



Microbial reductive transformation of iron-rich tailings in a column reactor and its environmental implications to arsenic reactive transport in mining tailings

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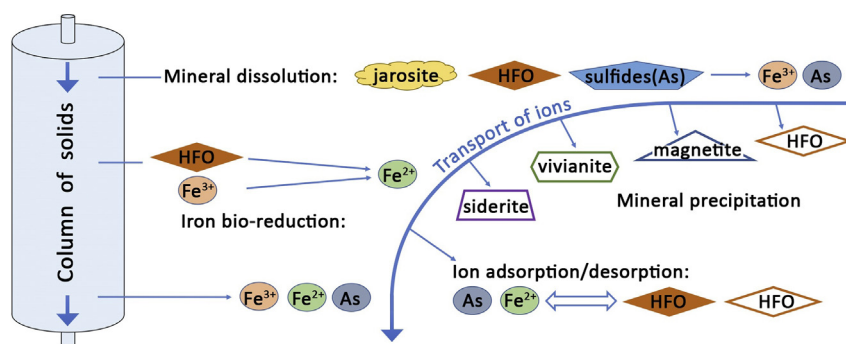
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HIGHLIGHTS

- Advective flow with reductive bacteria in tailings induces Fe-minerals transformation and As transport.
- Microbial iron reduction decomposes Fe^{3+} minerals in oxidized tailings and releases Fe^{2+} ions.
- Jarosite is decomposed while other iron oxides are newly formed in reaction column.
- Reactive transport model agrees with lab results of As release, transport and immobilization.

GRAPHICAL ABSTRACT



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ABSTRACT

The evolution of iron minerals under buried conditions is one of the most important processes controlling the mineral composition and heavy metal transportation in sediments. Microbial-mediated reduction plays a critical role in iron mineral transformation in natural environment. This study examined the transformation pathways of iron minerals mediated by bacteria and the changes of associated arsenic species in iron-rich mine tailings. Static and column reactions were designed to monitor variations of minerals and released iron and arsenic, a reactive transport model was simulated to support laboratory results. Laboratory experiments showed that major ferric minerals were preferentially dissolved and reduced by dissimilatory iron-reducing bacteria. The released Fe^{3+} in fluid promoted oxidative dissolution of pyrite and arsenopyrite, and precipitation of oxides and carbonates. The arsenic released to fluid was inferred to be immobilized by both pristine ferrihydrite and newly formed hydrous ferric oxides via surface complexation. The reaction system maintained a steady-state of iron mineral transformation and arsenic (im)mobilization. In the latter stage of column reactor experiments, continuous reaction and removal of dissolved Fe^{3+} and Fe^{2+} destabilized the state, leading to arsenic re-location and eventually rising concentration in fluid. The findings implicate that microbial-mediated iron mineral evolution remarkably influence the natural mineral assemblages and the fate of contaminant transport in the environment, and that deposition of iron oxides is essential in environmental protection and pollution recovery.

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1. Introduction

Iron-containing minerals are ubiquitous in various natural systems and industrial facilities. In these systems, iron (Fe) is present at both Fe(II) and Fe(III) valence states, and occurs in the forms of iron sulfides, iron (hydro)oxides, sulfates, carbonates, phosphates, silicates, and so on (Allard et al., 2002; Duckworth et al., 2009; Granina et al., 2004; Hansel et al., 2001; Noubactep, 2015; Perret et al., 2000). These minerals have great potential to incorporate toxic metals, for example, arsenopyrite host both Fe and As in its crystal structure, ferrihydrite adsorb heavy metals (e.g. As, Cu, and Pb) due to its great surface area (Brümmer et al., 2013; Duan et al., 2019; Karapinar, 2016; Li et al., 2017; Meng et al., 2014; Uddin, 2017; Zhu et al., 2010). They take part in iron cycling via dissolution, precipitation, as well as iron redox processes (Chen et al., 2011; Duan et al., 2019; Mattisson et al., 2004; Patrick and Jugsujinda, 1992; Rawson et al., 2016; Schippers and Jørgensen, 2002). The formation and decomposition of these iron minerals not only dictate iron pathways but also influence mobility of heavy metals (Guo et al., 2016; Warner et al., 2012; Zhu et al., 2015; Zou et al., 2016). These processes occur in environmental systems such as soil systems, aquifer sediments, and mining areas (Duan et al., 2019; Li et al., 2017; Lindsay et al., 2015; Lu and Wang, 2012), among which mining environments provide unique conditions to research iron cycling and heavy metal transport. These researches will have implications for diagnosing potential contamination to the surrounding environments.

