of the overall arsenic mobility in these systems.

![AFM height mode images after 1 day (A1, B1, and C1) and 7 days (A2, B2, and C2) in the 10 mM sodium nitrate, 10 mM sodium chloride, and wastewater systems at room temperature (22°C) and under aerobic conditions. Dotted lines indicate where the image was cut to produce the height profile graphs below each image. The scan size for these images is 3 microns and the height scale is 100 nm. Images of the unreacted coupon can be found in Figure 3-S2 in the SI.](image)
energies ranged between 30 and 50 kJ/mol. However, our numbers are slightly different from the literature as we are focused on the overall arsenic mobility, i.e., the balance between arsenic release and attenuation, in MAR-related systems. Interestingly, for the wastewater system, the activation energy did not change between the aerobic and anaerobic systems. Despite the lower activation energy for 10 mM sodium nitrate and 10 mM sodium chloride in anaerobic systems, the mobility of arsenic was 3.5 times higher in the nitrate system and 1.5 times higher in the chloride system compared to the wastewater system. This indicates that other factors, such as the availability of reactants, contributed to decreased arsenic mobilization in wastewater. To investigate these observed trends and to determine secondary mineral effects on aqueous arsenic mobilization, the differences in secondary mineral formation and phase transformation were studied between sodium nitrate, sodium chloride, and wastewater systems.

**Secondary Mineral Morphology and Coverage.** Differences in secondary mineral precipitation among the three aqueous systems yield further insight into the observed trends in arsenic mobilization. Figure 3.2 shows the AFM height mode images after 1 day and 7 days in the 10 mM sodium chloride, 10 mM sodium nitrate, and wastewater systems at room temperature (22°C) and under aerobic conditions. Images at additional time points are provided in Figure 3-S3 in the SI. For all time points, multiple images were taken over the entire sample surface to confirm observations. The images in Figure 3.2 showed very distinct differences in precipitate morphology between the three systems. For the 10 mM sodium nitrate system, after 1 day there was a significant amount of small precipitates covering the entire surface (Figure 3.2A1). After 7 days, these precipitates grew in quantity and size, and at the end of the reaction period there was a variety of both larger and small particles, indicating continued nucleation and growth for the entire period (Figure 3.2A2). For the 10 mM sodium chloride system (Figure 3.2B), particles
after 1 day were larger in size and sparse on the surface. After 7 days, these particles appeared to aggregate to form a continuous coating on the surface. Unlike the sodium nitrate system, there was not much evidence of continued nucleation because the size and morphology of precipitates was very different between days 1 and 7. For the wastewater system (Figure 3.2C), there was little precipitation after 1 day and both the size and morphology of precipitates did not change significantly over 7 days. Under anaerobic conditions, there was no observed precipitation on the coupons for all three systems even after 7 days (Figure 3-S4 in the SI).

**Secondary Mineral Phase Identification.** Identification of secondary mineral phases in aerobic systems was accomplished using Raman spectroscopy (Figure 3.3). The characteristic spectra for different iron oxide minerals were determined by measuring standard samples on the

![Figure 3.3. Optical microscope images and Raman spectra for arsenopyrite coupons reacted in sodium nitrate (A, B), sodium chloride (C, D), and wastewater (E, F) systems. Optical microscope images for the 7-day sodium nitrate system (A) shows a uniform coating of maghemite, as indicated by the characteristic Raman peaks (B). For the sodium chloride system, after 7 days, the surface was covered in a non-homogeneous coating (C) of hematite (α-Fe₂O₃) and maghemite (D). No precipitation was observed in the wastewater system (E, F).](image-url)
Raman instrument. For the anaerobic system, there was no precipitation detectable by Raman spectroscopy and AFM (Figure 3-S4 in the SI).

Early in the reaction period (< 1 day), there was no detectable secondary mineral precipitation on the surface for any system. In the sodium nitrate system, the characteristic peaks of maghemite (γ-Fe₂O₃), an iron(III) oxide polymorph, become detectable after 1 day of reaction (Figure 3.3B). By 7 days, the entire coupon surface in the sodium nitrate system was coated by maghemite (Figure 3.3A). For the sodium chloride system, no precipitation was detected after 1 day owing to the small quantity of precipitates. After 7 days, however, the surface was covered in a non-homogeneous coating of hematite (α-Fe₂O₃) and maghemite (Figure 3.3D). The visual difference between these two mineral phases is apparent on the arsenopyrite surface (Figure 3.3C). For the wastewater system, there was no detectable precipitation even over the 7-day reaction period. 6-line ferrihydrite, magnetite, and goethite standards were also considered, but the spectra did not match the reacted samples.

**Mechanism of Secondary Mineral Phase Transformation in Nitrate and Chloride Systems.**

Hematite is the most thermodynamically stable iron oxide polymorph and is the final form resulting from the transformation of less thermodynamically stable iron(III) (hydr)oxides. The occurrence of hematite in the sodium chloride system and not the sodium nitrate system after 7-days reaction time was confirmed by multiple replicates. The faster transformation of iron(III) (hydr)oxides in the presence of sodium chloride compared to sodium nitrate is an interesting new observation, and can greatly impact arsenic mobilization from arsenopyrite.

Previous research conducted into the effects of chloride and nitrate on heterogeneous and homogeneous iron(III) (hydr)oxide nucleation and growth provides insight into this
phenomenon. Using time-resolved small angle x-ray scattering (SAXS) and grazing-incidence SAXS, Hu et al.\textsuperscript{56} observed that in the presence of chloride ions, Ostwald ripening was the dominant process controlling heterogeneous precipitation, whereas continuous nucleation, growth, and aggregation occurred in the nitrate system.\textsuperscript{56} Ostwald ripening describes the growth mechanism wherein smaller precipitates dissolve and form larger and more thermodynamically stable precipitates on the surface, resulting in an increase in particle size while the total number of particles decreases. In other words, through Ostwald ripening the particles can undergo phase transformation from less stable iron(III) (hydr)oxide polymorphs such as ferrihydrite into more stable forms, such as maghemite and, eventually, hematite.\textsuperscript{238}

The differences reported by Hu et al. in the iron(III) (hydr)oxide growth mechanisms are observable in AFM images of arsenopyrite coupons after 1 and 7 days of reaction time (Figure 3.2). In the sodium nitrate system, small particles are always visible on the surface in addition to larger aggregates, indicating continued nucleation, growth, and aggregation. Based on size analyses of more than 100 particles, particle height increased in the sodium nitrate system, from 10–30 nm after 1 day to 50–80 nm after 7 days. In the sodium chloride system, larger particles of around 40 ± 10 nm with a smaller number of particles are visible after 1 day. This height did not increase after 7 days, while lateral dimension of particles increased greatly, forming a continuous iron(III) (hydr)oxide coating after 7 days (Figure 3.2B2). Furthermore, there is a lack of smaller precipitates in both the 1- and 7-day samples, indicating that primary particles may have gone through Ostwald ripening processes. The prevalence of Ostwald ripening as a growth mechanism can also explain the faster phase transformation observed in the sodium chloride system. In the presence of chloride, soluble ferric chloride complexes can form.\textsuperscript{239} These complexes would decrease the apparent saturation ratio with respect to iron(III) (hydr)oxides in the system. Due to
the lower saturation ratio, it will be more thermodynamically favorable to form stable crystalline phases rather than metastable phases, which require larger saturations.\textsuperscript{240, 241} This phenomenon may explain why iron(III) (hydr)oxides in the sodium chloride system will form the more stable polymorph, hematite, within 7 days, while this phase is not present in the sodium nitrate system. However, additional mechanistic studies are needed to fully elucidate the role of chloride in this system.

The Ostwald ripening phenomenon will have secondary effects on arsenic mobility in the sodium nitrate and sodium chloride systems. Increased iron(III) (hydr)oxide nucleation in the sodium nitrate system leads to a large number of smaller particles. The high cumulative surface area of these precipitates can lead to more available surface sites for the sorption of aqueous arsenic anions, resulting in lower arsenic concentrations. Sorption quantities would also affect aqueous arsenic speciation. At pHs below 7, which were observed for 7 day batch reactor experiments (Figure 3.4), As(V) will sorb more readily to iron(III) (hydr)oxides.\textsuperscript{115} Over the reaction period, the percentage of aqueous As(V) decreased for the sodium nitrate system from 62.7\% As(V) (i.e., 37.3\% As(III)) at 1 day to 53.1\% at 7 days. The percentage of aqueous As(V) increased from 55.3\% to 65.9\% for sodium chloride and 59.3\% to 77.1\% for reclaimed water. These trends indicate that for the sodium nitrate system, aqueous As(III) was oxidized to As(V) and sorbed onto iron(III) (hydr)oxide precipitates, while for the sodium chloride system and reclaimed water system there was less capacity for As sorption. This would occur because the reclaimed water system had less precipitation compared to sodium nitrate system, and the sodium chloride had more crystalline precipitates (e.g., hematite).

This mechanism is consistent with observations of enhanced arsenic mobilization from arsenopyrite in the sodium chloride system compared to sodium nitrate (Figure 3.1).
increased reaction time, iron(III) (hydr)oxide undergoes aging processes to form maghemite in the sodium nitrate system and a mixture of maghemite and hematite in the sodium chloride system. Hematite, due to its increased crystallinity, has less sorption capacity for arsenic than maghemite. However, it is important to note that the transformation of iron(III) (hydr)oxides into more stable iron(III) oxide polymorphs can lead to the irreversible sorption of associated arsenic anions. Therefore, although these systems will have less capacity for arsenic sorption, the arsenic attenuated by the iron(III) (hydr)oxides in early stages will become strongly bound within the iron(III) oxide matrix. This inferred trapping mechanism can be beneficial for the long term fate and transport of arsenic in oxic or hypoxic groundwater systems where ferric iron minerals are stable.

**Inhibited Secondary Mineral Precipitation in the Wastewater System.** Another interesting new observation is the lack of precipitation in the system containing wastewater in comparison to both the sodium nitrate and sodium chloride systems. Currently, there are no studies which have reported on this apparent inhibition of iron(III) (hydr)oxide precipitation. Nonetheless, studies which model arsenic mobilization during MAR operations have assumed the formation of
ferrihydrite as an attenuation mechanism during arsenic transport in MAR. However, this modeling study did not utilize reclaimed water as the secondary water source.

We examined this aspect further for our system by monitoring the oxidation–reduction potential (ORP) and pH over the 7-day reaction period for the wastewater, sodium nitrate, and sodium chloride aqueous solutions. ORP is a measure of the tendency of the solution to gain or lose electrons. A positive redox potential indicates oxidizing conditions, meaning that the aqueous solution is more likely to gain electrons from arsenopyrite, thereby becoming reduced while arsenopyrite is oxidized. Evolution trends in pH and ORP for aerobic reactors can be found in Figure 3.4. Dissolved oxygen (DO) was also monitored, but no clear trend was observed.

For the 10 mM sodium nitrate and sodium chloride systems, similar evolutions were observed for pH and ORP measurements. pH decreased steadily over the 7-day period. This is likely due to the continuous oxidative dissolution of arsenopyrite through reaction eq. 1.2, which produces arsenous acid. For the wastewater system, the pH increased initially from 7.0 to 8.4, before decreasing again to around 7. The wastewater has a higher alkalinity than our model systems, which results in a high buffering capability. This may prevent the decreases in pH observed in the nitrate and chloride systems. At a lower pH, increased arsenic mobilization could occur due to proton-promoted dissolution; however lower pH will also favor arsenic sorption onto iron(III) (hydr)oxides. Higher iron concentrations would result in higher saturation indices with regard to iron(III) (hydr)oxide precipitates. However, the higher pH in the wastewater should also contribute to higher saturation indices due to the increased hydroxide ion concentration (reaction eq. 1.5). Because water chemistry effects on iron(III) (hydr)oxide saturation indices are contradictory, additional factors may be contributing to the inhibited precipitation for wastewater. Bicarbonate effects were also tested but could not account for
observed trends in arsenic mobilization for the wastewater system. Information on bicarbonate tests can be found in the SI.

The ORP values provide further insight into precipitation trends. The ORP increased over the 7-day period and was generally positive for the sodium nitrate and sodium chloride systems. In contrast, the ORP in the wastewater system fluctuated but always remained negative over the reaction period. The formation of iron(III) (hydr)oxides is contingent on the oxidation of Fe$^{2+}$, released through reaction eq. 1.2, to Fe$^{3+}$. The negative redox potential in the wastewater system indicates that the condition is a reducing environment for arsenopyrite. This could prevent the oxidation of Fe(II) and precipitation of iron(III) (hydr)oxides, a process consistent with our AFM and Raman experimental observations.

The lower ORP conditions in the wastewater system can be prevalent in reclaimed wastewater being considered for reuse in MAR. During secondary wastewater treatment, low ORP conditions are used to facilitate biological denitrification and phosphorus removal processes.$^{243}$ These redox reactions are further promoted by the addition of dissolved organic carbon (DOC) serving as the electron donor. Although much of the DOC present in wastewater is removed prior to effluent discharge and reuse, DOC levels can still be elevated when compared to groundwater concentrations.$^{244}$ In this study, wastewater samples had a non-purgeable organic carbon (NPOC) concentration of 12.42 mg C/L, while concentrations in the two model systems were negligible. This factor may be the root of observed differences in precipitation, as the presence of DOC could prevent the oxidation of Fe(II) and passivate the arsenopyrite surface, preventing heterogeneous iron(III) (hydr)oxide precipitation.
While our work involving nitrate and chloride model wastewaters has revealed many important new insights on the expected reactivity of arsenopyrite at MAR field sites, results have also raised questions about the observed difference in reactivity between arsenopyrite in our model systems and in reclaimed wastewater samples. Therefore, the effects of DOC on arsenopyrite dissolution and secondary mineral precipitation were examined next to help elucidate the mechanism behind secondary mineral precipitate inhibition in the reclaimed water system.

### 3.4.2. NOM inhibits secondary mineral formation and increases arsenic mobilization

In order to determine DOC effects, arsenic mobilization was first investigated for systems containing 10 mM sodium nitrate and/or chloride with and without NOM. The concentration of aqueous arsenic for systems containing sodium nitrate and NOM or sodium chloride and NOM under aerobic and anaerobic conditions is shown in Figure 3.5.

