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Model-Based Analysis of Arsenic Immobilization via Iron Mineral Transformation under Advective Flows

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Abstract

Recent laboratory studies have demonstrated that co-injection of nitrate and Fe(II) (as ferrous sulfate) to As-bearing sediments can produce an Fe mineral assemblage containing magnetite capable of immobilizing advected As under a relatively wide range of aquifer conditions. This study combined laboratory findings with process-based numerical modeling approaches, to quantify the observed Fe mineral (trans)formation and concomitant As partitioning dynamics and to assess potential nitrate-Fe(II) remediation strategies for field implementation. The model development was guided by detailed solution and sediment data from our well-controlled column experiment. The modeling results demonstrated that the fate of As during the experiment was primarily driven by ferrihydrite formation and reductive transformation and that different site densities were identified for natural and neoformed ferrihydrite to explain the observations both before and after nitrate-Fe(II) injection. Our results also highlighted that when ferrihydrite was nearing depletion, As immobilization ultimately relied on the presence of magnetite. On the basis of the column model, field-scale predictive simulations were conducted to illustrate the feasibility of the nitrate-Fe(II) strategy for intercepting advected As from a plume. The predictive simulations, which suggested that long-term As immobilization was feasible, favored a scenario that maintains high dissolved Fe(II) concentration during injection periods and thereby converts ferrihydrite to magnetite.

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ASSOCIATED CONTENT

Supporting Information

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Notes

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Graphical Abstract

INTRODUCTION

Groundwater arsenic (As) contamination is a prevalent naturally occurring problem worldwide, especially in South and Southeast Asia, where it affects the health of more than 100 million people.^{1,2} Arsenic is also currently the second most common contaminant of concern and the first priority hazardous substance at the National Priorities List (also known as “Superfund”) sites in the U.S., many of which have posed a significant threat to groundwater resources.^{3,4} Unfortunately, As-contaminated aquifers have remained difficult to remediate in a timely and cost-effective manner. One of the investigated pathways for remediating groundwater As contamination involves stimulating iron (Fe) mineral (trans)formations and immobilizing dissolved As by sorption onto and/or coprecipitation into the Fe minerals.^{4,5} Despite intense research, the long-term effectiveness of current As immobilization strategies is severely compromised by the fact that under the prevailing redox conditions typical at many sites targeted for remediation, the neoformed Fe minerals are often susceptible to microbially mediated redox transformations and subsequent remobilization of As.^{6–8}

In contrast, magnetite (Fe_3O_4), which retains As by both adsorption and structural substitution,^{9–13} appears to be a more effective host-mineral for As immobilization. Unlike many Fe minerals, magnetite is stable under a relatively wide range of conditions including both oxic and Fe(III)-reducing conditions typical of many As-contaminated aquifers.^{14,15} In our recent microcosm and column experiments,^{14,15} we observed that coinjection of nitrate and Fe(II) (as ferrous sulfate) into aquifer sediments can produce an Fe mineral assemblage containing nanoparticulate magnetite and ferrihydrite. During its formation, magnetite can coprecipitate As into its structure and, once formed, can serve as a dispersed reactive filter to immobilize advected As even under prolonged microbial reduction.^{15,16} These experimental observations are affected by a multitude of biogeochemical processes, such as (1) nitrate-Fe(II) injection leads to the *formation* of fresh Fe minerals; (2) the presence of dissolved Fe(II) from injection and microbial reduction promote the reductive *transformation* of reactive Fe(III) minerals; and (3) such (*trans*)*formation* is accompanied by the gain or loss of the structural and sorption sites available for As. Many of these biogeochemical processes

co-occur and evolve along the flow path under hydrodynamic conditions, rendering it difficult to characterize their rates directly based on experimental data alone. Additionally, sediments from As-contaminated aquifers naturally contain a range of aged Fe minerals, which have different properties from their fresh analogues and further confound the understanding of the individual processes. However, an in-depth analysis of these biogeochemical processes, and the rates at which they occur spatiotemporally, is essential for understanding what controls dissolved As concentrations and mass fluxes in contaminated groundwater systems. To this end, numerical models become invaluable tools for distilling complex systems into their salient components. Based on data collected from experimental studies, reactive transport models have been successfully exploited in the rigorous, process-based quantification of various redox transformations and the associated fate of metal(loid)s in porous media, at both bench and field- scale.^{17–21}

In this study, we develop a process-based quantification framework for Fe mineral (trans)formations and the concomitant changes in As mobility induced by nitrate-Fe(II) injection. The model development was constrained by data collected from our well-controlled, multistage column experiment (1400+ solution and solid-phase observations) during which effluent As concentration varied by 2 orders of magnitude. The model was subsequently used to illustrate the feasibility of *in situ* magnetite formation as a sustainable groundwater remediation technique. This was achieved by a small set of predictive field-scale model simulations that explored possible chemical and operational strategies to optimize the effectiveness of nitrate-Fe(II) amendments for immobilizing dissolved As. The development and application of a process-based quantification approach contribute to a deeper understanding of the complex Fe and As reaction network and eventually to an improved design of this remediation strategy.

METHODS

Laboratory Column Experiment.