In sulfide mines, numerous iron minerals at different redox levels are exploited and disposed of to the surroundings (Lindsay et al., 2015; Lu and Wang, 2012). In exposed sulfide mining areas, acid mine drainage (AMD) is produced due to microbial-chemical oxidation of the sulfide minerals, the AMD in turn facilitates intensive release of iron and heavy metals to waters (Dopson and Johnson, 2012; Hallberg et al., 2010; Lu and Wang, 2012). As the water seeps through solid materials and reduce acidity, iron and heavy metals will likely be immobilized. Moving further deep into the buried tailings, iron will be present in reduced forms due to low levels of oxidizing agents. In addition, microbial activities are discovered to participate in iron redox processes in environments including groundwater aquifer, mining areas, and benthic systems (Kappler and Straub, 2005; Lovley et al., 2004; Weber et al., 2006). The comprehensive iron mineral species and intensive microbial activities in sulfide mining areas make it a critical location to study and unravel microbial-chemical-mediated mineral speciation as well as heavy metal mobility.

Previous studies have proposed mechanisms for microbial reduction and oxidation of iron minerals. Microbial oxidation of iron minerals has been studied in-depth since 1950s (Bryner and Jameson, 1958). Pathways of electron transport and mineral transformation have been discovered and coupled direct-indirect contact mechanisms have been proposed to explain iron sulfide oxidation mediated by microbial activities (Corkhill et al., 2008; Sand et al., 2001; Schippers and Sand, 1999). Dissimilatory iron reduction was proposed to explain microbial activities in iron reduction under buried environments, where anaerobic bacteria acquires energy via reducing Fe(III) (Lovley, 1991; Lovley et al., 2004). In particular, *Shewanella oneidensis* MR-1 is well-known for its iron reduction capacity and its ubiquitous distribution in natural environments (Hansel et al., 2003; Lovley, 1991; Lovley et al., 2004). During dissimilatory reduction of Fe(III) minerals by *S. oneidensis* MR-1, a variety of secondary minerals are produced, with examples including green rust, goethite, magnetite, siderite, and vivianite (Hansel et al., 2003; Ouyang et al., 2014). These secondary minerals have great potential to sequester heavy metals and influence both iron and contaminant behaviors.

Reported studies on microbial-mediated iron mineral transformation are mainly focused on the following aspects. 1) Iron redox pathway for single minerals (Hansel et al., 2003; Li et al., 2016; Ouyang et al., 2014); 2) The influences of various factors (e.g. temperature, pressure, presence of other chemicals) on the redox processes (Clément et al.,

2005; Guo et al., 2010; Han et al., 2018; Picard et al., 2012; Wang et al., 2018); 3) Isotope fractionation (Guo et al., 2013; Heimann et al., 2010; Percak-Dennett et al., 2011); 4) Bacteria, protein, and genome identification (Beblawy et al., 2018; Gescher et al., 2008; Kulichevskaya et al., 2014; Ross et al., 2009). The evolution of buried natural iron minerals as well as heavy metal transport patterns under the influence of bacteria, especially dissimilatory iron reducing bacteria, are seldom discussed. One good example of such research is by Sun et al. (2018), whose work was model-based and dominated by injection of nitrate-Fe²⁺ fluid. Their results provided useful parameters and references for further research. By employing the published parameters, we intend to study the reactions that are controlled by activities of *Shewanella oneidensis* MR-1 and monitor the changes of ferrous ions and arsenic. Specifically, we propose to investigate the microbial-mediated evolution pathways of iron-rich mine tailings, and determine its impact on heavy metal transport.

In this study, we designed static and column reactor batch experiments to 1) identify natural iron mineral evolution pathways under the effects of microbial activities in anoxic and buried conditions; and 2) determine the distribution and fates of aqueous iron species as well as hazardous arsenic during iron mineral transformation. 3) A reactive transport model using the PHREEQC program was also conducted to explore and predict the unmeasured results and controlling processes.

2. Materials, experiments and methods

2.1. Field sampling

Iron-rich mine tailings were sampled from unlined wastewater impoundments on the Yangshanchong tailings dam at the Dongguashan Cu-Au mine in Tongling, Eastern China (30°54.483'N 117°53.643'E). Each individual impoundment is about 0.5 m deep and 5 m wide. Water samples were collected in 5 L polypropylene buckets from the center of impoundments, filtered through a 0.22 µm membrane to remove solids and bacteria, and stored at 4 °C. Solid samples were also collected in 1 gal polyethylene ziploc bags from the tailing profiles at the bottom of the impoundments, freeze-dried, and stored at 4 °C. Solid samples were autoclaved prior to use in static and column experiments described in Section 2.3.