**Figure 3.5. Aqueous arsenic concentration evolution for systems containing sodium nitrate and NOM or sodium chloride and NOM under aerobic and anaerobic conditions.**

<table>
<thead>
<tr>
<th>A. Sodium nitrate + NOM</th>
<th>B. Sodium nitrate + NOM</th>
<th>C. Sodium chloride + NOM</th>
<th>D. Sodium chloride + NOM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerobic</td>
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<td>Aerobic</td>
<td>Anaerobic</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Aqueous system</th>
<th>Aerobic</th>
<th>Anaerobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM sodium nitrate + NOM</td>
<td>57.3 ± 5.2</td>
<td>39.1 ± 3.2</td>
</tr>
<tr>
<td>10 mM sodium chloride + NOM</td>
<td>44.0 ± 6.7</td>
<td>49.3 ± 4.0</td>
</tr>
</tbody>
</table>

**Table 3.3. Empirically determined activation energies for NOM-containing systems**

(kJ/mol)
nitrate or 10 mM sodium chloride and 12.5 mg/L NPOC from SRNOM (Figure 3.5). After 6 hours, the highest arsenic concentration was 0.34 ± 0.01 μM in the sodium nitrate + NOM system, compared to 0.33 ± 0.02 μM for the sodium nitrate system in the absence of NOM. For the sodium chloride system, the highest concentration was 0.73 ± 0.14μM after 6 hours in the NOM-containing system, compared to 0.55 ± 0.04 μM in the absence of NOM. The activation energies were calculated in Table 3.3.

These results indicate that the presence NOM does not inhibit arsenopyrite oxidation for either system, and thus cannot explain the lower arsenic mobilization in the reclaimed water system observed in the previous section. Furthermore, NOM was found to preferentially enhance arsenic mobility in the chloride system. Since NOM is not expected to impact arsenic mobilization from arsenopyrite directly, NOM effects on the aqueous water chemistry and secondary mineral precipitation were explored.

First, pH and ORP were monitored in the sodium chloride + NOM and sodium nitrate + NOM systems (Figure 3.6). For the sodium nitrate + NOM system, both pH and ORP trends are nearly identical to the systems without NOM. This may explain why the
arsenic concentrations are nearly identical in the two systems, despite NOM being present. For the sodium chloride + NOM system, the pH was increased and the ORP was decreased, similarly to the wastewater system (Figure 3.6A and B). However, the ORP was still positive for the chloride + NOM system over the first 6 hours of reaction, while the ORP negative for the wastewater system after 6 hours. This may account for the higher arsenic mobilization in the sodium chloride + NOM system compared to the wastewater system. Potential causes for this difference are discussed later in this section.

Next, secondary mineral precipitate quantities were examined. Figure 3.7 shows AFM images of the arsenopyrite surface after 6 hours, 1 day, 4 days, and 7 days of reaction in the sodium nitrate + NOM and sodium chloride + NOM systems. For both systems, some precipitation was observed on the surface. However, quantities were less than in the absence of NOM. The morphology was also very different for the sodium chloride system with NOM compared to without NOM. Rather than forming large particles and surface coatings, precipitates

Figure 3.7. AFM images for arsenopyrite coupons reacted in NOM-containing systems. The scan size is 20 microns and height scale is 100 nm.
in the sodium chloride + NOM system were small and distinctly separate on the arsenopyrite surface.

The phase of these precipitates was also investigated. Figure 3.8 shows optical microscope images and Raman spectra for nitrate and chloride systems with NOM. For the nitrate + NOM system, some discoloration was observed on the surface after 7 days. Raman spectra appear to show some fluctuation which may be similar to maghemite. However, these peaks are much weaker than the samples without NOM. This may be because the precipitate quantity is too small or because the secondary precipitate phase is less crystalline, e.g., ferrihydrite, which does not have any observable peaks using our Raman settings. For the chloride + NOM system, no discoloration was observed.
using the optical microscope.

These observation can in part be linked to the observed effects of NOM on iron(III) (hydr)oxide precipitation described in Chapter 2. GISAXS and HRXRD results indicate that the presence of NOM leads to the formation of smaller volumes of iron(III) (hydr)oxides and less crystalline phases. This effect may be strongest for the chloride system because in the absence of NOM, chloride formed more crystalline phases, thus the discrepancy would be larger between the presence and absence of NOM. In addition, arsenic concentrations were higher for the chloride system, and, as observed in Chapter 2, the presence of arsenic together with NOM can lead to even smaller volumes of precipitated iron(III) (hydr)oxides.

From these tests, we can conclude that the presence of NOM will inhibit iron(III) (hydr)oxide precipitation and crystallization for both nitrate and chloride systems, and may be the root cause of inhibited precipitation in the wastewater system. In the case of chloride, this inhibition also lead to higher arsenic mobilization, likely due to NOM and arsenate effects on secondary mineral precipitation, as described in Chapter 2. However, arsenic mobilization was lower for the wastewater system than for our two model systems with NOM. This may be because the ORP is negative for the first 6 hours of reaction in the wastewater system. While NOM can decrease the ORP, additional factors may be at play. For instance, biological activity in the wastewater can led to increased oxygen demands, thus less oxygen will be available for arsenopyrite oxidation. Chemical reducing agents such as sodium sulfite salts and sulfur dioxide can also be added to wastewater during treatment to reduce hazardous metals, including hexavalent chromium and lead, for easier removal.\textsuperscript{245} In addition, the ORP value of injected water at MAR field sites can vary significantly (Table 1.2) and elevated ORP values have been observed both in secondary water sources and in groundwater aquifers after MAR operation. ORP and DOC will be key
factors to monitor with regard to secondary water quality, as they appear to play an important role both in arsenic mobilization and secondary mineral precipitation.

In order to further study the effects of ORP, preliminary investigation was carried out on pyrite samples using electrochemical AFM. These results can be found in the SI.

**3.4.3. Fe(III) increases arsenic mobilization and secondary mineral precipitation and aging**

Next, the role of additional oxidants was examined. For these experiments, the complexity of sodium nitrate and sodium chloride model systems was increased through the addition of 1.5 μM ferric ions (Fe$^{3+}$), as described in Section 3.3. The role of ferric ions is of interest due to both its potential effects as an arsenopyrite oxidant (eq. 1.3) and because of complex redox interactions which can take

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**Figure 3.9. AFM height images for arsenopyrite flat coupons reacted for 7 days in batch reactors containing 1.5 μM Fe$^{3+}$ and 10 mM sodium nitrate (A1), 1.5 μM Fe$^{3+}$ and 10 mM sodium chloride (A2), 10 mM sodium nitrate (B1), and 10 mM sodium chloride (B2). The colored area under the AFM line cuts indicates where on the surface there appears to be secondary mineral precipitation compared to the background roughness.**
place when Fe$^{2+}$ and Fe$^{III}$ coexist. The effects of Fe$^{3+}$ on arsenopyrite dissolution and secondary mineral precipitation are outlined in the following section. For clarity, iron in solution is referred to as Fe$^{3+}$ (although it can be present as reactive Fe(III)-OH colloids, e.g., Fe(OH)$_3$, and as hydroxo-Fe$^{3+}$ complexes at circumneutral pHs) and iron in the solid phase is referred to as Fe$^{III}$. Results indicate that Fe$^{3+}$ effects on arsenopyrite oxidative dissolution are threefold, as described in the following sections.

**More secondary mineral precipitation in Fe$^{3+}$ systems.** AFM images (Figure 3.9) show significantly more precipitation in the systems with additional Fe$^{3+}$ after 7 days compared to the systems without Fe$^{3+}$. With additional Fe$^{3+}$, precipitation was smaller (10–50 nm height from > 100 precipitates) for the sodium nitrate system compared with the sodium chloride system (50–100 nm from > 50 precipitates). For the sodium chloride system with Fe$^{3+}$, the surface was much rougher (RMS = 3.51 nm for the system without added Fe$^{3+}$, compared to 23.9 nm for the system with added Fe$^{3+}$), indicating more extensive dissolution and secondary mineral precipitation. Interestingly, in the absence of Fe$^{3+}$, there was less precipitation observed for the chloride system (Figure 3.9B2) compared to the nitrate system (Figure 3.9B1).

The AFM observations are consistent with CBD measurements of the total Fe$^{III}$ precipitated on arsenopyrite powder after 7 days reaction. Even after subtracting out the Fe$^{3+}$ initially added to batch reactors (0.375 µmol Fe$^{3+}$ per batch reactor), the total precipitated Fe$^{III}$ quantities per reactor were 2.45 ± 0.30 and 2.81 ± 0.14 µmol Fe(OH)$_3$ for the nitrate and chloride systems, respectively. Without additional Fe$^{3+}$, the total quantities were 0.69 ± 0.0015 and 0.65 ± 0.14 µmol Fe(OH)$_3$ for the nitrate and chloride systems. Thus, the addition of Fe$^{3+}$ led to more extensive precipitation.
Figure 3.10. Arsenic concentration evolutions for batch reactors containing arsenopyrite powder and 1.5 µM Fe$^{3+}$ over a six hour reaction period for aerobic sodium nitrate, aerobic sodium chloride, anaerobic sodium nitrate, and anaerobic sodium chloride systems. The dotted lines indicate the maximum concentration seen for the reactors without added Fe$^{3+}$ at 35°C for each system.

Higher arsenic mobilization in Fe$^{3+}$ systems. As shown in Figure 3.10, after 6 hours with added 1.5 µM Fe$^{3+}$, the concentration of arsenic increased to a maximum of 0.45 ± 0.05 µM for the sodium nitrate system and 0.65 ± 0.06 µM for the sodium chloride system, under aerobic conditions at the highest temperature, 35°C. These values represent a 36% increase in arsenic concentration for the nitrate system and 18% increase for the chloride system compared to same systems without added Fe$^{3+}$. We also expect that for the aerobic 35°C system, the impacts of secondary mineral formation on arsenic concentration are the most exaggerated, as previous testing has showed increased iron(III) (hydr)oxide precipitation at higher temperatures (Figure 3-S6 in the SI). While the differences in arsenic concentration are not striking, particularly for lower temperatures, the increase is troubling in the context of the increased secondary mineral formation in Fe$^{3+}$-containing systems. Our results indicate that these minerals may not be an effective enough sink to entirely mitigate arsenic, despite their large quantity.
In order to test whether the increases in arsenic concentration could be due to the oxidation of arsenopyrite by Fe\textsuperscript{3+} in addition to dissolved oxygen, these experiments were repeated under anaerobic conditions. Interestingly, the maximum arsenic concentrations for the anaerobic nitrate and chloride systems containing Fe\textsuperscript{3+} were $0.17 \pm 0.02$ $\mu$M and $0.18 \pm 0.06$ $\mu$M, respectively. These values were similar, for the chloride case, or even lower, for the nitrate case, than those of the anaerobic systems without additional Fe\textsuperscript{3+}, indicating that for circumneutral pH conditions in the absence of dissolved oxygen, Fe\textsuperscript{3+} is not able to oxidize arsenopyrite to a

Figure 3.11. Optical microscope images of arsenopyrite coupons reacted in systems containing 1.5 $\mu$M Fe\textsuperscript{3+} and 10 mM sodium nitrate for 7 days (A1) and 14 days (A2), or 1.5 $\mu$M Fe\textsuperscript{3+} and 10 mM sodium chloride for 7 days (B1) and 14 days (B2). Colored symbols indicate where the Raman spectra (C) were taken. Maghemite was the dominant phase identified for the 14 day sample from the chloride system, while for all other systems, hematite was the dominant phase. The macro-scale mechanism for secondary mineral phase transformation is shown (D). The spectra for ferrihydrite can be found in the SI.
significant extent.\textsuperscript{246}

The increased arsenic concentration under aerobic conditions, thus, cannot be attributed to the contribution from the oxidation of arsenopyrite by Fe\textsuperscript{3+}, even though additional Fe\textsuperscript{3+} increased secondary mineral formation. Possibly without dissolved oxygen, the concentration of Fe\textsuperscript{3+} was not high enough to mobilize arsenic from arsenopyrite: The added Fe\textsuperscript{3+} concentration was only 1.5 \(\mu\text{M}\), compared to 6.19 mM dissolved O\textsubscript{2}. However, it is clear that when Fe\textsuperscript{3+} and dissolved oxygen coexist during arsenopyrite oxidative dissolution, both iron(III) (hydr)oxide formation and arsenic release are increased. We explore this mechanism further in the later discussion.

Faster secondary mineral phase transformation with additional Fe\textsuperscript{3+}. Although the addition of Fe\textsuperscript{3+} led to increased secondary mineral precipitation, this increase did not mitigate arsenic mobility, as one might expect due to the natural attenuation of arsenic by iron(III) (hydr)oxides, but rather arsenic concentrations were increased. Mobilized arsenic quantities may exceed what can be attenuated by secondary minerals. In addition, the sorption capacity of these minerals is related to their phase. To investigate the responsible process, the phase of the secondary minerals was investigated using Raman spectroscopy (Figure 3.11). In our previous study without added Fe\textsuperscript{3+}, only maghemite was observed on the arsenopyrite surface for the nitrate system, while both maghemite and hematite were observed for the chloride system. Furthermore, for the nitrate system, only maghemite was observed, even after 14 days reaction.\textsuperscript{246}

For both systems with additional Fe\textsuperscript{3+}, maghemite was the first detectable secondary phase after 4 days. By 7 days, the maghemite had undergone phase transformation, becoming hematite. With increasing time, maghemite precipitates were again observed on the surface of these
coupons, even on areas coated in the blueish precipitates. These blueish precipitates were consistently identified as hematite during our previous study of arsenopyrite oxidation. Additional CBD analysis was conducted on arsenopyrite powder reacted for 14 days, showing that the iron(III) (hydr)oxide quantities per batch reactor increased with time from 2.83 ± 0.30 μmol at 7 days to 3.36 ± 0.17 μmol at 14 days for the nitrate system and from 3.19 ± 0.14 μmol at 7 days to 3.47 ± 0.28 μmol at 14 days for the chloride system. If the phase transformation of hematite back into maghemite were the main mechanism, the total Fe(III) quantity would not increase. Thus, we concluded that the observed maghemite spectrum results from maghemite precipitates forming on surfaces already coated with hematite (Figure 3.11D). These Raman observations show that additional Fe$^{3+}$ not only led to increased precipitation, but also accelerated phase transformation.