In our bench-scale experiment,¹⁶ triplicate columns were loaded with aquifer sediments from the Dover Municipal Landfill Superfund Site (New Hampshire), where groundwater As contamination is a concern.^{22,23} Detailed descriptions of the Dover site and the sediment sampling procedures have been provided else-where.^{22,24} Total Fe content in the Dover sediments was 0.28 mol kg⁻¹ (1.57%), which existed primarily as nonreactive Fe-bearing silicates with lesser quantities of carbonates, oxides, and sulfides, but did not contain magnetite. Total As content was 44 μmol kg⁻¹ (3.3 mg kg⁻¹), with 61% as As(III) and 39% as As(V), which was associated with amorphous and crystalline Fe(III) oxides. The columns had an inner diameter of 4 cm, a length of 20 cm, and therefore a volume of ~250 mL. The effective porosity was ~0.30. Four oxygen-depleted experimental stages with varying influent compositions were conducted, to represent the various stages of site remediation. Artificial groundwater (A-GW) was used, which consisted of Milli-Q water amended with 0.02 mM NH₄Cl, 1 mM KCl, 0.4 mM CaCl₂, 0.4 mM MgSO₄, and 1 mM Na-lactate. The A-GW was amended with additional chemicals in Stages I to IV and maintained at pH 7 with 10 mM PIPES buffer. Stage I used 38 pore volumes (PVs) of A-GW with 1.33 μmol L⁻¹ (100 μg L⁻¹) As(III), to equilibrate the sediments and mimic As transport under the

characteristic geochemical conditions found at landfills. Stage II used 38 PVs of A-GW with $1.33 \mu\text{Mmol L}^{-1}$ ($100 \mu\text{g L}^{-1}$) As(III), 4 mM FeSO_4 , and 10 mM NaNO_3 , to produce Fe minerals and test if they could immobilize As (followed by 4 PVs of A-GW to clean residual nitrate-Fe(II)). Stage III used 45 PVs of A-GW with 10 mM Na-lactate, to further enhance microbial reduction and test if the neoformed Fe minerals were stable. Stage IV used 120 PVs of the same influent with Stage I, to return to landfill conditions and test if the neoformed minerals could immobilize additional advected As. The influents were injected at 2 PVs per day, equal to a flow velocity of 0.4 m day^{-1} . The effluent pH was close to 7 except for Stage II, which was half a pH unit lower (Figure 1). The effluent As, Fe, Ca, and nitrate concentrations varied considerably between stages. The effluent P, nitrite, and sulfide concentrations were not detectable. Based on the spectroscopic, magnetic, and chemical extraction analyses of sediments collected from triplicate columns sacrificed at the end of Stages II, III, and IV (Figure 2), magnetite and ferrihydrite precipitated as a result of nitrate-Fe(II) injection, followed by a phase in which ferrihydrite underwent significant reduction while magnetite remained stable. The concentration of As(III) increased in the sediments, especially in the vicinity of the column inlet, where As(III) was injected. The As partitioning between different Fe oxides varied between stages, and As-bearing sulfides were mostly not detectable. Full details of the experimental setup and results are given in Sun et al.¹⁶

Modeling Tools and Procedures for the Column Model.

The geochemical model PHREEQC²⁵ was used to reconstruct the initial solution and solid (mineral and surface) equilibrium that prevailed within the unamended columns. Subsequently, MODFLOW²⁶ and PHT3D²⁷ were used to simulate flow and reactive transport across the columns during influent injections. Based on experimental observations, a reaction network consisting of a mixture of equilibrium and kinetically controlled reactions was defined in the PHREEQC/PHT3D reaction database and successively refined to reproduce the observations. The refinement of the model, and associated improved agreement between simulation results and observations, was achieved by evaluating a range of conceptual models in combination with a parameter estimation procedure that began with trial-and-error, followed by automatic calibration using an implementation of Particle Swarm Optimization (PSO). The most critical changes compared to the standard PHREEQC database were made with respect to Fe mineral reactions and their role on As mobility. The developed reaction network for Fe and As- related reactions addresses three major aspects: (1) the process-based description of the Fe mineral (trans)formation; (2) the identification of a suitable approach to quantify the impact of the mineralogical changes on sorption characteristics and associated surface species including As; and (3) the simulation of the As structural substitution within magnetite.¹⁶ Neoformed magnetite and ferrihydrite from nitrate-Fe(II) injection were represented as Fe_3O_4 and $\text{Fe}(\text{OH})_3$, respectively; natural amorphous and crystalline Fe(III) oxides in the Dover sediments were represented as ferrihydrite $\text{Fe}(\text{OH})_3$ and goethite FeOOH , respectively, both for simplicity and to account for natural variation.^{18,28} Additionally, an exchanger site was implemented in the model to account for the evolution of cations in the effluent when influent compositions were changed between the experimental stages.¹⁶ In the following, we provide the details for the three Fe- and As- related aspects of the employed reaction network. All other reactions remained

consistent with the standard PHREEQC database, and the relevant reactions, stoichiometries, and thermodynamic constants are provided in Supporting Information (SI) Table S1.

Iron Reaction Network.

Reactions Induced by Nitrate-Fe(II) Injection (Stage II).—The injected nitrate-Fe(II) amendment precipitated as ferrihydrite and magnetite.^{15,16} Consistent with previous studies,^{19,20} the oxidation of dissolved Fe(II) to dissolved Fe(III) in the presence of nitrate in mildly acidic to neutral water was modeled as

$$r_{Fe^{II}-ox} = k_{Fe^{II}-ox} \times (A_{OH^-})^2 \times C_{NO_3^-} \times C_{Fe^{II}} \quad (1)$$

where $k_{Fe^{II}-ox}$ is the rate coefficient, A_{OH^-} is the hydroxyl ion activity, and $C_{NO_3^-}$ and $C_{Fe^{II}}$ are the concentrations of dissolved nitrate and Fe(II), respectively. The product of nitrate reduction was not determined during the column experiment, and dinitrogen gas was assumed to be the ultimate product in the model.²⁹ Ferrihydrite is known to be the initial, fast precipitate from hydrolysis of Fe(III)-containing solutions,³⁰ and therefore ferrihydrite precipitation was modeled as a thermodynamically controlled equilibrium reaction. Attributed to the large amount of dissolved Fe(II), which subsequently sorbed on the surface of ferrihydrite, magnetite was allowed to form via a solid-state conversion of the ferrihydrite surface:^{30,31}