The solid samples collected from the mine tailings are rich in quartz, jarosite and goethite, and contain very small percentages of ferrihydrite, pyrite, arsenopyrite, and possibly chalcopyrite (See Fig. S1 in supporting information (SI)). Among these minerals, pyrite, arsenopyrite and chalcopyrite are pristine ore minerals. After exposure to the air and water, part of the sulfide minerals underwent (microbial-mediated) oxidation, and transformed into secondary minerals such as jarosite, ferrihydrite, and goethite (Lu and Wang, 2012). Some secondary minerals like ferrihydrite and amorphous iron oxides are unstable in natural environment and thus transformed to more stable forms, such as jarosite and goethite. As a result, the abundances of the more stable jarosite and goethite in final products of sulfide weathering are relatively high. Arsenic could be accommodated in these secondary minerals, such as oxides, sulfate, arsenates and amorphous Fe-As minerals (Lu and Wang, 2012; Zhu et al., 2015).

In the water collected from the AMD impoundment, the elemental composition is Al 214.07 ppm, As 1.45 ppm, Co 0.61 ppm, Cu 24.99 ppm, Fe 245.88 ppm, Mg 116.22 ppm, Mn 33.21 ppm, Ni 0.59 ppm, P 0.86 ppm, Si 47.17 ppm, and Zn 46.23 ppm. The high concentration of Fe in the wastewater is in accordance with the iron-rich mineral composition in the mine tailings. It is unclear about the transformation pathways of the secondary iron minerals and arsenic transport patterns in mine tailings under fluid. We address these questions with observations from static and column experiments as described in Section 2.3.

2.2. Bacteria and medium

This study chose *Shewanella oneidensis* MR-1 as the iron reducing bacteria. *Shewanella oneidensis* was first isolated from sediments of Lake Oneida in New York State (Arnold et al., 1990; Myers and Nealson, 1990, 1988). It is a facultative anaerobic gamma proteobacteria that couples the incomplete oxidation of lactate to acetate with Fe(III) reduction.

Defined-minimal medium (DM medium) (Myers and Nealson, 1988) was used throughout the experiment. The medium ingredients include: 1.2 g/L $(\text{NH}_4)_2\text{SO}_4$, 1 g/L K_2HPO_4 , 0.4 g/L KH_2PO_4 , 0.17 g/L NaHCO_3 , 0.25 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.072 g/L $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, trace elements (0.2 mg/L MnCO_3 , 1 mg/L $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 0.28 mg/L ZnCl_2 , 0.8 mg/L $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 3.5 mg/L H_3BO_3 , 1 mg/L $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.05 mg/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.2 mg/L Na_2SeO_4 , and 22 mg/L Na_2EDTA), and amino acid solution (20 mg/L L-arginine hydrochloride, 20 mg/L L-glutamate, and 20 mg/L L-serine). A 15 mM sodium lactate was added as electron donor, 10 mM NaHCO_3 was added as pH buffer. The medium was autoclaved and purged with N_2 for 5 min prior to inoculation to eliminate dissolved oxygen.

2.3. Experimental design

Two types of experiments were designed: 1) static batch experiment and 2) column reactor experiment. Static batch experiment consisted of four condition combinations - anaerobic condition with only mine tailings (short for Anaero-Taili), with only bacteria (short for Anaero-Bio), and with both mine tailings and bacteria (short for Anaero-Taili-Bio); aerobic condition with both mine tailings and bacteria (short for Aero-Taili-Bio). Each condition had two identical parallel experiments. The reaction took place in 500 mL conical flasks with 0.5 g iron-rich mine tailings added in 250 mL sterile DM medium, the experiments with bacteria were inoculated *Shewanella oneidensis* MR-1 at a density of $\sim 10^7$ cell/mL. Solutions were sampled throughout the experiment to examine the stage of reactions. At the end of 30-day reaction, the solids were harvested for further analysis.