**Mechanism of Fe$^{3+}$–arsenopyrite interactions.** We propose a mechanism analogue to the discussion by Moses and Herman for circumneutral pyrite oxidation. First, the additional Fe$^{3+}$ can sorb on the surface. Fe$^{II}$ in the mineral can then donate its electron to Fe$^{3+}$, forming Fe$^{III}$ and either directly reducing Fe$^{3+}$ to Fe$^{2+}$ or forming an Fe$^{2+}$/Fe$^{3+}$ complex with a delocalized electron. This Fe$^{2+}$ or Fe$^{2+}$/Fe$^{3+}$ complex will donate its electron to dissolved oxygen, forming Fe$^{3+}$ again and repeating the cycle. With time, Fe$^{III}$ on the surface will form iron(III) (hydr)oxide secondary mineral precipitates. The phase transformation of these minerals can be accelerated due to electron transfer and atom exchange between Fe$^{2+}$ and Fe$^{3+}$, and the precipitation extents will be greatly increased due to the increased oxidative dissolution by Fe$^{3+}$. Colloidal Fe$^{III}$ phases can also potentially adsorb onto the arsenopyrite surface and undergo phase transformation to form more aged iron(III) (hydr)oxide minerals such as maghemite. This phase transformation can be accelerated by Fe$^{2+}$ present from arsenopyrite dissolution. However, even if all of the added
Fe$^{3+}$ formed Fe$^{III}$ colloids which deposited on the arsenopyrite surface, this could only account for less than 12% and 13% of the total precipitated secondary minerals for the chloride and nitrate systems, respectively. Therefore, this mechanism may be less significant than the precipitation due to the oxidation of arsenopyrite.

During this oxidation process, arsenic can be dissolved from the exposed arsenopyrite surface. Even after 14 days of reaction, there was still some arsenopyrite surface exposed to the solution that could be seen using the Raman optical microscope. However, this process may become slower as more of the surface is coated in secondary minerals.

In addition, if iron(III) (hydr)oxide solids on the arsenopyrite surface become charged with Fe(II) due to the delocalization of electrons, they can be continuously oxidized by dissolved oxygen, which explains the increased precipitation quantities even after 14 days, when much of the surface is coated by precipitates. Electron transfer kinetics can also be different in the presence of these iron(III) (hydr)oxides. For example, if electron transfer from arsenopyrite to maghemite to oxygen is faster than transfer from arsenopyrite to oxygen, oxidation can occur more rapidly. Furthermore, because the electrical conductivity of sodium chloride exceeds that of sodium nitrate at ambient temperatures, electron transfer would be faster in sodium chloride compared to sodium nitrate.$^{248}$ Thus, this mechanism bolsters our observation of faster dissolution and more extensive precipitation in the chloride system rather than the nitrate system (Figure 9A1 and 9A2).

Our findings call immediate attention to the role of additional Fe$^{3+}$ in arsenopyrite oxidative dissolution kinetics at circumneutral pHs. We have found that Fe$^{3+}$ can still be highly reactive towards arsenopyrite, resulting in both faster dissolution and more extensive secondary mineral
precipitation. These species can be present along with precipitating iron(III) (hydr)oxides as the system approaches equilibrium. Future investigations are needed to delineate the exact mechanism of reaction including (1) the potential formation of Fe\(^{2+}/Fe^{3+}\) complexes and (2) the fate of sulfur and arsenic speciation from arsenopyrite in our experimental systems. This study gives insight into arsenic transport in aquatic systems, where the quantities and phase of iron(III) (hydr)oxides can significantly impact arsenic concentrations. These findings also have vital implications for MAR, where Fe\(^{3+}\) can be introduced along with dissolved oxygen to subsurface systems containing arsenic-bearing sulfides.

3.5. Environmental implications

The redox cycling of iron in the Earth’s subsurface regulates the fate and transport of many elements of concern. Engineered processes such as MAR can have a drastic effect on the redox potential of groundwater environments, triggering the oxidative dissolution of reduced iron minerals including arsenopyrite. Ferric ions released from these minerals will form iron(III) (hydr)oxide minerals, attenuating mobilized arsenic. This work showed that the presence of high concentrations of chloride ions will inhibit the continued nucleation of iron(III) (hydr)oxides. In addition, the promotion of Ostwald ripening could lead to the faster phase transformation of iron(III) (hydr)oxides. As a result, the arsenic mobility is higher in systems which contain sodium chloride rather than sodium nitrate. Sites implementing MAR should therefore carefully monitor chloride concentrations in injected reclaimed water. In order to fully benefit from the effects of arsenic sorption onto nanoscale iron(III) (hydr)oxide precipitation, pretreatment should be utilized to minimize chloride concentrations. However, it is also important to note that the transformation of iron(III) (hydr)oxides into more stable iron(III) oxide polymorphs can lead to
the irreversible sorption of associated arsenic anions, which can be beneficial for better sequestration of arsenic in oxic or hypoxic groundwater systems.

In addition, it was determined that the presence of wastewater inhibited iron(III) (hydr)oxide precipitation and decreased the ORP for this system, potentially due to the presence of DOC. This point was further investigated by examining the effects of NPOC from Suwanee River NOM on arsenic mobilization from arsenopyrite and secondary mineral precipitation. It was found that NOM inhibited secondary mineral precipitation, as was also seen in nanoscale studies conducted in Chapter 2. For the chloride + NOM system, arsenic mobilization was further enhanced, likely due to NOM altering the quantities and morphology of secondary mineral precipitates. Therefore, DOC is also a factor which may need to be monitored at MAR sites and controlled in order to promote iron(III) (hydr)oxide precipitation.

Lastly, the effects of additional of Fe$^{3+}$ on arsenopyrite oxidation and secondary mineral precipitation were tested. We found that even low concentrations of Fe$^{3+}$ had a catalytic effect on secondary mineral formation and phase transformation under oxic conditions. Fe$^{3+}$ presence also led to increased arsenic concentrations in these systems. These observations are particularly concerning due to the very low concentration of iron tested. Moving forward, Fe$^{3+}$ must be a consideration for secondary water utilized in MAR operations. Furthermore, other redox sensitive metals should be tested for their interactions with arsenopyrite in order to determine whether similar mechanisms can take place.

Comparison of water quality between our experiments (Table 3.1), and injection water quality at other studied MAR sites (Table 1.2) shows similarities in the pH, iron concentration, and TOC. Therefore, we can reason that the dominant geochemical reactions will be similar
between our wastewater experimental system and MAR field sites. However, we expect that the reactions can differ for the sodium nitrate case, because the nitrate concentration in these sites is much lower than 10 mM, which was used in our model system.

While our experimental systems can provide a good model for anthropogenic arsenic mobilization during MAR, these mobilization mechanisms can differ from systems with natural arsenic mobilization. For example, in Bangladesh, arsenic mobilization will frequently occur due to natural recharge with low ORP water, which can trigger the dissolution of arsenic-bearing iron(III) (hydr)oxide minerals. While our experimental systems do not model this process, we provide important insight into the secondary iron(III) (hydr)oxide mineral phases which can form during MAR. These minerals can also dissolve when exposed to reducing conditions, such as during recovery of injected water, when there is an influx of anaerobic groundwater towards the well. In this scenario, the presence of hematite would be favorable since it is the more stable iron(III) oxide polymorph.

Our findings have significant environmental implications for the longer term fate and transport of arsenic in groundwater aquifers; arsenic associated with these stable iron(III) oxide minerals will be trapped as long as the aqueous environment is favorable for Fe(III) formation (e.g., oxidative environments). Activation energies for arsenic mobilization in aerobic and anaerobic model wastewater and wastewater samples were also experimentally determined. Differences in activation energies between the systems indicate that the mechanisms controlling arsenopyrite dissolution and the propensity for arsenic mobilization can vary with water quality and can therefore be useful for determining MAR operating conditions which limit arsenic release from arsenic containing pyrite minerals. Outcomes can be used as a basis for developing more complex model MAR systems on the laboratory scale. This basis will allow us to better
interpret how future changes to the aqueous phase (e.g., addition of DOC, bicarbonate anions, and aqueous metals in Table 3.1) and solid phase (e.g., utilization of arsenopyrite-soil mixtures, field site samples, and arsenian pyrite (< 0.5–10 wt% As$^{185}$), can impact the mechanisms of arsenopyrite oxidation and secondary mineral precipitation during MAR.

3.6. Acknowledgments

We are grateful for support received from Washington University’s Faculty Startup and National Science Foundation (EAR-1424927). CWN acknowledges the generous support of the Mr. and Mrs. Spencer T. Olin Fellowship. We wish to thank Environmental NanoChemistry Group members for valuable discussion. A portion of this study (Section 3.4.1) was a part of the EPA Water Resources Adaptation Program (WRAP) research conducted with partial sponsorship under EPA Contract No. EP-C-09-041. The research in Section 3.4.1 was been subjected to the Agency’s administrative review and approved for external publication. Any opinions expressed are those of the authors and do not necessarily reflect the views of the Agency; therefore, no official endorsement should be inferred.
3.7. **Supporting information for Chapter 3**

Contents: Experimental details

- 8 figures (3-S1 – 3-S8)
- 1 table (3-S1)

**Sample and Solution Preparations**

*Arsenopyrite Sample Preparation and Characterization*

**FeAsS Characterization.** X-Ray Diffraction (XRD) was carried out on powdered arsenopyrite samples using a Rigaku D-MAX/A Diffractometer. Spectra were fitted using Jade Plus. Results showed that arsenopyrite samples contained a mixture of arsenopyrite and quartz (Figure 3-S1A). Raman spectroscopy was conducted using an inVia Raman Microscope (Renishaw, UK) on unreacted arsenopyrite. Raman measurements were carried out with a 514 nm laser and a grating of 1800 lines/mm. Two different spectra were observed on different areas of the polished arsenopyrite coupon surface (Figure 3-S1B). These spectra were identified as quartz and arsenopyrite, using literature and scans of standard samples. The spectra in Figure 3-S1B are from the natural arsenopyrite coupon.
Figure 3-S1. Characterization of natural arsenopyrite samples by XRD (A) and Raman (B) showing a mixture of quartz and arsenopyrite.
**FeAsS Cleaning.** Sieved arsenopyrite samples were sonicated and washed to remove fine arsenopyrite powder from the surface. The samples were then stirred in a 10% HCl bath for two hours to remove any oxidation from the surface. Finally, samples were filtered and washed with ethanol before drying in the anaerobic chamber. Samples were stored in the anaerobic chamber prior to use to prevent re-oxidation. SEM-EDX was used to confirm that this procedure removed detected oxygen from the surface. Flat arsenopyrite coupons were cleaned using acetone, ethanol, and isopropanol prior to use. A clean and uniformly flat surface was confirmed by AFM prior to the experiments (Figure 3-S2).

![Figure 3-S2. Tapping mode AFM image of unreacted arsenopyrite coupon. Height scale: 200 nm.](image-url)
10 mM Sodium Nitrate and Sodium Chloride Batch Reactor Experiments

Four small pieces of flat FeAsS coupon were placed in each batch reactor and removed after 6 hours, 1 day, 4 days, and 7 days. Smaller-scale images (3 micron) in Figure 3.2 showed detailed information on precipitate morphology, while larger images (Figure 3-S3) provided better pictures of overall precipitates coverage and trends during the 7 day reaction period. Larger-scale images were also used to demonstrate the lack of precipitation in anaerobic systems compared to aerobic systems (Figure 3-S4).

Bicarbonate Experiments

The impacts of bicarbonate present in reclaimed water were examined in order to test whether bicarbonate presence could explain observed trends in arsenic mobilization and secondary mineral precipitation for the reclaimed water system. The inorganic carbon (IC) content of reclaimed water was measured to be 2.6 mM. Six-hour room temperature batch reactor experiments and 7-day batch reactor coupon experiments were conducted for systems containing 10 mM sodium nitrate with 3 mM sodium bicarbonate and 7 mM sodium nitrate with 3 mM sodium bicarbonate. The arsenic concentration after 6 hours in both bicarbonate-containing systems was more than twice as high as the concentration in the system containing sodium nitrate only. Since the arsenic concentration in the reclaimed wastewater system was lower than the arsenic concentration in the sodium nitrate system, the presence of bicarbonate in the reclaimed water cannot explain the observed trends, as bicarbonate presence at a comparable concentration should cause an increase in arsenic mobility. This mobility increase may be due to competitive sorption between bicarbonate and arsenate on secondary mineral precipitates. Furthermore, Raman analysis of 7-day reacted coupons in the bicarbonate-containing systems
showed the formation of an amorphous surface layer which was not observed in reclaimed water system after 7 days. Therefore, while the addition of bicarbonate is an important factor which must be investigated further, it may not be the most influential aqueous component impacting the dissolution behavior of arsenopyrite in our reclaimed water system.
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**Figure 3-S3.** Tapping mode AFM Images of reacted FeAsS coupons in 10 mM sodium nitrate or 10 mM sodium chloride. All systems were at pH 7.0 ± 0.2, room temperature, and equilibrated with atmospheric oxygen. Images are 20 × 20 μm and the height scale is 100 nm.
**Figure 3-S4.** Comparison between secondary mineral precipitation in the aerobic and anaerobic systems for 10 mM sodium nitrate and 10 mM sodium chloride. All systems were at pH 7.0 ± 0.2 and room temperature. Images are 20 × 20 μm and the height scale is 100 nm.
Fe\(^{3+}\)-containing Batch Reactor Experiments

\textit{Fe}^{3+} \textit{batch reactor solution preparation}

The reaction medium used for these experiments was 10 mM sodium nitrate or sodium chloride from reagent-grade salts. Ferric nitrate was added to the systems from a stock solution to achieve a concentration of 1.5 \(\mu\)M Fe\(^{3+}\). The stock solution was made immediately prior to reaction to prevent extensive hydrolysis of the ferric nitrate salt.

The pH of the sodium nitrate and sodium chloride solutions was adjusted to 7.0 ± 0.2 using nitric or hydrochloric acid for the sodium nitrate or chloride solutions, respectively. The pH and ionic strength of these solutions were chosen to match values observed both in natural soil solutions and in wastewater samples collected for our previous investigation. All solutions were made fresh for each replicate trial using deionized water.

In order to account for this additional Fe\(^{3+}\), when total quantities of Fe\(^{III}\) were measured using CBD extraction, the quantity of Fe\(^{3+}\) added initially was subtracted from the measured Fe\(^{III}\). The additional Fe\(^{3+}\) accounted for 13\% of the Fe\(^{III}\) formed in the nitrate system and 12\% of the Fe\(^{III}\) formed in the chloride system. Furthermore, after subtracting out the added Fe\(^{3+}\), the precipitated quantities in the nitrate and chloride system were 3.5 and 4.3 times higher, respectively, than the same systems without additional Fe\(^{3+}\).