Similar to other recent studies,^{17,18,32} the conversion from ferrihydrite to magnetite was modeled as

$$r_{mgt-pptn} = -k_{mgt-pptn} \times \max\left(0, \left[1 - \frac{1}{SR_{mgt}}\right]\right) \times \left(\frac{[Fh] - C_m}{[Fh]}\right) \times \left(\frac{C_{Fe^{II}}}{K_{mgt-pptn}^{thres} + C_{Fe^{II}}}\right)^3 \quad (3)$$

where $k_{mgt-pptn}$ is the effective rate coefficient, SR_{mgt} is the saturation ratio of magnetite, $[Fh]$ is the concentration of ferrihydrite, C_m is the concentration at which ferrihydrite secondary mineralization effectively stalls, and $K_{mgt-pptn}^{thres}$ is a threshold term describing the dissolved Fe(II) concentration required for transformation of ferrihydrite to magnetite that was adapted from Tufano et al.³² Note that Rawson et al.¹⁶ also evaluated a slightly different rate expression consisting of a sorbed Fe(II) threshold term with identical results. The initial

estimates of $K_{mgt-pptn}^{thres}$, C_{m} , and $K_{mgt-pptn}^{thres}$ were based on literature values^{17,18,32} but allowed to deviate during the model calibration process.

Furthermore, the investigated Dover sediments have previously been shown to contain Fe(II) sulfides, presumably mackinawite (FeS).^{16,22,24} Therefore, mackinawite oxidation by nitrate was also included in the Fe reaction network:

The employed rate expression was modified from the commonly used rate expression for pyrite oxidation by nitrates^{19,20,33,34}

$$r_{FeS-ox} = 10^{k_{FeS-ox}} \times \left(C_{NO_3^-}\right)^{0.5} \times \left(A_{H^+}\right)^{-0.11} \times \left(\frac{[FeS]}{[FeS]_0}\right)^{0.67} \quad (5)$$

where k_{FeS-ox} is the effective rate coefficient for mackinawite oxidation, $C_{NO_3^-}$ is the concentration of dissolved nitrate, A_{H^+} is the proton activity, and $([FeS]/[FeS]_0)^{0.67}$ is a factor that accounts for changes in mackinawite surface area due to the progressing reaction.

Reactions Induced by Microbial Reduction (Stages I, III, and IV).—In the column experiment highly labile organic matter, lactate, was amended to the influent. The associated microbial degradation led to significant Fe(III) reduction in the columns during Stages I, III, and IV and therefore constitutes an important aspect of the Fe-related reaction network. In contrast to exogenous lactate, natural sediment-bound organic matter was not considered due to its much lower reactivity. Given that sulfate-reducing bacteria (SRBs) are ubiquitous in natural sediments and as sulfate was present in the A-GW influents, sulfate reduction coupled to the transformation of lactate to acetate was considered:³⁵

Furthermore, while magnetite remained stable under prolonged microbial reduction, ferrihydrite was the most bioavailable Fe(III) mineral for dissimilatory Fe(III)-reducing bacteria (FeRBs) using lactate or acetate as electron donor:^{7,8,36}

Similar to Rawson et al.,¹⁸ microbial reduction coupled with organic matter degradation (Reactions 6 and 7) was modeled as the first-order reactions

$$r_{OM_Fh/OM_sulfate} = k_{OM_Fh/OM_sulfate} \times C_{OM} \quad (8)$$

where $k_{OM_Fh/OM_sulfate}$ refers to the rate coefficient of either sulfate reduction or Fe(III) reduction, and C_{OM} is the concentration of organic matter (in this case, lactate or acetate). Microbial sulfate reduction usually produces dissolved sulfide (Reaction 6); however, this was never detected in the column effluent.¹⁶ The reason for the absence of sulfides was most likely that the dissolved sulfides reductively reacted with ferrihydrite and were therefore successively consumed within the Dover sediments.^{6,8,37}

The rate of chemical ferrihydrite reduction by dissolved sulfide was modeled as⁸

$$r_{sulfide_Fh} = k_{sulfide_Fh} \times (C_{sulfide})^{0.5} \quad (10)$$

where $k_{siderite}$ is the rate coefficient, and $SR_{siderite}$ is the dissolved sulfide concentration. The exponent was set to 0.5 in accordance with Poulton et al.⁸ In addition, both the pH changes and the bicarbonate produced from organic matter degradation affected the evolution of the Fe(II) carbonate mineral, siderite.¹⁶ Siderite was therefore also included in the Fe reaction network with a rate expression^{18,20}

$$r_{siderite} = k_{siderite} \times (1 - SR_{siderite}) \quad (11)$$

where $k_{siderite}$ is the rate coefficient, and $SR_{siderite}$ is the saturation ratio of siderite. Crystalline Fe(III) oxides such as goethite can also undergo reduction in a similar manner with ferrihydrite (i.e., similar to Reactions 7 and 9), but the goethite related rates must have been slow when ferrihydrite was present,^{7,36,38} and the amount of goethite was indeed found to be relatively stable during the experiment.^{7,16,36,38,16} Therefore, similar to Rawson et al.,¹⁸ the reduction of crystalline Fe(III) oxides was not considered in the model. A conceptual diagram of the Fe reaction network is provided in Figure S1.