The column reactor experiments included two types of reactions: one with the presence of bacteria (short for Flow-taili-Bio) and the other is a blank control (short for Flow-Sedi). The reaction happened inside of a vertical column by continuously pumping DM medium at a steady rate of 0.2 mL/min. The DM medium for Flow-taili-Bio experiment was inoculated with $\sim 10^8$ cell/mL bacteria. The vertical column was made of glass, 24 cm in length and 3 cm in inner diameter, with 5 sample-lets evenly spaced along one side of the column. For a reaction column, an inlet connecting to source medium was designed at the bottom and an outlet connecting to waste sink was designed at the top (see diagram of column design in Fig. 1). Each of the columns was filled with 375 g of the iron-rich mine tailings collected from sulfide mine impoundments and 36 mL fluid was added. Prior to reaction, the medium was pumped for 12 h in order to stabilize the solid-fluid system in each column reactors. The medium fluid was pumped from the bottom to the top of the vertical column in order to reduce fluid distribution heterogeneity across the solids. Because the rates for diffusion of ions and relocation of particles are negligible compared to the flow rate, the profiles of the columns in this study with flow direction that go from bottom to top will resemble that of a transport from top to bottom in homogeneous and saturated solids. In the Results section, we explain data in a normal buried order (outlet at the bottom and inlet at the top) so that the interpretation of the experiment is consistent with common understanding of leaching transport and simulations in later sections. Throughout the reaction, fluids were collected from each sample-let. The rest of the fluid running through the solids was collected daily at the end of the columns. This cumulative fluid represented the general trend of the solution across the reaction period, and was therefore referred to as “bulk fluid” in the Results section. The remaining solids were collected at the end of the 20-day experiment.

2.4. Analytical methods

All fluid was filtered through a 0.22 μm membrane during sampling prior to measurement. Concentrations of Fe^{2+} and Fe^{3+} was measured following o-phenanthroline method (Harvey et al., 1955) as described in Ouyang et al. (2014). The concentration of As was tested by an Optima 5300DV inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer, San Diego, USA). The number of active bacteria was counted in fluid under a CKX41SF OLYMPUS inverted biological microscope (Ouyang et al., 2014).

The solids before and after experiments were analyzed for surface morphologies, elemental valence state and mineral compositions. The reacted solids were observed using a JSM-6490 scanning electron microscope coupled with energy dispersive spectrometer (SEM-EDS) (JEOL Ltd., Tokyo, Japan). A PHI 5000 VersaProbe X-ray photoelectron spectroscopy (XPS) (UIVAC-PHI, Japan) was employed to examine the valence states of iron in reacted solids (see details in Ouyang et al., 2014). The mineral composition was determined by ARL X'TRA X-ray diffraction (XRD) (Thermo Electron, Switzerland) and JY HR800 Raman spectroscopy (Jobin Yvon, France). The XRD spectra were further analyzed using Rietveld refinement in the MAUD software, with calculated errors approximately 2.00% (Lutterotti et al., 1999).

2.5. Modeling of the column reaction

The geochemical software PHREEQC (Parkhurst and Appelo, 2013) was used to simulate bio-mediated mineral dissolution-precipitation and reactive transport of aqueous species across the columns during continuous pump of flow. The simulation was referred to as reactive transport model in this study and incorporated the following processes: 1) Dissolution-precipitation kinetics of the major iron minerals, including jarosite, goethite, ferrihydrite, and magnetite; 2) Oxidative dissolution kinetics of arsenopyrite by dissolved Fe^{3+} ; 3) Bio-reduction kinetics of ferrihydrite; 4) Surface complexation of arsenic to available ferrihydrite binding-sites; and 5) fluid transport. Reaction kinetics of siderite was not included in the simulation because siderite was not detectable from XRD results; with published parameters, siderite did not precipitate over the experimental period either. Over the course of this experiment, ferrihydrite is the predominant Fe(III)-mineral for dissimilatory iron reduction, thus only ferrihydrite bio-reduction kinetics was considered in the model. Total Fe concentration was calculated by summing the released Fe from all Fe-containing minerals. Total arsenic concentration was composed of the arsenic from both arsenopyrite and As-containing iron (hydr)oxides (e.g. ferrihydrite, magnetite, goethite), which was suggested to contain approximately 0.3% As in the mine tailing environment (Zhu et al., 2013). Detailed parameters were chosen from published studies via trial-and-error simulations and were listed in Table 1. The reactions and thermodynamic parameters of arsenic were extracted from the PHREEQC llnl database, all other parameters were supported by the PHREEQC minteq.v4 database.