\textit{Fe}^{3+} \textit{batch reactor setup}

A series of batch reactor experiments were utilized to observe the extents of arsenic mobilization for the different aqueous systems, as well as compare new findings with our previous results. Reactors contained 250 mL of 10 mM sodium nitrate or sodium chloride. First, 0.05 g of
arsenopyrite powder was added before the reactor was stirred. Immediately after the powder was added, 500 μL of 0.75 mM Fe(III) stock solution was added to each reactor. The reactor was then put on the stir plate and the first sample was taken. Aliquots of 2 mL were taken from the reactors at 0, 0.5, 1, 2, 3, 4, 5, and 6 hours. Samples were immediately filtered using a 0.2-μm polytetrafluoroethylene (PTFE) membrane syringe filter, acidified to 2% v/v acid with nitric acid, and capped to prevent evaporative losses. Arsenic concentrations for these samples were then measured using inductively coupled plasma mass spectrometry (ICP-MS) (7500ce, Agilent Technologies, CA). The temperature was controlled at 5, 22, or 35 ± 1 °C using a hot water or ice bath during reaction in order to calculate activation energies (Table 3-S1). These batch experiments were repeated in the anaerobic chamber to determine the effects of dissolved oxygen and the potential for arsenopyrite oxidation by Fe$^{3+}$ in the absence of oxygen. For these systems, deoxygenated deionized water was used to create all solutions. Solutions were created in the chamber and samples were collected and filtered in the chamber.

In order to observe precipitate morphology and phase, flat, polished 1-mm thick arsenopyrite sections, called “coupons”, were utilized. These coupons were prepared by Burnham Petrographics, LLC (Rathdrum, Idaho, USA) from the same arsenopyrite ore as the powder samples. The quality of these coupons was confirmed using atomic force microscopy (AFM, Veeco Inc.) and Raman spectroscopy (inVia Raman Microscope, Renishaw, UK). These thin sections were stored in the anaerobic chamber after creation to prevent surface oxidation. Prior to reaction, coupons were cleaned using acetone, ethanol, and isopropynol to remove any surface organic compounds and rinsed with deionized water. Coupons were added to the batch reactors for the aqueous conditions outlined in the previous section. Coupons were reacted for 4 days, 7 days, 10 days, and 14 days at room temperature (22°C) to observe changes in morphology,
coverage, and phase over a longer time frame (Figure 3-S5). After reaction, coupons were rinsed with deionized water, dried with high purity nitrogen gas, and stored in the anaerobic chamber between analyses to prevent aging of heterogeneous secondary mineral precipitates.

**Solid phase analysis with AFM and Raman**

Coupons were analyzed using tapping mode AFM to observe the height, amplitude, and phase of nanoscale precipitates on the arsenopyrite surface. The tapping mode probes utilized were 125 μm long with phosphorus (n) doped silicon tips (nominal tip radius of 10 nm, MPP-11100-10, Bruker probes). For imaging, a scanning rate of 0.988 Hz and drive frequencies between 312 and 320 kHz were used. Each sample was imaged at multiple points across the surface to confirm observed trends in the coverage. Nanoscope 7.20 software was used to process images.

The phase of secondary mineral precipitates was determined using Raman spectroscopy. Raman measurements were conducted with a 514 nm laser and 1800 lines/min grating. In order to prevent artificial aging of the Fe(III)-containing minerals, a 20x objective and decreased power were utilized. Beam induced phase transformation of maghemite was investigated using our settings (Figure 3-S7). We found that even if the sample was scanned multiple times in the same spot (up to four times), no phase transformation occurred. Thus, no phase transformation is expected to occur during our sample measurement.

The spectra of reacted arsenopyrite samples were compared with standards run on the same instrument in order to identify the secondary mineral phase. Raman spectroscopy was valuable for analyzing the mineral phase in these experiments because it is a surface sensitive technique. Although transmission XAS was attempted on these samples after reaction, it was not able to detect the oxidized iron or arsenic over the signal from the bulk powder.
Quantification of Fe(III) with citrate-bicarbonate-dithionite (CBD) Extraction

The total quantities of Fe\textsuperscript{III} precipitated on the surface of the arsenopyrite powder were quantified using CBD extraction.\textsuperscript{226} This procedure allows us to selectively dissolve Fe\textsuperscript{III} off the surface of the Fe(II)-containing arsenopyrite, allowing us to quantify the amount of oxidized iron (i.e., iron(III)) that has precipitated on the arsenopyrite surface during reaction. This information provides a valuable basis for comparing the extent of iron oxide precipitation under different aqueous conditions. For this procedure, 0.1 g of arsenopyrite powder was placed in a 50 ml centrifuge tube. Next, 20 ml of 0.3 M sodium citrate and 2.5 ml of 1 M sodium bicarbonate solutions were added to the tube and it was immersed in a water bath and brought to 80°C. Once it reached the proper temperature, 1 g of sodium dithionite powder was added to the flask. The solution was stirred continuously for one minutes, and then periodically for 15 minutes. To stimulate flocculation, 5 ml of saturated NaCl solution and 5 ml of acetone was added to the flask. The suspension was mixed in a warm water bath and centrifuged at 2000 rev/min for 30 minutes. Finally, the supernatant was decanted and iron concentrations in the supernatants were measured using ICP-MS. CBD extraction was carried out on arsenopyrite powder reacted for 7 and 14 days in the presence and absence of Fe\textsuperscript{3+} to compare the effects of Fe\textsuperscript{3+} on the total quantity of secondary minerals in these systems.
Figure 3-S5. Additional optical microscope images and Raman spectra for arsenopyrite coupons reacted in batch reactors containing 10 mM sodium nitrate or sodium chloride and 1.5 μM Fe$^{3+}$ over a 14 day period, showing the reemergence of maghemite on the arsenopyrite surface after 10 days of reaction for both the nitrate and chloride systems.
<table>
<thead>
<tr>
<th>Temperature</th>
<th>Amplitude Image</th>
<th>Height Image</th>
<th>Width Distribution</th>
<th>Height Distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td><img src="image" alt="Amplitude" /></td>
<td><img src="image" alt="Height" /></td>
<td><img src="image" alt="Width" /></td>
<td>Avg: 17.8 ± 6.6 nm</td>
</tr>
<tr>
<td>3µm x 3µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35°C</td>
<td><img src="image" alt="Amplitude" /></td>
<td><img src="image" alt="Height" /></td>
<td><img src="image" alt="Width" /></td>
<td>Avg: 49 ± 12.6 nm</td>
</tr>
<tr>
<td>3µm x 3µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45°C</td>
<td><img src="image" alt="Amplitude" /></td>
<td><img src="image" alt="Height" /></td>
<td><img src="image" alt="Width" /></td>
<td>Avg: 65.2 ± 9.9 nm</td>
</tr>
<tr>
<td>3µm x 3µm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3-S6.** Temperature dependence of iron(III) (hydr)oxides on arsenopyrite. Higher temperatures had increased particle growth.

**Figures 3-S7.** Raman spectroscopy of maghemite samples scanned multiple times in the same place. Raman measurements were conducted using a 514 nm laser with an 1800 lines/min grating. A 20x objective and decreased power of 10% were utilized to minimize aging. These settings were also utilized for phase identification. After multiple scans, we saw no change in the iron oxide phase.
Table 3-S1. Calculated activations energies for aerobic systems containing 10 mM sodium nitrate or sodium chloride with and without Fe$^{3+}$. For the anaerobic systems containing Fe$^{3+}$, no temperature trend was observed, thus the activation energies were not able to be calculated.

<table>
<thead>
<tr>
<th>System</th>
<th>With 1.5 μM Fe(III)</th>
<th>Without 1.5 μM Fe(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mM sodium nitrate</td>
<td>49.3 ± 3.8 kJ/mol</td>
<td>40.8 ± 3.5 kJ/mol</td>
</tr>
<tr>
<td>10 mM sodium chloride</td>
<td>53.1 ± 6.5 kJ/mol</td>
<td>36.9 ± 2.3 kJ/mol</td>
</tr>
</tbody>
</table>

Figure 3-S8. Raman spectrum for ferrihydrite
Electrochemical AFM investigation of applied potential on pyrite oxidation in the presence and absence of arsenate

In order to study the effect of ORP, pyrite was utilized rather than arsenopyrite because the presence of quartz in natural arsenopyrite samples insulated the applied current. A potential of 500 mV was chosen because it was the lowest potential where surface morphological changes were observable over our reaction time frame. Solutions contained 10 mM sodium nitrate or 10 mM sodium nitrate and $10^{-5}$ M As(V). Samples were reacted in stagnant batch systems with a volume of 0.1 mL.

Contact mode images in solution were taken after 1 hour and 3 hours of reaction. Figure 3-S7 shows the AFM images and line cuts for the samples in solution. Figure 3-S8 shows the samples imaged with tapping mode after being rinsed and dried.

Figure 3-S7. Electrochemical AFM contact mode images and line cuts for pyrite samples reacted for up to 3 hours under an applied potential of 500 mV.
For pyrite reacted in the presence of 10 mM nitrate only, iron(III) (hydr)oxide precipitates formed with a variety of sizes. For the system with arsenate, precipitates were all uniformly sized and coated the entire surface. Thus, As(V) may promote heterogeneous nucleation on pyrite, while in the absence of As(V), homoepitaxial growth may be preferred. In our outcomes from Chapter 2, we found that heterogeneous precipitates in systems which contain arsenate are less crystalline and contain more water. Thus, we would expect precipitates in the arsenate containing system to be larger, but this was not the case. Therefore, additional mechanisms may be taking place in environments with an applied potential. For example, phase transformation can be electrochemically induced. Changes in morphology for the nitrate only system, such as the aggregation of particles, may be indicative of this phase transformation. Since precipitates which contain arsenate will be less crystalline and more hydrated, phase transformation can be slowed.

Figure 3-S8. Tapping mode images and line cuts for samples reacted using ECAFM
Chapter 4: Macroscale: Applying scientific findings to arsenic reactive transport modeling in larger scale model MAR systems

4.1. Overview

Chapters 1 and 2 provide important knowledge about the fundamental science behind arsenic mobilization under MAR conditions. However, predicting arsenic mobility at MAR sites will be further complicated by site-specific factors such as aquifer mineralogy, aquifer hydrology, and various MAR operating parameters, including injection rates and durations. A better understanding of these factors and how they will influence arsenic mobilization and attenuation processes is vital in developing safer and more sustainable MAR operations. Therefore, while previous tasks focused on using controlled parameters to examine nanoscale and microscale geochemical processes, the final task will focus on applying our scientific findings to larger scale experiments which better mimic MAR operations.

For this study, column reactors packed with a mixture of arsenopyrite and acid washed sand were used to mimic arsenic transport in groundwater aquifers. Arsenic concentrations were monitored from ports at different distances along the column over the course of 30 days. After reaction, samples were taken from each port and sequential extraction was used to compare iron and arsenic mineralogy at different distances and between different aqueous systems.

Next, reactive transport modeling was used to simulate the soil column system. Activation energies calculated in Chapter 3 were incorporated into the model to provide a better estimation of arsenic mobility in these systems. While good agreement was observed between empirical
arsenic concentrations and model values using the calculated activation energies, improvement is still needed to better model arsenic association with secondary mineral phases.

4.2. Introduction

Systematic investigation of nano- and microscale arsenopyrite dissolution and secondary mineral precipitation processes, as carried out in Chapters 1 and 2, provides a strong scientific basis for exploring and understanding arsenic mobilization in larger scale column reactor systems. However, for these larger scale systems, additional factors must be considered. For example, due to vertical zoning in column reactors, the water chemistry can vary with distance from the injection port, an effect that has also been observed in MAR field sites. Thus, these systems provide a better model of how geochemical reactions can change with distance from the secondary water injection well. In accordance with these zoning effects, we can expect that close to the injection port of the column, water will be oxygen-rich, resulting in the formation of arsenopyrite oxidation products such as hematite and maghemite, while further down the column oxygen can become depleted due to oxidation reactions, resulting in less arsenopyrite oxidation and less secondary mineral precipitation.

The soil column reactor set-up is also a particularly good model for MAR in the case of Aquifer Storage, Transfer, and Recovery (ASTR), an MAR method wherein secondary water is injected into one well and recovered downstream to facilitate soil–aquifer treatment. This process allows for extended interactions between the injected water and aquifer formation minerals, which can help cleanse reclaimed wastewater used as the secondary water source. However, these interactions can also lead to arsenic mobilization as previously described. By characterizing arsenic mobility and secondary mineral phase formation along different lengths of the column, we can gain insight into the role these secondary minerals play in attenuating
arsenic. A better understanding of this system can help inform MAR field site design aspects, such as distances between wells and injection rates, to allow sufficient time for secondary mineral precipitation and arsenic attenuation, minimizing the risk for arsenic contamination in recovered water.

In addition, column reactors have increased reaction times which better mimic MAR systems. These increased times can greatly influence secondary mineral precipitation, and in turn affect arsenic mobility. For example, the aging of ferrihydrite leads to the formation of more stable iron(III) oxide minerals such as hematite and maghemite, irreversibly immobilizing arsenic sorbed prior to phase transformation. These mineral transformations are expected to occur at MAR sites, where dissolved oxygen in known to persist for months after secondary water injection. In addition, the identity of secondary mineral phases can be directly related to the local water chemistry. For example, previous studies have shown that arsenic-containing minerals such as scorodite (FeAsO$_4$$\cdot$2H$_2$O) can form during arsenopyrite oxidation at near neutral pH, while acidic or reducing conditions can transform arsenopyrite into realgar (α-As$_4$S$_4$) or orpiment (As$_2$S$_3$). These minerals have very different reactivities and release arsenic under different aqueous conditions. Thus, it is important to determine whether arsenic is associated with less crystalline or more crystalline phases, and to ascertain the conditions under which arsenic can be mobilized from its associated phases.

Lastly, we must scale up laboratory findings to time frames and transport distances expected to occur at MAR field sites. Reactive transport modeling is one powerful tool that can be used to couple the physical and geochemical processes occurring at MAR sites to predict the risk of arsenic groundwater contamination. However, many uncertainties can compromise the outcomes of these reactive transport models (RTMs). For example, Maher et al. found that
calculated dissolution rate constants from their model were $10^2$ to $10^5$ times smaller than the experimentally measured values. This discrepancy was attributed to differences in reactivity on the mineral surface compared to the bulk mineral, and the authors suggested that direct measurement of the surface reactivity is needed to accurately predict mineral dissolution rates. Nitzsche et al.\textsuperscript{254} also found prediction uncertainty in their model as a result of uncertainty in their thermodynamic database.