Surface Complexation Reactions.

Adsorption and desorption of As oxyanions on mineral surfaces often play a key role in regulating dissolved As concentrations in groundwater.^{16,17,39} In the case of the Dover columns, surface-bound As was found to be associated primarily with Fe(III) oxyhydroxides and magnetite.¹⁶ To accurately quantify sorption under the dynamic biogeochemical conditions, it is necessary to link the sorption characteristics with the presence and abundance of multiple types of Fe oxide minerals and to define a sorption model for As and all other important solution species to account for the influence from pH changes and

potential competitive sorption effects. The final conceptual/ numerical model implementation considered four types of Fe oxides — (1) neoformed ferrihydrite and (2) magnetite, as well as (3) natural amorphous and (4) crystalline Fe(III) oxides — that are mainly characterized by different surface site densities. The initial densities of strong and weak sites on neoformed ferrihydrite were set to those for hydrous ferric oxides (Hfo) as originally provided by Dzombak and Morel,⁴⁰ and the initial site densities on neoformed, nanoparticulate magnetite were set to 20% of those for neoformed ferrihydrite. Similar to Rawson et al.,¹⁸ natural amorphous and crystalline Fe(III) oxides within unamended Dover sediments were assumed to have lower site densities compared to neoformed minerals. The total number of sorption sites on each mineral was stoichiometrically linked with the temporally varying mineral concentration. Sorption of anions (e.g., As) and cations (e.g., Fe(II) and Ca) was assumed to occur as surface complexation reactions. In the simulations, sorption was quantified using an electrostatic double layer model.⁴⁰ The stoichiometries of the considered surface complexation reactions on both strong and weak sites are listed in Tables S1 and S2. The surface complexation constants were based on Dzombak and Morel⁴⁰ and Dixit and Hering.³⁹

Arsenic Coprecipitation within Magnetite.

Besides surface-bound As on different Fe oxides, As immobilization can occur through coprecipitation with magnetite, as substitution within magnetite crystal structure or as surface precipitate.^{10,12,16} To model this process, we adopted the approach previously used by Rawson et al.^{17,18} The stoichiometries of As(III) and As(V) coprecipitation were assumed to be

The rates of As(III) and As(V) coprecipitation with magnetite are both stoichiometrically linked with the rate of magnetite precipitation (eq 3). Rawson et al. could only hypothesize that As was coprecipitated with magnetite.^{17,18} In contrast, structurally bound As within magnetite was indeed observed in our column experiment, and the amount was determined by sequential extraction.¹⁶ The As:Fe molar ratio within magnetite, from $Fe_3O_4As_2O_3(s)$ and $Fe_3O_4As_2O_5(s)$ fractions, was constrained based on sediment extraction data throughout the model calibration process.

Model Calibration and Sensitivity Analysis.

The parameters used in the numerical model were initially selected based on literature values. The parameters were then refined such that the sum of the squared residuals between observations and model-simulation equivalents was minimized, while still subject to the constraint that the parameters agreed with their corresponding literature values as closely as possible. Following an initial manual trial-and-error step, the parameters were further refined

by an automatic calibration step using the heuristic PSO method due to the significant nonlinearity common in similar geochemical and reactive transport models.^{17,21,41} The PSO code was written within the PEST++ platform using the YAMR run manager⁴² and linked with PHT3D. The calibration process was constrained by not only the observed temporal changes in the effluent composition but also the observed temporal and spatial mineralogical changes. Specifically, the calibration was constrained by the effluent data from the column that was terminated at the end of Stage IV and the sediment data from the unamended Dover sediments and all three columns that were terminated at the end of Stages II, III, and IV, respectively.¹⁶ The observations on sediment Fe mineralogy and As distribution were based on sequential extraction, and sediment As speciation was based on linear combination fitting of XANES spectra. Observation weights were assigned based on magnitude (e.g., pH vs concentration value), the number of observations available (e.g., solution vs solid-phase data), and the uncertainty inherent in each observation type. More details about weight assignment are provided in the Supporting Information. The parameters to be calibrated included a number of reaction rate coefficients, surface site densities of specific Fe minerals, As:Fe ratio within magnetite, cation exchange capacity, etc. (Tables 1 and S2). The PSO calibration was set with a swarm size of 100, and 100 iterations of the algorithm were conducted in parallel on a high-performance computer cluster. The parameter estimates from PSO were subsequently used as initial values for the Gauss-Levenberg-Marquardt method contained in PEST++ for final calibration refinement and sensitivity analysis.^{41,43} Tikhonov regularization was also employed on this final step to provide prior information for parameters, alleviating any issues associated with overfitting or parameter insensitivity which may result in high posterior variance and unreasonable parameter estimates.⁴⁴

Predictive Model of Potential Field-Scale Implementation.

To illustrate the feasibility of the nitrate-Fe(II) remediation strategy for intercepting As at the field-scale, 2D predictive simulations were conducted. These simulations also provided a tool to explore operational considerations, e.g., how to adjust the composition of the nitrate-Fe(II) injectant to increase the fraction of magnetite precipitation relative to ferrihydrite. The field-scale model was constructed as a single-layer 90 m × 90 m grid, with 3 m × 3 m model cells and a thickness of 3 m. The hydrogeological parameters were based on typical aquifer conditions at the Dover Superfund site.²³ A heterogeneous hydraulic conductivity (K) random field was generated with an average K of 12 m day⁻¹ (Figure S2). The effective porosity was 0.25 similar to Dover site characteristics (between 0.20 and 0.33) and lower than the porosity of the Dover columns of 0.30 to reflect the fact that silica sand was mixed in the columns to improve flow properties.^{16,23} Longitudinal (0.2 m) and lateral transverse (0.02 m) dispersivities were set to values representing local-scale dispersivities. Ambient groundwater flow was assumed to occur at an average velocity of 50 m year⁻¹. Ambient groundwater was for simplicity assumed to have the same composition as the “landfill” injectant used in Stages I and IV of the column experiment.

Two injection scenarios were defined and compared: (1) the same nitrate-Fe(II) composition used in Stage II of the column experiment, i.e., 4 mM Fe(II) and 10 mM nitrate, was injected continuously for 4 weeks, and (2) the nitrate-Fe(II) concentrations were doubled, i.e., 8 mM Fe(II) and 20 mM nitrate, in week 1, while 8 mM Fe(II) without nitrate was used in week 4

(an equal amount of Fe(II) was injected between the two scenarios). pH can regulate the product of this nitrate-Fe(II) injection, with lower pHs slowing down Fe(II) oxidation (eq 1) and potentially limiting microbial growth.^{45,46} To eliminate pH differences between the two scenarios for comparison purposes, the concentration of the buffer was also doubled in scenario #2. The injection was simulated through two wells at a rate of 30 m³ day⁻¹ per well. Using the calibrated parameters from the column model (Tables 1 and S2), the 2D simulations included the Fe(II) oxidation, ferrihydrite, and magnetite precipitation reactions, surface site densities, cation exchange capacity, and all the related surface complexation and exchange reactions. The total simulation time was 10 years. More details of the 2D model setup are given in Table S3.

RESULTS AND DISCUSSION

Column Model — Iron Mineral (Trans)formation and the Fate of Arsenic.

Overall, the developed reactive transport model provides an excellent description of the observed breakthrough behavior of all the measured species during all four experimental stages (Figure 1). Moreover, simulations also agreed well with the observed temporal and spatial evolutions in both concentration and speciation of As and Fe in the sediments (Figure 2). This close agreement suggests that our conceptual model and its implementation into a numerical model framework provides a good representation of the key redox and surface processes occurring in the Dover columns.

Pre-Equilibration Stage (Stage I).—Based on experimental observations,^{16,23,24} the Dover sediments naturally contained As-bearing ferrihydrite and goethite,^{16,22,24} the presence of which initially sorbed the injected As but then released As under microbial reduction (Figure 1A). The model-based data interpretation revealed a consistent narrative. In the final calibrated model, the site densities of natural ferrihydrite and goethite were determined to be relatively low (Table 1). Moreover, the model suggested that due to microbial ferrihydrite reduction, along with microbial sulfate reduction and subsequent intrusion of sulfide that traveled with the flow and chemically reduced ferrihydrite, the abundance of ferrihydrite was decreasing along the length of the column during Stage I (sediment characterization unavailable in this stage¹⁶). Therefore, although the available sorption sites could initially host the injected As, attenuation was quickly overcome by *in situ* As release due to the destruction of sorption sites. Consequently, dissolved As accumulated along the flow path and eventually eluted from the column (Figure 1D). An effluent As concentration peak (increase and then decrease), instead of a continuous increase, was observed in all the triplicated Dover columns (Figures 1 and S3). The observed decrease was replicated by the model as a result of ferrihydrite successively becoming depleted within the column, which causes a slowing release of As. Furthermore, the model suggested that ferrihydrite dissolution occurred concomitantly with siderite and mackinawite precipitation, which limited Fe elution (Figure 1B vs Figure S4) and suppressed Fe(II)-induced ferrihydrite conversion to magnetite because of low porewater Fe(II) concentrations (eq 3).^{16,17,31,32}

Nitrate-Fe(II) Injection Stage (Stage II).—A characteristic feature of the observed breakthrough behavior during Stage II is the lag between nitrate and Fe breakthrough (Figure 1BC). This observed lag is reproduced by the model as a result of nitrate migrating unretarded through the column, while the transport of ferrous Fe was retarded by cation exchange (a model variant without cation exchange is given in Figure S6). Cation exchange also governed the evolution of effluent Ca (Figure 1F vs Figure S6). Once a new exchange equilibrium was attained throughout the column, Fe elution increased but remained substantially below the concentrations amended to the influent. In the model, the amount of Fe retained on the exchange site only contributed ~5% to the overall Fe loss by the end of Stage II, which agreed with sediment extraction data (Figure S5). Instead, the observed Fe loss within the column was primarily a result of the simulated partial oxidation of Fe(II) to Fe(III) due to the presence of nitrate, combined with an immediate precipitation as Fe minerals. The estimated rate of Fe(II) oxidation in the Dover columns ($\sim 2 \times 10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ during Stage II) was orders of magnitude slower than Fe(II) oxidation by oxygen under similar, circumneutral pH.^{47,48} This relatively slow oxidation was required to ensure that Fe mineral formation occurred, as observed, dispersed through the column rather than entirely concentrated at the influent end. The estimated rate of Fe(II) oxidation was also significantly faster than the uncatalytic, abiotic Fe(II) oxidation rate by nitrate reported by Straub et al.,⁴⁹ indicating that the reaction (eq 1) was chemically catalyzed and/or microbially mediated by nitrate-dependent Fe oxidizers and/or by denitrifiers.^{15,16,41,50} As discussed in Sun et al.,¹⁶ the data available were insufficient to reveal the exact mechanism(s) of Fe(II) oxidation in this column experiment. However, regardless of how eq 1 was accelerated, ferrihydrite neoformed because of its overwhelmingly fast kinetics. On the other hand, magnetite remained substantially oversaturated (saturation index >16, Figure S7) during Stage II and neoformed via Fe(II)-induced ferrihydrite recrystallization (Figure 2).^{30,31} The rate of partial conversion from ferrihydrite to magnetite $k_{mgt-pptn}$ was estimated to be on the order of $10^{-7} \text{ mol L}^{-1} \text{ s}^{-1}$ (Table 1). This rate is orders of magnitude faster than the rate ($10^{-12} \text{ mol L}^{-1} \text{ s}^{-1}$) estimated from a field experiment that was conducted in a Bengal Delta aquifer¹⁸ and comparable to the rate (10^{-4} - $10^{-6} \text{ mol L}^{-1} \text{ s}^{-1}$) estimated from a bench-scale column experiment that used ferrihydrite-coated sands,¹⁷ both of which employed the same rate expression as this study (eq 3).