For the current study, arsenopyrite dissolution was monitored over 30 days in a soil column containing acid washed sand. Aqueous samples were taken daily from sampling ports along the distance of the column and measured for arsenic concentration. Following reaction, soil samples were taken from each port and analyzed using sequential extraction for iron mineralogy and associated quantities of arsenic. Then, reactive transport modeling, which incorporated empirical values, was used to predict arsenic concentrations and secondary mineral precipitation extents. These values were compared with experimental soil column outcomes, and recommendations were made to improve the accuracy of the model.

4.3. Experimental approach

4.3.1. Materials and chemicals

Column reactors were packed with a mixture of 300-500 µm arsenopyrite, prepared and cleaned as described in Chapter 3, and sand. Sand was acid washed by
soaking it in an acid bath at pH 1 for 24 hours. After thoroughly rinsing with DI water, the sand was analyzed using X-ray diffraction (XRD, Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ=1.5418 Å)) (Figure 4.1). The sand was found to be primarily quartz (SiO₂) with small quantities of albite (NaAlSi₃O₈) and microcline (KAlSi₃O₈). As described in Chapter 2, quartz is a widely abundant mineral which can be found in many groundwater aquifers. Additional testing was also carried out for a shortened reaction period (1 week) using a soil sample which contained quartz and dolomite. These results can be found in the Supporting Information (SI).

10 mM sodium nitrate and 10 mM sodium chloride were used separately as the influent solutions for the column. All solutions were created using reagent grade salts and ultrapure water (resistivity > 18.2 MΩ·cm). The pH was adjusted to pH 7 in order to mimic reclaimed water samples and link our findings to previous experiments (Chapter 3).

4.3.2. Soil column set up

A 60 cm tall column reactor was built using polyvinyl chloride piping (1-1/2” I.D.). Figure 4.2 presents a schematic of this column. Five sampling ports were placed at 15 cm intervals along the column length.
Influent was pumped into the bottom of the column and effluent was collected from the top. The ratio of arsenopyrite to sand in the column was chosen to be 1 g/kg, a value higher than values generally seen in natural sediment. The average arsenic abundance in crustal rock is 1.5 mg/kg. Concentrations as high as 20-200 mg/kg have been measured in sulphide-rich shales, phosphatic rocks, and coal,\(^{117}\) while igneous and metamorphic rocks and carbonate minerals have measured concentrations in the range of 1-10 mg/kg.\(^ {256}\) The elevated concentration in our experiments was chosen to yield measurable concentrations of arsenic at steady state.

The porosity of the soil column was measured to be 0.260, using water displacement.\(^ {257}\) The flow rate was chosen to be 2.5 mL/min, giving the column a linear flow rate of \(~3.3\) cm/hours. This flow rate is generally faster than the rate for groundwater aquifers, though these rates can vary significantly. However, the flow rate is within the range for laboratory flow rates used in groundwater studies, which can range from \(0.1 - 14\) cm/hr.\(^ {258-260}\)

Over the course of the 30 day reaction period, 10 mL samples were taken daily from the five sampling ports. The pH, DO, and ORP were measured and then the sample was acidified. After 30 days of reaction, the samples were measured for arsenic and iron, using ICP-MS. However, because iron concentrations were all below the detection limit for the instrument, only arsenic concentrations are reported. Duplicate columns were run for the sodium nitrate and sodium chloride systems. Immediately after the 30\(^{th}\) day of reaction, the column was disassembled and soil samples were removed from each port. The samples were dried overnight in a desiccator, and sequential extraction was carried out on samples to determine the iron mineralogy and associated arsenic.
4.3.3. Sequential extraction method

A sequential extraction method, established by Jang et al., was used to quantify the fractions of iron and arsenic associated with different minerals or attenuation mechanisms. Table 4.1 shows the different steps for the sequential extraction, which was performed on 2.5 g of soil from each port. Between each step, samples were centrifuged for 10 minutes at 5000 RPM to separate the solids from the supernatant. The supernatant was then poured off and filtered using a 0.2 μm syringe filter to ensure that no particles remained. Aqueous samples were acidified to 1% v/v nitric acid, and iron and arsenic concentrations were measured using inductively coupled plasma-optical emission spectrometry (PerkinElmer Optima 7300DV ICP-OES). ICP-OES was used rather than ICP-MS due to the high salt concentrations in aqueous samples from the sequential extraction technique. The reported values for iron and arsenic percentages, with standard errors, were averaged from duplicate trials. Values for iron and arsenic quantities in mg/kg of soil can be found in Tables 4-S1 and 4-S2 in the SI. Table 4-S3 in the SI gives the sequential extraction results for unreacted soil and arsenopyrite.

Table 4.1. Sequential extraction procedure adapted from Jang et al.

<table>
<thead>
<tr>
<th>Step</th>
<th>Fractions</th>
<th>Extraction Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Soluble</td>
<td>0.2 M KCl (25 ml), stirring time (ST) (2 hours)</td>
</tr>
<tr>
<td>2</td>
<td>Adsorbed</td>
<td>0.1 M Na₂HPO₄ (25 ml, pH 8.0), ST (20 h)</td>
</tr>
<tr>
<td>3</td>
<td>Carbonate</td>
<td>1 M CH₃COONa (25 ml), ST (5 h), then 0.1 M Na₂HPO₄ (25 ml, pH 8.0), ST (20 h)</td>
</tr>
<tr>
<td>4</td>
<td>Organic matter</td>
<td>5% NaOCl (10 ml, pH 9.5) then heating at 70 ± 0.5 C, ST (30 min)</td>
</tr>
<tr>
<td>5</td>
<td>Easily reducible oxides</td>
<td>0.1 M NH₂OH (25 ml, pH 2.0), ST (30 min), then 0.1 M KOH (25 ml), ST (20 h)</td>
</tr>
<tr>
<td>6</td>
<td>Amorphous oxides</td>
<td>0.25 M NH₂OH/HCl (25 ml, 50 ± 0.5 C), ST (30 min), then 0.1 M KOH (25 ml), ST (20 h)</td>
</tr>
<tr>
<td>7</td>
<td>Crystalline minerals</td>
<td>Aqua regia [30 ml HCl (35-38%) and 10 ml HNO₃ (68-70%)], ST (1 h)</td>
</tr>
</tbody>
</table>
4.3.4. CrunchFlow modeling

Reactive transport modeling was carried out using CrunchFlow, a multicomponent reactive transport software. This software is specifically designed for efficient modeling and simulation of reactive flow and transport through porous media such as groundwater aquifers, soils, and sediments. CrunchFlow has been developed over about 20 years by Dr. Carl Steefel at Lawrence Berkeley National Laboratory. Many features of the software make it especially suited for modeling arsenic mobilization during MAR, including the incorporation of kinetically-controlled mineral precipitation and dissolution, multicomponent ion exchange on multiple sites, and multicomponent surface complexation based on the Dzombak and Morel double layer model, with site densities that are linked to evolving mineral concentrations.

To model our system, a number of assumptions were made for simplicity. First, it was assumed that ferrihydrite was the primary secondary mineral to form. Ferrihydrite was chosen because of its high sorption capacity for arsenic and because it is a precursor of more crystalline iron(III) (hydr)oxide secondary mineral phases. The pH was fixed at 7.0, and dissolved oxygen and CO₂ values were calculated to be at equilibrium with the atmosphere. Nitrate or chloride concentrations were set at 10 mM, and sodium concentrations were calculated using charge balance, since pH was primarily adjusted with NaOH. The redox conversion between As(III) and As(V) oxidation states was included in the modeling program.

Surface complexation constants for arsenic sorption onto iron hydroxide surface sites were taken from the literature, and these values can be found in Table 4.2. Ferrihydrite contains two sorption sites with different affinities: strong sites, which exist at a concentration of 0.005 mol/mol Fe, and weak sites, which exist at a concentration of 0.2 mol/mol Fe. Arsenic is assumed to be primarily associated with the more abundant weak sites. Arsenopyrite dissolution
was modeled using the activation energies and rate constants calculated in Chapter 3 for 10 mM sodium nitrate and 10 mM sodium chloride systems. Additional modeling parameters can be found in the SI.

4.4. Results and Conclusions

4.4.1. Arsenic mobility in soil columns differs for nitrate and chloride systems

The concentration evolution of arsenic in the soil column can be found in Figure 4.3. For both systems, arsenic concentration increased along the length of the column. This finding indicates that arsenic is being mobilized from the column, and that it is not being attenuated at a

<table>
<thead>
<tr>
<th>As complexation</th>
<th>Log(K) at 25°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;FeOH_weak + AsO\textsubscript{4}\textsuperscript{3-}+3H\textsuperscript{+}</td>
<td>29.31</td>
<td>Dzombak and Morel (1990)</td>
</tr>
<tr>
<td>&gt;FeOH_weak + AsO\textsubscript{4}\textsuperscript{3-}+2H\textsuperscript{+}</td>
<td>23.51</td>
<td>Dzombak and Morel (1990)</td>
</tr>
<tr>
<td>&gt;FeOH_weak + AsO\textsubscript{4}\textsuperscript{3-}</td>
<td>10.58</td>
<td>Dzombak and Morel (1990)</td>
</tr>
<tr>
<td>&gt;FeOH_weak + As(OH)\textsubscript{3}</td>
<td>5.41</td>
<td>Dzombak and Morel (1990)</td>
</tr>
</tbody>
</table>

The concentration evolution of arsenic in the soil column can be found in Figure 4.3. For both systems, arsenic concentration increased along the length of the column. This finding indicates that arsenic is being mobilized from the column, and that it is not being attenuated at a

**Figure 4.3. Arsenic mobility in nitrate (A) and chloride (B) soil columns**
rate which could prevent the accumulation of arsenic with distance along the column. For the nitrate system, a steady state concentration of $0.126 \pm 0.042 \mu M$ was reached after 8 days. For the chloride system, the steady state concentration was $0.095 \pm 0.020 \mu M$, reached after 9 days.

Although arsenic mobilization was higher in chloride systems for batch arsenopyrite dissolution (Chapter 3) compared to nitrate systems, for the sodium chloride column experiment, the mobile arsenic concentration was slightly lower. This reversal could stem from the formation of concentration gradients of dissolved oxygen in the column. As shown in Section 3.4.1, although arsenic mobilization was highest in the chloride system under aerobic conditions, under anaerobic conditions, the mobilization was highest in the nitrate system. Thus, if there are regions within the soil column where dissolved oxygen is depleted, these regions may still undergo arsenopyrite oxidation by nitrate, whereas in the chloride system, arsenic mobilization will be limited. Dissolved oxygen, pH, and ORP were measured for samples taken from Ports 1-5 over the reaction period, but no definitive trends were observed (Figure 4-S3 and 4-S4).

Table 4.3. Sequential extraction results for iron in the sodium nitrate (A) and sodium chloride (B) columns.

<table>
<thead>
<tr>
<th>Iron (%)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.31 ± 0.01</td>
<td>0.43 ± 0.28</td>
<td>0.1 ± 0.01</td>
<td>0.2 ± 0.33</td>
<td>0.31 ± 0.39</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.5 ± 0.61</td>
<td>0.85 ± 0.92</td>
<td>0.43 ± 0.11</td>
<td>0.55 ± 0.68</td>
<td>0.4 ± 0.55</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td>0.01 ± 0.01</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>0.19 ± 1.15</td>
<td>0.27 ± 2.51</td>
<td>1.66 ± 3.85</td>
<td>1.18 ± 3.43</td>
<td>0.58 ± 3.58</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>0.77 ± 2.34</td>
<td>0.27 ± 3.21</td>
<td>1.66 ± 1.85</td>
<td>1.18 ± 3.43</td>
<td>0.58 ± 3.58</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Iron (%)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.01 ± 0.01</td>
<td>0.02 ± 0.02</td>
<td>0.03 ± 0.02</td>
<td>0.02 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.06 ± 0.2</td>
<td>0.05 ± 0.3</td>
<td>0.15 ± 0.28</td>
<td>0.15 ± 0.28</td>
<td>0.15 ± 0.28</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.15 ± 0.22</td>
<td>0.09 ± 0.15</td>
<td>0.33 ± 0.29</td>
<td>0.88 ± 1.06</td>
<td>0.46 ± 0.51</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.01 ± 0.01</td>
<td>0.08 ± 0.10</td>
<td>0.03 ± 0.02</td>
<td>0.03 ± 0.02</td>
<td>0.02 ± 0.02</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>1.23 ± 1.17</td>
<td>0.74 ± 0.69</td>
<td>0.3 ± 0.68</td>
<td>0.74 ± 0.83</td>
<td>0.45 ± 1.12</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>1.47 ± 2.36</td>
<td>0.91 ± 1.33</td>
<td>1.22 ± 1.27</td>
<td>0.45 ± 1.12</td>
<td>0.45 ± 1.12</td>
</tr>
</tbody>
</table>
aqueous samples were taken from close to the injection port and measured in the atmosphere, so oxygen could have been introduced.

Sequential extraction results are reported in Tables 4.3A and 4.3B for iron distribution in the nitrate and chloride systems, respectively. Arsenic distributions are reported in Table 4.4A for the nitrate column and 4.4B for the chloride column. Results in mg/kg are reported in Table 4-S1 and 4-S2 in the SI. The cross bars in Tables 4.3 and 4.4 indicate samples where the iron or arsenic concentrations were below the detection limit. These distributions indicate the quantities of arsenic and iron in each phase which is in excess of the values measured for unreacted soil and arsenopyrite. For both the nitrate and chloride systems, the majority of the excess iron exists primarily in crystalline mineral phases. This is not a surprising result, as not only are significant quantities of arsenopyrite expected to remain in the soil, but also crystalline iron(III) oxide secondary mineral phases such as hematite and maghemite are known to form within 7 days of reaction, as seen in the outcomes of Chapter 3. Thus, it is difficult to distinguish the mineral phase using this

### Table 4.4. Sequential extraction results for arsenic in the sodium nitrate (A) and sodium chloride (B) columns.

#### A. 10 mM sodium nitrate column

<table>
<thead>
<tr>
<th>Arsenic (%)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.06 ± 0.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.04 ± 0.05</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.10 ± 0.14</td>
<td>0.17 ± 0.33</td>
<td>0.02 ± 0.14</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### B. 10 mM sodium chloride column

<table>
<thead>
<tr>
<th>Arsenic (%)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.36 ± 0.28</td>
<td>0.23 ± 0.60</td>
<td>0.62 ± 0.36</td>
<td>0.3 ± 0.64</td>
<td></td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.24 ± 0.02</td>
<td>0.42 ± 0.59</td>
<td>0.29 ± 0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.20 ± 0.15</td>
<td>0.29 ± 0.14</td>
<td>0.31 ± 0.09</td>
<td>0.40 ± 0.08</td>
<td></td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>0.59 ± 4.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>8.03 ± 8.87</td>
<td>17.85 ± 8.51</td>
<td>20.7 ± 7.13</td>
<td>24.89 ± 11.95</td>
<td>27.16 ± 8.11</td>
</tr>
</tbody>
</table>
sequential extraction method, and further testing, such as HRXRD and XAS, is needed to differentiate between different iron(III) oxide polymorphs, and between secondary minerals and arsenopyrite. However, large quantities of precipitates are necessary to detect secondary minerals over bulk arsenopyrite using these techniques. This is a good potential future measurement.

Arsenic in the nitrate and chloride systems was also primarily associated with crystalline mineral phases (Table 4.4A and 4.4B). This may be due to the sorption of arsenic onto less crystalline phases and subsequent phase transformation, incorporating arsenic into crystalline iron oxides. Furthermore, the percentages of arsenic-associated with crystalline minerals were increased further down the column, with the highest percentages at Port 5. This may result from the dissolution of arsenopyrite closer to the injection port, where oxygen levels should be highest, and subsequent arsenic transport toward the top of the column (e.g., Ports 4 and 5), before being incorporated into iron(III) (hydr)oxide precipitates and undergoing phase transformation to become more permanently sequestered in crystalline iron(III) oxide phases.

Next, CrunchFlow modeling was used to simulate arsenic concentrations at Ports 1-5 over the course of the 30 days of reaction. Quantities of precipitated ferrihydrite and associated arsenic were also calculated from the model and compared with empirically determined values to test the model validity.

4.4.2. CrunchFlow provides estimates of arsenic mobilization and secondary mineral precipitation

Reaction rates and activation energies were obtained from experiments described in Chapter 3. Rate constants for arsenic mobilization from arsenopyrite in the 10 mM sodium nitrate and 10 mM sodium chloride systems were incorporated into CrunchFlow reactive transport software\textsuperscript{264}
and used to model arsenopyrite dissolution and secondary mineral precipitation in the soil column. Additional rate constants and sorption coefficients were sourced from the database and literature, as described in Section 4.3.4.

Figure 4.4 shows the model prediction for the arsenic concentration evolution at our five port distances over the 30 day reaction period for the nitrate and chloride systems. For both the nitrate and chloride systems, the model required approximately 4 days to reach steady state. In addition, the large initial spike in arsenic concentration observed in the experiments was not simulated in either model system. This spike is likely due to the fast dissolution of smaller sized arsenopyrite particles which may remain adhered on the surface of the 300–500 µm arsenopyrite, despite sonication and acid washing. Because the early transient dissolution spike related to small particles is not possible to simulate without including an arsenopyrite crystal size distribution, it was not included in the comparison between experimental and model system results. Instead, the steady state concentrations of arsenic in both systems were compared.

For the simulated nitrate system, the maximum steady state arsenic concentration was 0.29

![Figure 4.4. CrunchFlow prediction of arsenic mobilization for the 10 mM sodium nitrate (A) and 10 mM sodium chloride (B) soil columns](image-url)
μM at Port 5. For the chloride system modeling results, the maximum steady state arsenic concentration at Port 5 was 0.46 μM. While the trends for both systems matched the experimental results relatively closely with regard to increasing arsenic concentration along the column distance, these maximum concentrations are higher than those observed in experimental systems (0.126 ± 0.042 μM and 0.095 ± 0.020 μM for the nitrate and chloride systems, respectively). In addition, the arsenic concentration for the nitrate model was lower than for the chloride model, while in the experimental systems, the arsenic concentration was higher for the nitrate system.

One possible reason for this discrepancy is the passivation of the arsenopyrite surface due to secondary mineral precipitation with longer reaction times, which is not captured in the model. Activation energies were calculated for the first 6 hours of reaction, over which time precipitation on the surface was minimal. However, as shown in Chapter 3, after 7 days of reaction, much of the arsenopyrite surface

### Table 4.5. Iron and arsenic mineralogy from CrunchFlow modeling

#### A. 10 mM sodium nitrate column model

<table>
<thead>
<tr>
<th>Location</th>
<th>Iron (wt%)</th>
<th>Arsenic (mol/g Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
<td>Measured</td>
</tr>
<tr>
<td>Port 1</td>
<td>0.00103</td>
<td>0.77 ± 2.34</td>
</tr>
<tr>
<td>Port 2</td>
<td>0.00225</td>
<td>0.27 ± 3.21</td>
</tr>
<tr>
<td>Port 3</td>
<td>0.00225</td>
<td>1.66 ± 1.85</td>
</tr>
<tr>
<td>Port 4</td>
<td>0.00225</td>
<td>1.18 ± 3.43</td>
</tr>
<tr>
<td>Port 5</td>
<td>0.00225</td>
<td>0.58 ± 3.58</td>
</tr>
</tbody>
</table>

#### B. 10 mM sodium chloride column model

<table>
<thead>
<tr>
<th>Location</th>
<th>Iron (wt%)</th>
<th>Arsenic (mol/g Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Model</td>
<td>Measured</td>
</tr>
<tr>
<td>Port 1</td>
<td>0.00107</td>
<td>1.47 ± 2.36</td>
</tr>
<tr>
<td>Port 2</td>
<td>0.00228</td>
<td>0.91 ± 1.33</td>
</tr>
<tr>
<td>Port 3</td>
<td>0.00228</td>
<td>1.22 ± 1.27</td>
</tr>
<tr>
<td>Port 4</td>
<td>0.00228</td>
<td>0.45 ± 1.12</td>
</tr>
<tr>
<td>Port 5</td>
<td>0.00228</td>
<td>0.45 ± 1.12</td>
</tr>
</tbody>
</table>
was coated by iron(III) oxide secondary mineral precipitates. Furthermore, for the chloride system, a more rapid mineral phase transformation to hematite was observed. As observed in AFM images, secondary precipitates in the chloride system formed a layer-like structure on the surface (Figure 3.2 in Chapter 3). Although the more crystalline minerals in the chloride system have less capacity for arsenic sorption, their patchy crystalline morphology may also act as a diffusion barrier, preventing further oxidation and dissolution of arsenopyrite. Thus, although higher concentrations would be expected for the chloride system based on the activation energy and reaction rate calculated over the 6-hour reaction time frame, for time frames larger than 7 days, mobilization may be less in this system, as was observed in soil column experiments. It is important that future models account for secondary mineral formation and phase transformation with regard to its role as a diffusion barrier.

Next, secondary mineral precipitation in the simulations was compared to that in the experimental system (Table 4.5). For the model systems, ferrihydrite was assumed to be the dominant secondary mineral for arsenic attenuation. The quantities of ferrihydrite calculated in the model were compared with the increased iron-containing crystalline mineral phase measured using sequential extraction. Although this phase is not amorphous or poorly-crystalline, as ferrihydrite is, our model did not consider phase transformation. Therefore, this value is the best indication of secondary mineral formation because iron quantities were elevated compared to the unreacted soil/FeAsS samples. CrunchFlow modeling output gave the weight percent of ferrihydrite formed at different distances along the column, which is shown in Table 4.5.

For arsenic, CrunchFlow modeling gave the total concentration of arsenic surface complexes in moles per gram of solid. These values were converted into moles per gram ferrihydrite using the mass fraction of ferrihydrite from the model. For the experimental system, the arsenic
concentration was calculated in moles per gram of iron-containing secondary mineral phase using the percentages of iron and arsenic measured by sequential extraction for crystalline phases, where concentration levels were increased compared to the unreacted samples. These values gave the empirical quantities of arsenic associated with the secondary minerals. However, these calculations were made assuming a molecular volume for ferrihydrite which may differ from experimental values due to differences in the crystalline nature of secondary mineral precipitates. This assumption may be one source of error in our values.

Tables 4.5A and B present the CrunchFlow modeling and experimental results for the 10 mM sodium nitrate and 10 mM sodium chloride systems. We found that both the experimental iron percentage and experimental associated arsenic amounts were higher than the values calculated using our model by several orders of magnitude. Although this discrepancy is much larger than the discrepancy between the modeled and experimentally measured aqueous arsenic concentrations, the values of iron and arsenic associated with solid phases are much smaller than the aqueous arsenic concentration. Thus, small changes in the measured or modelled iron and arsenic solid phase quantities can lead to large errors while not greatly impacting the aqueous arsenic concentration.

One potential issue which may contribute to this discrepancy is the large error associated with the experimental iron percentage. Within this error, measured values could potentially be as low as modelled values. In addition, this percentage may consist of other crystalline mineral phases in addition to ferrihydrite, which was the only phase incorporated into the model. One possible cause for the inconsistency in arsenic measurements is that arsenic may be co-precipitating with ferrihydrite in addition to complexing with the mineral surface. For example, if precipitates in this system contained 8.1 mol% arsenic, similar to the Fe-As co-precipitates
analyzed in Chapter 1, this incorporated arsenic would contribute an additional 0.00048 moles of arsenic per gram of ferrihydrite. Furthermore, we know from our findings in Chapter 1 that the presence of arsenic will decrease the crystallinity of iron(III) (hydr)oxides. This effect can in turn increase their reactive surface area and lead to more sorption than predicted by the model. The discrepancies in attenuated arsenic quantities may also be a reason for the higher aqueous arsenic concentrations observed in the model compared with experimental observations.

4.5. Environmental implications

Soil column experiments give insight into the dominant reactions expected to occur at MAR sites, which will influence the overall risk for arsenic mobility. For the sodium nitrate and sodium chloride systems, it was found that dissolved arsenic concentrations increased with increasing distance from the injection port. We also observed that mobilization was slightly lower for the sodium chloride system at steady state than for the sodium nitrate system. Dissolved oxygen gradients may have formed in the column, where nitrate can still oxidize arsenopyrite in the absence of dissolved oxygen. Furthermore, over time, passivation of the arsenopyrite surface in the sodium chloride system may have occurred, because the formation of more crystalline minerals will act as a barrier to dissolution.

Reactive transport modeling outcomes indicate that by utilizing experimentally determined reaction rates for arsenic mobilization in the sodium nitrate and sodium chloride systems, prediction of arsenic mobilization can be achieved within the same order of magnitude as observed values. However, the model must be improved with regard to its prediction of iron precipitation and arsenic attenuation by mechanisms other than sorption, such as co-precipitation. Better prediction of secondary mineral formation can also be accomplished by incorporating empirically determined nucleation rates, such as those measured using in situ
GISAXS in Chapter 1. Physicochemical characteristics of the Fe-As co-precipitates, such as surface area, must be incorporated into future models for better prediction of arsenic sorption. In addition, sorption can be influenced by arsenic speciation.\textsuperscript{133, 265, 266} It is important in the future to characterize the speciation of the arsenic in the column reactors and ensure that it matches the modelled speciation. Lastly, to prevent underestimation of arsenic mobilization, secondary mineral phase transformation and the potential impacts of heterogeneous crystalline secondary minerals on arsenopyrite dissolution must be fully explored and included in the model.

By improving these attenuation mechanisms and incorporating effects such as arsenopyrite surface passivation, mobile arsenic concentrations in the model can better reflect the lower values seen in the experimental systems. The further development of accurate RTMs of arsenic mobilization will be vital for scaling up laboratory findings to pilot scale MAR operations.

4.6. Acknowledgments

We are grateful for support received from Washington University’s Faculty Startup and the National Science Foundation (EAR-1424927). CWN acknowledges the generous support of the Mr. and Mrs. Spencer T. Olin Fellowship. We wish to thank Environmental NanoChemistry Group members for valuable discussion. We are also grateful to Dr. Carl Steefel for his mentorship on the use of CrunchFlow and his continued input and suggestions regarding the application and improvement of the model.
4.7. Supporting information for Chapter 4

Contents: Experimental details

4 figures (4-S1 – 4-S4)

2 tables (4-S1-4-S2)

Investigation of the effects of soil mineralogy

Preliminary experiments were conducted which used a soil column containing a mixture of dolomite and quartz. These results give some insight into how the presence of carbonate minerals in groundwater aquifers can impact arsenic mobilization. Results for aqueous arsenic mobility tests over a 7 day reaction period can be found in Figure 4-S1A. The arsenic concentration was much lower for the system with dolomite present, particularly during the initial spike which was observed for experimental systems. Furthermore, calcium and magnesium concentration evolutions show a high spike over the initial days of reaction.

Figure 4-S1. As, Ca, and Mg concentration evolutions in soil column containing dolomite
The high spike in dissolved calcium and magnesium ions due to dolomite dissolution can cause decreased arsenic mobility. Arsenic is known to sorb on calcium and magnesium solids such as CaCO$_3$ and Mg(OH)$_2$. In addition, aqueous Ca$^{2+}$ and Mg$^{2+}$ cations have been shown to increase arsenic sorption. This occurs because Ca$^{2+}$ and Mg$^{2+}$ cations can form outer sphere complexes with iron(III) (hydr)oxide secondary mineral precipitates, increasing their surface charge and promoting the sorption of negatively charged arsenic anions.

These preliminary results indicate that the site-specific mineralogy will be an important factor to consider when predicting arsenic mobility during MAR operation. Calcium and magnesium carbonate minerals in particular can be widely present in groundwater aquifers.

**Additional soil column experimental results**

The pH, DO, and ORP were measured over the 30 day reaction period for the 10 mM sodium nitrate and 10 mM sodium chloride soil columns in the study. While the system which contained dolomite had an increase in pH over the 7 day reaction period (Figure 4-S2A), this trend was not seen for the soil column which contained quartz and aluminosilicates. When carbonate minerals dissolve, aqueous CO$_3^{2-}$ can interact with and neutralize H$^+$, forming HCO$_3^-$ and increasing the
pH. Thus, this trend was likely not seen because carbonate minerals were not present. Instead, the pH remained close to 7 over the course of the 30 days reaction, while DO fluctuated between 4 and 8 mg/L and the ORP fluctuated between 100 and 250 mV. The lack of definitive trends for DO and ORP could be because samples were taken near the port and were exposed to oxygen during measurement. These trends can be seen in Figures 4-S3 for the sodium nitrate system and Figure 4-S4 for the sodium chloride system.