The simulated *in situ* precipitation of ferrihydrite and magnetite triggered a dramatic decrease in effluent As concentration (Figure 1A). In the model, a portion of the As immobilization occurred as coprecipitation within magnetite.¹⁶ An As:Fe molar ratio of ~1:2000 reproduced the magnitude of coprecipitation within magnetite measured by sediment extraction (Table 1 and Figure 2), which is significantly smaller compared to Rawson et al.,^{17,18} where the As:Fe molar ratio in magnetite was ~1:4. This discrepancy is plausible because a ratio of 1:4 is only likely to occur if a large part of As exists as an amorphous surface precipitate,^{10,12} which is unlikely to be as recalcitrant as the substituted As within the crystal structure of magnetite observed in the Dover columns.¹⁶ Arsenic(V) is believed more likely to be incorporated within magnetite than As(III).¹² In this column experiment, the estimated mole fraction of As(V) in magnetite was an order magnitude smaller than that of As(III), which probably reflects the fact that As(V) was much less abundant. Nevertheless, both model-estimated fractions have relatively large uncertainty,

calling for additional experiments to more explicitly determine the speciation of As in magnetite to better constrain the As structural incorporation process. With the current estimated As:Fe molar ratio of ~1:2000, structurally bound As within magnetite accounted for 12% of the solidphase As in the simulation by the end of Stage II (Figure 2). Consequently, surface-bound As contributed more significantly to the overall immobilization of As. Our model suggested that the neoformed magnetite possessed relatively high sorption site densities, agreeing with its nanoparticulate size confirmed by XRD and SEM analyses.¹⁵ Nevertheless, because the neoformed ferrihydrite had almost 4 times higher site densities compared to magnetite (Table 1), adsorption on ferrihydrite was most critical for As immobilization during Stage II, accounting for half of the solid-phase As (Figure 2) and in good agreement with sediment extraction data.¹⁶

Post-Nitrate-Fe(II) Injection Stages (Stages III and IV).—The stability of magnetite allowed it to persist once precipitated and to act as a reactive As filter (Figure 2). Contrastingly, although ferrihydrite was initially a predominant sink for the injected As, the As-bearing ferrihydrite became vulnerable under the reducing conditions enhanced by the 10 mM lactate amendment during Stage III. During this stage, the abundance of ferrihydrite and its total number of sorption sites decreased in the model due to a combination of microbial Fe(III) reduction and chemical reduction by sulfide. Nevertheless, in agreement with observations, the model suggested that the release of As from ferrihydrite transformation was accompanied by (re)adsorption on magnetite and goethite as well as on the remaining ferrihydrite (Figure 2). This explains why effluent As concentration remained low throughout Stage III (Figure 1AD).

Stage IV is characterized by a gradual As elution (Figure 1A). The conceptual model derived in the experimental study¹⁶ attributed this slow As progression to a low magnitude of reductive dissolution of goethite once ferrihydrite became depleted.^{7,36,38} Another alternative explanation could have been that a saturation of sorption sites induced As elution, but this would most likely have produced a more distinct, steeper As breakthrough. Differing from the earlier proposed conceptual model, our present model suggested that ferrihydrite bound As continued to be solubilized *in situ* by reductive transformation, which was then partially (re)-adsorbed along the flow path and partially eluted (Figure 1D). This model was able to closely reproduce observations of both effluent As concentration and speciation throughout Stage IV (Figure 1A). In contrast to Stage I during which effluent As concentration fluctuated rapidly, effluent As concentration was substantially lower than the influent level during the entire Stage IV, indicating that the majority of the advected As was still immobilized within the nitrate-Fe(II) amended sediments. The model suggested that while ferrihydrite became less and less capable of immobilizing As under prolonged reduction, adsorption on magnetite increasingly contributed to As immobilization, in agreement with sediment extraction data (Figure 2). Compared to ferrihydrite and magnetite, the contribution of goethite to As immobilization remained more or less stable over the entire experiment, also agreeing well with observations.

Neoformed vs Natural Ferrihydrite.—Data-constrained simulations with different model variants allowed us to elucidate the differences between natural and neoformed

minerals. Thereby the obtained good agreement between simulations and observations relied on a distinction in site density between neoformed and natural ferrihydrite. The natural ferrihydrite that existed in the Dover sediments prior to the experiment was determined to possess almost 4 times lower site density compared to its neoformed analogue (Table 1). Using the same calibration procedure as described previously, another calibrated model variant in which neoformed and natural ferrihydrite shared identical site densities failed to reproduce observations (Figure 3, variant (iii)). While little discrepancies were found for the effluent As dynamics prior to the nitrate-Fe(II) injection, the estimated ferrihydrite reduction rates were inadequately high such that effluent Fe concentrations differed from the corresponding observations.

Furthermore, effluent pH and As concentrations showed a severely poor agreement with observations during the 10 mM lactate amended stage after nitrate-Fe(II) injection (Figures 3 and S8). Although differing in their attributed site densities, neoformed and natural ferrihydrite appeared to have similar dissolution rates under reduction. To illustrate this behavior, another model variant was calibrated in which reduction rate coefficients were allowed to deviate independently, and the estimated rates from this calibration were found to be almost identical to the estimates derived in the present (final) model.

Importance of Arsenic Retention via Magnetite.—The numerical model also enabled the investigation of individual minerals or processes with respect to their importance for controlling the fate and transport of As. To illuminate the role of magnetite on As immobilization, a model variant was constructed on the basis of the final model where magnetite structural and surface-bound As was deactivated (Figure 3, variant (iv)). The results implied that in the short term, reductive transformation of ferrihydrite would not generate As elution until ferrihydrite and its associated sorption capacity were nearing depletion. The results also demonstrated that without retention via stable magnetite, substantially higher As elution would have occurred under prolonged reduction, underpinning the hypothesized long-term effect that magnetite has on attenuating As in reducing aquifers.

Field-Scale Predictive Simulations.

Using the calibrated parameters from the column model (Tables 1 and S2), two field-scale predictive simulations with varying injection scenarios were conducted to assess the efficacy of the nitrate-Fe(II) strategy to create stable As host-minerals *in situ* and intercept As plumes. Since magnetite is distinctly more stable than ferrihydrite under reducing conditions common within As-burdened aquifers, any optimized injection strategy would be targeted to preferentially produce magnetite rather than ferrihydrite. Between the two injection scenarios considered (Figure 4AB vs 4CD), the superior injection strategy (scenario #2) consisted of using Fe(II) without nitrate in the later portion of the injection; by doing so, high dissolved Fe(II) concentrations were maintained, thus stimulating a more sustained ferrihydrite conversion to magnetite.^{31,32} The predictive simulations suggested that the amount of minerals precipitated from a short injection would provide sufficient adsorption capacity to intercept As from the upgradient plumes for many years (Figure 4E-H). Following both injection scenarios, magnetite and ferrihydrite precipitated in the extended

vicinity of the injecting wells (Figure 4A-D). Based on the densities of ferrihydrite (3.8 g cm^{-3}) and magnetite (5.2 g cm^{-3}), the volume of mineral precipitation remained negligible, even in the direct vicinity of the injection wells ($\sim 2 \text{ cm}^3$ per m^3 of pore space, Figure S9) and should not restrict groundwater flow. Overall, we conclude that, with the aid of formal optimization methods, the nitrate-Fe(II)-based remediation technique can potentially produce a stable, dispersed reactive filter within the aquifer to immobilize dissolved As from contaminated groundwater as it migrates through the amended zone.

IMPLICATIONS

While being crucial for determining the long-term potential of the nitrate-Fe(II) strategy for groundwater As remediation, neither the underlying driver of the gradual As elution at the end of the column experiment nor the ultimate significance of magnetite on controlling As transport could previously be inferred from the experimental data.¹⁶ Combining experimental observations with reactive transport modeling, this study demonstrated that the (trans)formation of ferrihydrite played a dominant role in governing the dynamics of As, including the late gradual As elution. Injection of nitrate has been previously suggested as a possible treatment route for As-burdened groundwater systems;^{5,29} however, this may predominantly produce ferric oxyhydroxides, which are vulnerable under the typically prevailing reducing conditions in these systems.^{1,2} Stimulating the formation of magnetite by coinjecting Fe(II) can improve the long-term effectiveness of this route. Our model-based analysis of the column experiment suggested that magnetite effectively immobilized As by coprecipitation and adsorption. However, the importance of magnetite was not pronounced until ferrihydrite was depleted. As a result, the surface site density on magnetite could not be well constrained in the present model. To unambiguously, experimentally resolve the role of magnetite, future experiments will have to be performed and monitored long enough such that the effects of magnetite become evident. Furthermore, field-scale predictive modeling illustrated its potential for evaluating different chemical and operational factors that are likely to affect the implementation of a nitrate-Fe(II)-based remediation strategy in practice. While the predictive simulations conducted within this study were not comprehensive, the obtained results provided some important insights and will serve as hypotheses to be tested and amended by pilot field experiments. As demonstrated by both experimental and modeling results, a magnetite based As immobilization method by nitrate-Fe(II) injection is potentially a long-term, *in situ* remedial option for As-contaminated groundwaters, which now requires investigation and optimization under field-scale conditions.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

(A) Effluent As, (B) effluent Fe, (C) effluent nitrate, (D) porewater As, (E) effluent pH, and (F) effluent Ca concentrations during the column experiment. On subplot (A), As speciation is also shown for the portion where IC-ICP-MS measurements are available (speciation was not measured in the experiment until PV ~ 110). On the effluent subplots, symbols represent observations,¹⁶ solid lines represent the reactive model simulations, and dashed lines represent conservative model simulations. Due to an experimental failure,¹⁶ a few effluent As observations during Stage I were not included in the calibration and marked on subplot (A) as uncolored symbols. Shaded blocks or white dashed lines in each subplot represent the four experimental stages. For clarity, only observations from the column that was terminated at the end of Stage IV are shown. The observations from the other two columns that were terminated at the end of Stages II and III, respectively, are shown in Figure S3

Figure 2.

Simulations and observations of (top) Fe mineralogical composition, (middle) As distribution among different Fe minerals, and (bottom) As speciation in the initial (unamended) sediments and amended Dover sediments at the end of Stages II, III, and IV. Sid, Fh, Gt, Mgt, and FeS stand for siderite, ferrihydrite, goethite, magnetite, and mackinawite, respectively. Exchangeable Fe was also determined by extraction; however, the amount is small such that the top panel looks almost identical with or without exchangeable Fe (Figure S5).