**Figure 4-S3.** pH, DO, and ORP evolutions for the 10 mM sodium nitrate system

**Figure 4-S4.** pH, DO, and ORP evolutions for the 10 mM sodium chloride system
Additional modeling parameters

The following parameters were used for CrunchFlow modeling.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Initial volume fraction</th>
<th>Surface area</th>
<th>LogK_{sp} for dissolution (from literature unless otherwise noted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albite</td>
<td>0.05</td>
<td>100 m$^2$/m$^3$ porous media</td>
<td>-12.6</td>
</tr>
<tr>
<td>Quartz</td>
<td>0.89</td>
<td>100 m$^2$/m$^3$ porous media</td>
<td>-13.39</td>
</tr>
<tr>
<td>K-Feldspar</td>
<td>0.05</td>
<td>100 m$^2$/m$^3$ porous media</td>
<td>-12.85</td>
</tr>
<tr>
<td>Arsenopyrite</td>
<td>0.01</td>
<td>0.335 m$^2$/g (measured, approximate)</td>
<td>-6.778 (calculated using empirical data)</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>--</td>
<td>200 m$^2$/g (from literature$^{102}$)</td>
<td>-5.30</td>
</tr>
</tbody>
</table>

| Temperature   | 25°C (room temperature) |
| pH            | 7 (controlled parameter) |
| HCO$_3^-$     | Equilibrated with atmosphere ($P_{CO_2} = 3.15 \times 10^{-4}$) |
| O$_2$(aq)     | Equilibrated with atmosphere ($P_{O_2} = 0.21$) |
| NO$_3^-$ (or Cl$^-$) | 0.01 M |
| Na$^+$        | Calculated using charge balance |
| Porosity      | 0.260 (measured, fixed) |
| Flow rate     | 3.29 cm/hr (controlled parameter) |

Sequential extraction results in mg/kg

Iron and arsenic mineralogy were also calculated in mg Fe/kg soil. These values were not used for comparison between systems because soil samples had variations in the total quantities,
which may result from samples containing different amounts of arsenopyrite. However, the
distribution in percent iron and arsenic for these systems was consistent for different mg/kg
ratios, as reported in the main text. The contribution of unreacted arsenopyrite and sand was also
unable to be subtracted from Tables 4-S1 and 4-S2 due to these variations.

Table 4-S1. Iron and arsenic mineralogy in mg/kg for duplicate nitrate column experiments

<table>
<thead>
<tr>
<th>Iron (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>Sorbed</td>
<td>11.80</td>
<td>12.50</td>
<td>10.16</td>
<td>6.30</td>
<td>5.08</td>
</tr>
<tr>
<td>Carbonate</td>
<td>6.05</td>
<td>10.47</td>
<td>16.15</td>
<td>7.10</td>
<td>3.74</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>37.04</td>
<td>40.63</td>
<td>39.27</td>
<td>32.56</td>
<td>24.01</td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>39.98</td>
<td>48.58</td>
<td>46.60</td>
<td>38.90</td>
<td>29.21</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>1732.3</td>
<td>2128.0</td>
<td>2275.5</td>
<td>2067.7</td>
<td>1342.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Arsenic (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.51</td>
<td>0.76</td>
<td>0.33</td>
<td>0.30</td>
<td>0.18</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.00</td>
<td>0.15</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.24</td>
<td>0.12</td>
<td>0.29</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>11.94</td>
<td>17.57</td>
<td>2.20</td>
<td>12.59</td>
<td>4.88</td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>1.61</td>
<td>2.04</td>
<td>0.39</td>
<td>1.38</td>
<td>0.68</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>136.13</td>
<td>200.01</td>
<td>61.66</td>
<td>104.48</td>
<td>60.52</td>
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<table>
<thead>
<tr>
<th>Iron (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.04</td>
<td>0.05</td>
<td>0.06</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Sorbed</td>
<td>4.81</td>
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<td>5.53</td>
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<td>Carbonate</td>
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</tr>
<tr>
<td>Organic matter</td>
<td>0.03</td>
<td>0.02</td>
<td>0.04</td>
<td>0.04</td>
<td>0.01</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>20.84</td>
<td>20.70</td>
<td>16.11</td>
<td>21.52</td>
<td>21.64</td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>27.39</td>
<td>19.29</td>
<td>17.64</td>
<td>17.73</td>
<td>22.74</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>705.87</td>
<td>553.53</td>
<td>553.87</td>
<td>555.43</td>
<td>553.02</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Arsenic (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.04</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.02</td>
<td>0.10</td>
<td>0.00</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>8.26</td>
<td>3.97</td>
<td>1.82</td>
<td>4.21</td>
<td>1.78</td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>0.75</td>
<td>0.48</td>
<td>0.50</td>
<td>1.03</td>
<td>0.46</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>19.25</td>
<td>12.21</td>
<td>7.49</td>
<td>22.74</td>
<td>36.19</td>
</tr>
</tbody>
</table>
Table 4-S2. Iron and arsenic mineralogy in mg/kg for duplicate chloride column experiments.

<table>
<thead>
<tr>
<th>Iron (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.24</td>
<td>0.11</td>
<td>0.18</td>
<td>0.24</td>
<td>1.00</td>
</tr>
<tr>
<td>Sorbed</td>
<td>3.19</td>
<td>2.39</td>
<td>2.86</td>
<td>0.28</td>
<td>5.79</td>
</tr>
<tr>
<td>Carbonate</td>
<td>3.44</td>
<td>3.58</td>
<td>5.51</td>
<td>5.37</td>
<td>7.70</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.08</td>
<td>0.13</td>
<td>0.15</td>
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<tr>
<td>Easily reducible oxides</td>
<td>28.27</td>
<td>36.34</td>
<td>45.26</td>
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<td>72.24</td>
</tr>
<tr>
<td>Amorphous oxides</td>
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<td>46.70</td>
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<td>1166.35</td>
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<td>1297.93</td>
<td>1237.98</td>
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<table>
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<tr>
<th>Arsenic (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
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<td>0.00</td>
<td>0.18</td>
<td>0.49</td>
<td>0.73</td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.03</td>
<td>1.71</td>
<td>0.46</td>
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<td>1.17</td>
</tr>
<tr>
<td>Carbonate</td>
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<td>0.00</td>
<td>0.54</td>
<td>0.00</td>
<td>0.17</td>
</tr>
<tr>
<td>Organic matter</td>
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<td>0.57</td>
<td>0.35</td>
<td>0.45</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>12.23</td>
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<td>33.51</td>
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<td>11.41</td>
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<tr>
<td>Amorphous oxides</td>
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<td>3.05</td>
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</tr>
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<td>Crystalline minerals</td>
<td>22.30</td>
<td>131.12</td>
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<table>
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<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
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<tbody>
<tr>
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<td>0.34</td>
<td>0.63</td>
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<td>Sorbed</td>
<td>5.22</td>
<td>3.41</td>
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<td>12.13</td>
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<tr>
<td>Carbonate</td>
<td>5.34</td>
<td>4.10</td>
<td>11.64</td>
<td>31.16</td>
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<tr>
<td>Organic matter</td>
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<td>0.64</td>
<td>0.71</td>
<td>0.71</td>
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<td>Easily reducible oxides</td>
<td>1.45</td>
<td>17.80</td>
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<td>Amorphous oxides</td>
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<td>Crystalline minerals</td>
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<td>917.91</td>
<td>1402.02</td>
<td>1494.91</td>
<td>1832.79</td>
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<table>
<thead>
<tr>
<th>Arsenic (mg/kg)</th>
<th>Port 1</th>
<th>Port 2</th>
<th>Port 3</th>
<th>Port 4</th>
<th>Port 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.00</td>
<td>0.11</td>
<td>0.26</td>
<td>0.29</td>
<td>0.31</td>
</tr>
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<td>Sorbed</td>
<td>0.00</td>
<td>0.22</td>
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<td>3.07</td>
<td>5.17</td>
<td>4.95</td>
<td>1.98</td>
<td>1.52</td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>1.08</td>
<td>1.34</td>
<td>1.13</td>
<td>1.04</td>
<td>1.04</td>
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<td>Crystalline minerals</td>
<td>10.56</td>
<td>30.13</td>
<td>25.27</td>
<td>46.36</td>
<td>29.30</td>
</tr>
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Table 4-S3. Iron and arsenic mineralogy for unreacted sand and arsenopyrite

<table>
<thead>
<tr>
<th></th>
<th>Iron (%)</th>
<th>Arsenic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.00 ± 0.00</td>
<td>0.40 ± 0.07</td>
</tr>
<tr>
<td>Sorbed</td>
<td>0.33 ± 0.01</td>
<td>0.41 ± 0.06</td>
</tr>
<tr>
<td>Carbonate</td>
<td>0.26 ± 0.11</td>
<td>0.00 ± 0.00</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.00 ± 0.00</td>
<td>0.06 ± 0.08</td>
</tr>
<tr>
<td>Easily reducible oxides</td>
<td>4.13 ± 0.61</td>
<td>35.88 ± 5.82</td>
</tr>
<tr>
<td>Amorphous oxides</td>
<td>2.69 ± 0.60</td>
<td>3.62 ± 0.76</td>
</tr>
<tr>
<td>Crystalline minerals</td>
<td>92.59 ± 1.10</td>
<td>59.63 ± 6.67</td>
</tr>
</tbody>
</table>
Chapter 5: Conclusions and Future Directions

5.1. Conclusions

To establish safe and sustainable MAR operations, we must fully characterize and understand the geochemical reactions which impact arsenic mobilization from arsenopyrite. This MAR system is especially complex because arsenic is not only mobilized from arsenopyrite as it undergoes oxidative dissolution, but also simultaneously attenuated by newly-formed iron(III) (hydr)oxide secondary mineral precipitates. With MAR utilizing reclaimed wastewater in mind, the impact of water chemistry on arsenopyrite dissolution was systematically investigated on the nano- to macroscale through three tasks.

Task 1 focused on nanoscale iron(III) (hydr)oxide nucleation and growth in the presence of water constituents known to exist during MAR, including arsenate and NOM. Task 2 determined how microscale secondary mineral precipitation on arsenopyrite is altered by different model wastewater constituents, and how these alterations impact aqueous arsenic mobility. Finally, Task 3 incorporated the findings of Tasks 1 and 2 to help understand and model arsenic transport in soil column reactors.

In Task 1, the nucleation and growth of iron(III) (hydr)oxide nanoparticles on quartz under different aqueous conditions were studied using in situ, time-resolved GISAXS. For the first effort of this study, the effects of phosphate and arsenate oxyanions were investigated. We learned that the iron(III) (hydr)oxide particle sizes were largest in the arsenate system, followed by the phosphate system. The Fe(III) only system had the smallest iron(III) (hydr)oxide nanoparticles. However, while growth was promoted, the oxyanion systems had suppressed nucleation compared to the Fe(III) only system. In addition, the presence of these oxyanions
decreased the crystallinity of iron(III) (hydr)oxides and increased their water content, particularly in the case of arsenate. This work provided the first in situ observation of iron(III) (hydr)oxide formation in the presence of arsenate and phosphate. New observations included larger particle sizes for newly-formed precipitates in the oxyanion-containing systems, which occurred as a result of oxyanion bridging and increased water contents.

Next, we investigated the effects of NOM and NOM and arsenate together on the nucleation and aggregation of iron(III) (hydr)oxides. In the presence of NOM, iron(III) (hydr)oxides were smaller and formed fractal aggregates on the quartz surface. These new precipitates contained significant quantities of organic carbon and had a much higher water content than those in the Fe(III) only system. In the presence of both NOM and arsenate, interestingly, iron(III) (hydr)oxides interacted exclusively with the two components, forming a fraction of larger precipitates, where iron(III) (hydr)oxides are interacting primarily with arsenic, and other smaller fractal aggregates, where iron(III) (hydr)oxides are interacting primarily with NOM. As a result, the water content of these precipitates was between that of the Fe(III) + NOM system and that of the Fe(III) + As(V) system. The volume of precipitates in Fe(III) + As(V) + NOM system was also much lower than those in the Fe(III) only and other binary systems. These results give new insight into unique iron(III) (hydr)oxide formation and aggregation behavior in the presence of both NOM and As(V), a scenario relevant to many natural and engineered aqueous systems.

In Task 2, arsenopyrite dissolution was investigated at the microscale in the presence and absence of dissolved oxygen for a number of model reclaimed water systems. Secondary mineral formation was also investigated on flat, polished arsenopyrite coupons. First, systems containing either 10 mM sodium nitrate or 10 mM sodium chloride were investigated and results were compared with reclaimed water. Arsenic mobility was highest in the sodium chloride system.
under aerobic conditions, followed by the sodium nitrate and wastewater systems. Under anaerobic conditions, arsenic mobility was highest for the nitrate system. In addition, examination of secondary mineral precipitation showed faster phase transformation in the chloride system, where a mixture of hematite and maghemite was observed, than in the nitrate system, where only maghemite was observed. Contrarily, no precipitation was observed in the reclaimed wastewater system. In order to explain these observations, secondary mineral precipitation was explored on arsenopyrite in the presence of NOM, and NOM was found to inhibit secondary mineral precipitation. However, arsenic mobility was still elevated in the NOM systems, likely due to their increased ORP compared to reclaimed wastewater. For the wastewater system, ORP can be controlled by microbial behavior or by the presence of reducing agents. Thus, while the decreased precipitation in the reclaimed water system may result from the presence of DOC, the lower ORP can account for the lower arsenic mobility.

New observations from this study have important implications for understanding arsenic mobility at MAR field sites. For example, faster mineral aging in chloride systems will impact attenuated arsenic quantities because more crystalline iron(III) oxide minerals will have less reactive surface area for arsenic sorption. However, over longer time frames, arsenic incorporated into these crystalline minerals will be more stable and can be more permanently sequestered. Furthermore, the extents and crystallinity of secondary minerals will impact their ability to passivate arsenopyrite surfaces. Therefore, it is important that we monitor the chloride concentration at MAR field sites because it can significantly impact both arsenic mobilization and secondary mineral phase transformation.

The effect of additional oxidants was also explored through the addition of a small concentration of Fe$^{3+}$ to the 10 mM sodium nitrate and 10 mM sodium chloride model
wastewater systems. We observed for the first time that the addition of Fe\textsuperscript{3+} increases both arsenic mobilization from arsenopyrite and the extent and aging of secondary mineral precipitates. We explained this by suggesting a mechanism similar to that proposed by Moses and Herman,\textsuperscript{188} where iron sorbed on the mineral surface acts as a conduit for electrons, resulting in the fast oxidation of Fe\textsuperscript{II} in the mineral structure. Furthermore, electron transfer and atom exchange between Fe\textsuperscript{2+} and Fe\textsuperscript{III} in secondary minerals can contribute to faster mineral aging through dissolution and reprecipitation pathways. Due to both more extensive dissolution and faster mineral aging, higher mobile arsenic concentrations were measured for systems with added Fe\textsuperscript{3+}. These results demonstrate the significance of considering redox-sensitive metal concentrations in reclaimed wastewater, because even small concentrations of Fe\textsuperscript{3+} had a large impact on arsenic mobilization. Sites implementing MAR with secondary water must minimize the concentration of these redox-sensitive minerals, because they can promote the dissolution of arsenic-containing sulfide minerals.

In Task 3, to expand our understanding to the macroscale, arsenopyrite mobilization was studied in soil column reactors, which better mimicked the conditions in MAR field sites. We observed that for these reactors, arsenic mobilization was slightly higher for the 10 mM sodium nitrate system at steady-state than for the 10 mM sodium chloride system. Arsenopyrite may have been oxidized by nitrate in regions of the column where oxygen was depleted. In addition, the formation of more crystalline minerals on the arsenopyrite surface in the sodium chloride system may have limited dissolution by acting as a diffusion barrier. Reactive transport modeling using CrunchFlow was then carried out to link our experimental data with the geochemical reactions prevailing in the soil column and enable us to predict aqueous chemistry changes and precipitation extents. We found that aqueous arsenic concentrations were slightly higher in the
model. In addition, the secondary mineral precipitation extent and quantity of arsenic attenuated in the model were much lower than measured values determined using sequential extraction. However, this model provided a good estimate of the steady state arsenic concentration, which was within the same order of magnitude as experimental measurements.

Results from this task indicate that by incorporating empirical values for arsenic mobilization, measured under conditions relevant to MAR, arsenic mobilization can be predicted accurately. However, there is still room for improvement of these models by incorporating surface passivation, arsenic co-precipitation, and additional secondary mineral phase formation and transformation. In addition, our improvements to arsenic reactive transport modeling during MAR can be useful for simulating other ground and surface water systems with pervasive arsenic contamination. For example, acid mine drainage sites often have issues with arsenic contamination due to arsenic-containing pyrite dissolution. Bangladesh also has problems with natural seasonal arsenic contamination due to the reduction of arsenic-bearing ferrihydrite. Improvements to the simulation of both arsenopyrite oxidation and arsenic sorption by secondary iron(III) (hydr)oxide precipitates can help mitigate the risk to human health.

5.2. **Recommended future directions**

Over the course of our study, we observed how different reclaimed water components can have a significant impact on arsenic mobilization and secondary mineral precipitation. Further studies must focus on the effects of additional constituents which are commonly present in reclaimed wastewater. In addition to abiotic factors, we must define how microbial activity both in the native groundwater and in secondary injected water can influence arsenic mobilization. Often, the reduction–oxidation potential of groundwater is mediated by microbial activity within the aquifer. The impact of microbial activity on the kinetics of arsenic release is a key
consideration because microbes can catalyze both the oxidative dissolution of arsenic-bearing pyrite and the reduction of iron(III) (hydr)oxides. Under the anaerobic conditions expected within deeper groundwater aquifers, there could be native iron-oxidizing or -reducing bacteria, as well as sulfur-oxidizing or -reducing bacteria. A previous study has shown that arsenopyrite dissolution can be enhanced by iron-oxidizing bacteria.\textsuperscript{269} In addition, reclaimed water will likely contain elevated levels of TOC, which can stimulate microbial activity; the average TOC of groundwater is 2.95 mg C/L, while reclaimed water samples have between 10 and 20 mg C/L.\textsuperscript{270} The TOC in reclaimed water can lead to groundwater geochemistry changes locally in the injection area. These local condition changes can cause heterogeneity in remobilized As distribution in groundwater aquifers, particularly in the case of arsenic mobilization through the reduction of arsenic-bearing iron(III) (hydr)oxides. While this mechanism has not been a focus of the current dissertation, it is an important future consideration, as it can occur both at MAR field sites and in regions such as Bangladesh, where high concentrations of arsenic occur naturally in the groundwater.\textsuperscript{73, 76, 212}

In addition, reclaimed water can contain other redox-sensitive metals in addition to iron, such as lead and chromium.\textsuperscript{271} We must characterize whether these elements will have as large an impact on arsenopyrite dissolution as iron. Reclaimed water can also contain significant concentrations of pharmaceuticals and personal care products (PPCPs). The fate and transport of these PPCPs is largely unknown in environmental systems, and will add risk to the wide application of reclaimed water in MAR. It is crucial to characterize how these constituents can influence arsenic mobility. For example, PPCPs will also sorb to iron(III) (hydr)oxides, and could therefore potentially compete with arsenic for sorption sites.\textsuperscript{272} In addition, outcomes from Chapter 3 indicate that the ORP of wastewater will have a significant impact on arsenopyrite
dissolution and secondary mineral precipitation. In particular, the presence of potential reducing agents in wastewater can influence ORP conditions. Westerhoff et al.\textsuperscript{273} have shown that DOC in wastewater can have more organic nitrogen than is found in Suwanee River fulvic acid. We must characterize how these organic compounds can interact differently with arsenopyrite. Additionally, it is important to determine the reactivity of other arsenic-bearing sulfide minerals, such as arsenian pyrite, under these different aqueous conditions.

Finally, while this work has begun connecting empirical dissolution-precipitation experiments with nano- to macroscale reactions, it is imperative to continue improving reactive transport models for arsenic mobilization from arsenopyrite. Attenuation mechanisms must be fully quantified and incorporated into models to give more accurate outputs for the steady state aqueous arsenic concentration. The role of secondary mineral coatings in passivating the reactive mineral surface should also be incorporated, particularly due to the heterogeneous precipitation of more crystalline minerals. The effect of mineralogy must also be further studied, because preliminary results have indicated that the presence of dolomite can measurably decrease arsenic mobilization. For example, Fakhreddine et al.\textsuperscript{274} found that the addition of quicklime (Ca(OH)\textsubscript{2}) and dolomitic lime (CaO-MgO) decreased arsenic mobilization by promoting arsenic sorption to clay minerals. The mineralogy at MAR field sites will be much more heterogeneous than the acid washed sand utilized in our experimental systems. In the future, we must not only experimentally determine the influence of additional minerals on arsenic fate and transport, but also incorporate into our models the means to alter aquifer mineralogy and still accurately predict arsenic mobilization.

This study has qualified and quantified the nano- and microscale changes occurring during arsenopyrite dissolution under conditions relevant to MAR. The outcomes provide important
new insights into the different factors which can increase or mitigate the risk of arsenic groundwater contamination at sites undergoing recharge with reclaimed wastewater. Further directions for study are suggested, which can help to establish best practices for MAR and improve reactive transport modeling for arsenic mobilization in these systems.
5. References

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135. Liu, G.; Fernandez, A.; Cai, Y., Complexation of arsenite with humic acid in the presence of ferric iron. Environmental science & technology 2011, 45, (8), 3210-3216.
141. Le, X.; Ma, M., Speciation of arsenic compounds by using ion-pair chromatography with atomic spectrometry and mass spectrometry detection. Journal of Chromatography A 1997, 764, (1), 55-64.


222. Cornell, R. M.; Giovanoli, R.; Schneider, W., Review of the hydrolysis of iron (III) and the crystallization of amorphous iron (III) hydroxide hydrate. *Journal of Chemical Technology and Biotechnology* 1989, 46, (2), 115-134.


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Appendix

7.1. *Curriculum vitae*
7.2. *Peer reviewed publications*
CHELSEA WREN NEIL
Department of Energy, Environmental and Chemical Engineering
Washington University in St. Louis
Email: cwneil@wustl.edu • Phone: (908) 489-4463

EDUCATION

Washington University in St. Louis: St. Louis, Missouri 2010-2015
Ph.D., Energy, Environmental and Chemical Engineering
Graduate Advisor: Dr. Young-Shin Jun
GPA: 3.87

Tufts University: Medford, Massachusetts 2006-2010
B.S., Chemical Engineering, Magna Cum Laude

EMPLOYMENT

Washington University in St. Louis: St. Louis, Missouri 2010-Current
Research Assistant in the Environmental NanoChemistry Laboratory
- Applied advanced analytical techniques, including electrochemical and fluid-cell atomic force microscopy, inductively-coupled plasma mass spectroscopy, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy, and Raman spectroscopy
- Utilized synchrotron-based X-ray techniques, including X-ray absorption spectroscopy and grazing-incidence small angle X-ray scattering, at the U.S. Department of Energy National Laboratories (in collaboration with Drs. Byeongdu Lee and Matt Newville at Argonne National Laboratory)
- Carried out collaborative projects with Dr. Jeffrey Yang (U.S. Environmental Protection Agency) and engineers at CB&I (Environmental Remediation Company)
- Conducted reactive transport modeling (CrunchFlow) in collaboration with Dr. Carl Steefel at Lawrence Berkeley National Laboratory
- Contributed to a successful National Science Foundation grant proposal (co-sponsored by Geobiology and Low-Temperature Geochemistry and Environmental Engineering) related to my dissertation and conducted the funded research projects

Tufts University: Medford, Massachusetts 2009-2010
Undergraduate researcher and Summer Scholars program participant
- Conducted independent research in the Environmental Engineering department through the Summer Scholars program
- Expanded research to develop senior thesis on arsenic release from synthetic lightweight aggregates made with coal fly ash
HONORS AND AWARDS

- **Environmental Science & Technology: Best Papers of 2014**
  April 2015

- **Graduate Student Research Award**
  Department of Energy, Environmental, and Chemical Engineering
  March 2015

- **2015 Graduate Student Award in Environmental Chemistry**
  American Chemical Society: Environmental Chemistry Division
  January 2015

- **Invited speaker at Gordon Research Seminar**
  Environmental Science: Water
  June 2014

- **Mr. and Mrs. Spencer T. Olin Fellowship**
  2010-2014

- **Early Career Travel Award for Synchrotron Environmental Science VI**
  September 2014

- **Certificate of Merit: ACS Division of Environmental Chemistry**
  May 2011

PUBLICATIONS


Hu, Y., **Neil, C.W.**, Lee, B., and Jun, Y.-S., “Control of Heterogeneous Fe(III) (Hydr)oxide Nucleation and Growth by Interfacial Energies and Local Saturations,” Environmental Science & Technology, **2013**, 47(16), 9198-9206. DOI: 10.1021/es401603g


*Submitted/In review*

PRESENTATIONS AND CONFERENCE PROCEEDINGS


Presented by co-authors


Successful Synchrotron National Facility Beamtime Proposals
(Peer-Reviewed and Highly Competitive)


COMPUTER SKILLS

Microsoft Word, Microsoft Excel, Microsoft PowerPoint, Igor, MATLAB, Geochemist’s Workbench, CrunchFlow (multicomponent reactive transport modeling software), Adobe Photoshop

MEMBERSHIPS

- Member of American Chemical Society (ACS)
- Member of Clay Mineral Society (CMS)
• Member of the Society of Women Engineers (SWE)
• Member of the Air & Waste Management Association
• Member of American Institute of Chemical Engineers (AIChE)

TEACHING & MENTORING EXPERIENCE

• **Guest lecturer** for Aquatic Chemistry (EECE 543/443), *Fall semester, 2014 & 2015*
• **Teaching assistant** for Engineering Analysis of Chemical Systems (ChE 351) *Fall semester, 2011 and 2012*
  • Core course for Chemical Engineering sophomores, focusing on mass and energy conservation balances in natural and engineered systems
  • Attended all lectures, held weekly office hours and recitation sessions, and proctored exams
  • Graded homework and exams with a partner and answered questions related to coursework and grading
• **Teaching assistant** for Molecular Transport Processes and Chemical Kinetics (ChE 359), *Spring semester, 2012*
  • Core course for Chemical Engineering sophomores, focusing on molecular motions and chemical kinetics
  • Held weekly office hours and worked with students to help them solve tough homework problems using software such as MATLAB
  • Graded homework, and proctored and graded exams
• **Graduate mentor** for an undergraduate student and three high school students working in the ENCL lab through the Students and Teachers as Research Scientists (STARS) program
  • **Ms. Yanzhe Zhu** (former undergraduate student at Washington University, recently graduated) worked on cerium oxide nanoparticle fate and transport. Co-advised with Jessica Ray.
  • **Mr. Andrew Dong** (former rising senior at Parkway South High School, June 2014-July 2014) worked on cerium oxide nanoparticle fate and transport
  • **Ms. Chloe An** (former rising junior at Ladue Horton Watkins High School Mo, June 2012-July 2012) worked on an MAR related project. Chloe’s final paper was awarded an LMI Aerospace Inc. Award for Excellence in Research for outstanding paper in the area of engineering. Chloe currently attends Pomona College.
  • **Ms. Dabin Choe** (former rising junior at Mary Institute and Saint Louis Country Day School, July 2011-August 2011) worked on an MAR related project. Dabin currently attends MIT.

OUTREACH

• Speaker, Hot topics “Human Impacts on the Environment” Workshop
  This workshop introduced recent environmental challenges and educational modules which middle school teachers in St. Louis and Southern Illinois area can implement in their classes.
Washington University in St. Louis, MO, USA
July 1st and July 31st, 2015
- Led lab demonstrations for “Moving and Shaking: An Introduction to Engineering” for students in grades 6-8
  St. Louis Area Gifted Resource Council, St. Louis, MO
- Graduate student mentor for the Students and Teachers as Research Scientists (STARS) Program, which promotes the early exposure of rising high school juniors and seniors and their teachers to STEM fields by pairing them with successful scientists in research institutions.
- Created and demonstrated a lab activity to a science class at Brittany Woods Middle School through an outreach initiative by ENCL and Washington University’s Institute for School Partnership
  Brittany Woods Middle School, St. Louis, MO
  May 28th, 2014
- Participated as a demonstrator for a Hands-on Workshop on Environmental Engineering for high school students and teachers to celebrate Women in Engineering Day
  Washington University Chapter of the Society of Women Engineers, St. Louis, MO
  February 23, 2013 and February 28, 2015

DEPARTMENTAL PARTICIPATION

- Member of the Association of Graduate Engineering Students (AGES) 2013-present
  - Organized events to facilitate dialogue between graduate engineers in different departments, including happy hours, BBQs, coffee breaks, and annual float trips
  - Led the initiative for AGES events that support the community, including a food drive for the St. Louis Food Bank and toy drive for Toys for Tots
- Participated in department recruiting events by meeting with prospective students and giving lab tours, February/March 2013, 2014, and 2015
- Washington University Green Labs Representative 2011-2012
  - Led the Environmental NanoChemistry Laboratory’s participation in the Green Labs Initiative
  - Took baseline energy readings and made changes to reduce our energy use and promote recycling as part of the campus-wide initiative
- Check-in coordinator for the Mid-American Environmental Engineering Conference (MAEEC) hosted by Washington University in St. Louis
  September 21, 2013
7.2. Peer-reviewed publications