Figure 3.

Model simulations illustrating effluent (A) As and (B) Fe concentrations, with 4 variants: (i) a conservative model, (ii) a calibrated reactive model with neoformed and natural ferrihydrite having different site densities (the final model, two Fh), (iii) another calibrated reactive model with neoformed and natural ferrihydrite sharing the same site densities (one Fh), and (iv) the final model without structural or surface-bound As in the presence of magnetite. Model variants (i) and (ii) are the ones shown in Figure 1.

Figure 4.

Comparison between (A)(B) nitrate-Fe(II) injection scenario #1 and (C)(D) scenario #2 for the distributions of (A)(C) ferrihydrite and (B)(D) magnetite and simulated groundwater As concentration following injection scenario #2 after (E) 100 days, (F) 1 year, (G) 3 years, and (H) 10 years. Groundwater As plume from upstream contains $1.33 \mu\text{mol L}^{-1}$ ($100 \mu\text{g L}^{-1}$) dissolved As(III), and groundwater flow direction is from left to right (horizontal to x-axis).

Key Kinetic Rate Parameters, Cation Exchange Capacity, and Surface Site Densities Employed in the Final Calibrated Model, as Estimated by PEST/PSO^a

Table 1.

parameter	estimated parameter value	prior standard deviation	posterior standard deviation	% variance reduction	coefficient of variation	composite scaled sensitivity
Reaction Rate Coefficients and Related Parameters [unit]						
iron(II) oxidation $k_{Fe_{ox}} [L^3 mol^{-3} s^{-1}]$	5.15×10^{12}	1.25×10^{13}	5.44×10^{11}	96%	1.06×10^{-01}	1.63×10^{-06}
magnetite precipitation $k_{mgc_pptn} [mol L^{-1} s^{-1}]$	1.55×10^{-07}	1.25×10^{-06}	2.04×10^{-08}	98%	1.31×10^{-01}	1.87×10^{-06}
magnetite stall concentration $C_m [mol L^{-1}]$	8.46×10^{-03}	2.50×10^{-02}	2.70×10^{-03}	89%	3.20×10^{-01}	1.27×10^{-06}
magnetite threshold $k_{mgc_thres} [mol L^{-1}]$	8.12×10^{-04}	2.50×10^{-03}	1.35×10^{-04}	95%	1.66×10^{-01}	2.65×10^{-06}
mackinawite oxidation $k_{FeS_{ox}} [mol^{0.61} L^{-0.61} s^{-1}]$	-7.48×10^{00}	1.00×10^{00}	5.63×10^{-02}	94%	7.52×10^{-03}	4.30×10^{-06}
microbial sulfate reduction $k_{QML_sulfate} [s^{-1}]$	9.34×10^{-06}	2.50×10^{-05}	7.39×10^{-07}	97%	7.92×10^{-02}	5.36×10^{-06}
microbial ferrirhydrite reduction $k_{QML_Fh} [s^{-1}]$	1.54×10^{-05}	2.50×10^{-05}	9.74×10^{-07}	96%	6.33×10^{-02}	6.42×10^{-06}
ferrirhydrite reduction by sulfide $k_{sulfide_Fh} [mol^{0.5} L^{-0.5} s^{-1}]$	7.22×10^{-07}	2.50×10^{-06}	2.97×10^{-07}	88%	4.12×10^{-01}	3.64×10^{-07}
siderite dissolution and precipitation $k_{siderite} [mol L^{-1} s^{-1}]$	2.99×10^{-07}	2.50×10^{-06}	5.65×10^{-07}	77%	1.89×10^{00}	5.98×10^{-08}
$Fe_3O_4As_2O_5(s)$ fraction in magnetite [unitless]	5.83×10^{-04}	1.50×10^{-02}	3.44×10^{-04}	98%	5.91×10^{-01}	3.23×10^{-07}
$Fe_3O_4As_2O_5(s)$ fraction in magnetite [unitless]	7.52×10^{-05}	1.50×10^{-02}	3.27×10^{-04}	98%	4.35×10^{00}	4.23×10^{-08}
Exchange Species [mol L⁻¹]						
EX sites	2.00×10^{-02}	3.25×10^{-03}	1.31×10^{-03}	60%	6.57×10^{-02}	5.47×10^{-07}
Surface Site Densities [mol of sites per mol of mineral]						
neoformed magnetite by nitrate-Fe(II) injection (Mgt_w)	2.99×10^{-02}	4.90×10^{-02}	3.47×10^{-02}	29%	1.16×10^{00}	4.50×10^{-07}
neoformed ferrirhydrite by nitrate-Fe(II) injection (Hfo_w)	1.07×10^{-01}	7.25×10^{-02}	4.53×10^{-02}	38%	4.23×10^{-01}	4.08×10^{-07}
natural ferrirhydrite in unamended Dover sediments (Fh_w)	3.02×10^{-02}	4.98×10^{-02}	1.32×10^{-02}	73%	4.38×10^{-01}	1.24×10^{-06}
natural goethite in unamended Dover sediments (Gt_w)	3.33×10^{-03}	2.50×10^{-02}	1.79×10^{-03}	93%	5.38×10^{-01}	2.05×10^{-06}

^aThe upper and lower bounds for each parameter during automatic calibration are selected based on literature data and expert knowledge. The exchange site was implemented with reactions based on the standard PHREEQC database and listed in Table S1. The stoichiometries and constants (logKs) of surface complexation reactions are given in Tables S1 and S2.