3. Results

3.1. Results from static experiment

The static experiment showed intensive iron mineral reduction mediated by microbial activities. The concentrations of Fe^{2+} in anoxic experiment inoculated with bacteria (anaero-taili-bio) was approximately 3 times higher than that for other experiments after reaction for 10 days (Fig. 2a). Despite the same phenomenon observed for Fe^{3+} in anaero-taili-bio experiment, the Fe^{3+} concentration quickly dropped to less than half of its peak value (Fig. 2b). The variation in Fe^{2+} and Fe^{3+} concentrations suggested that bacteria dominated iron mineral reduction under anoxic conditions and thus released both Fe^{2+} and Fe^{3+} ions to solution. The released Fe^{3+} was re-precipitated rapidly after day 13, but the decline in Fe^{2+} concentration was gentle and was in accordance with the

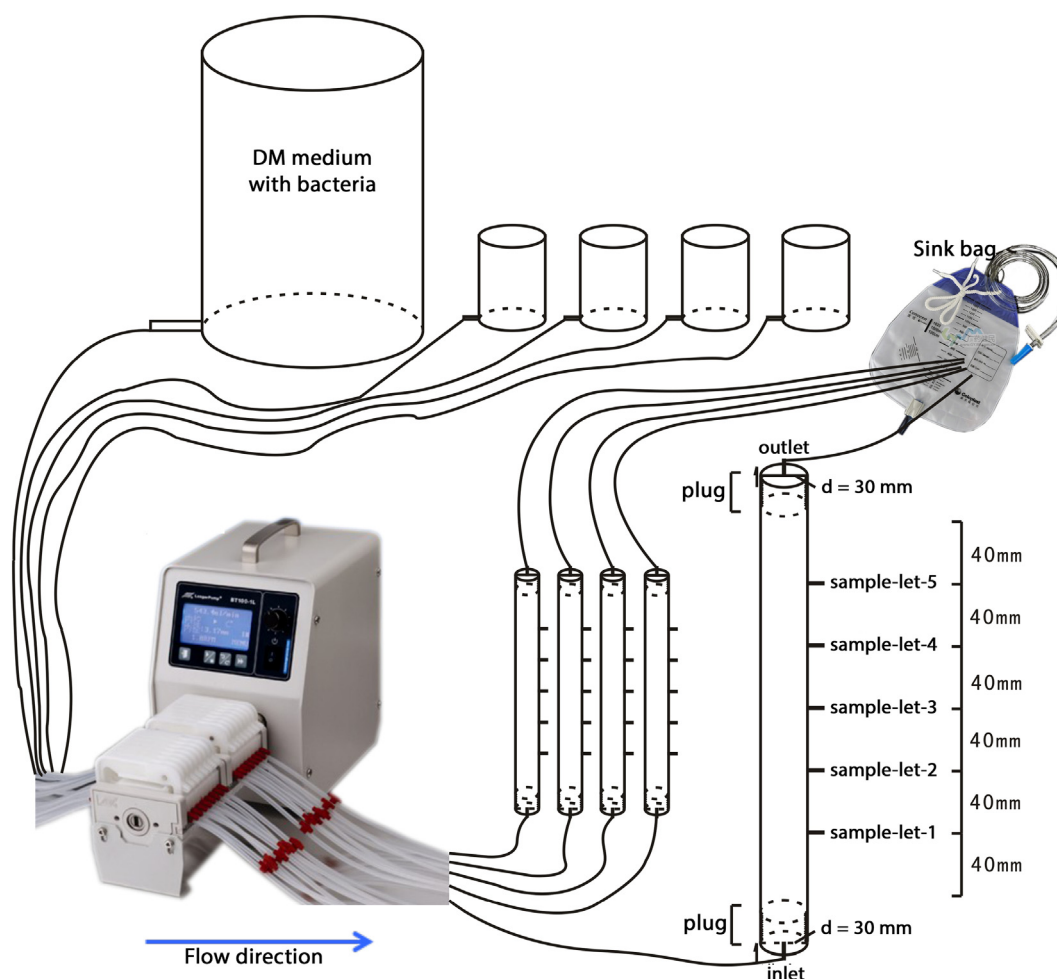


Fig. 1. Diagram of the designed column reactor.

activity of bacteria (Fig. 2d). Arsenic, on the other hand, was continuously released in anaero-taili-bio experiment during the entire reaction period, indicating that effective immobilization of arsenic did not happen immediately after the formation of new iron minerals (Fig. 2c).

New minerals were observed in the experimental samples after microbial-mediated iron reduction. On the 20th day of reaction, needle aggregates of goethite (Fig. 3a) and elongated vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$) (Fig. 3b) were observed in anaero-taili-bio experiment. Interestingly, most of the bacteria were observed to attach onto Fe(III) minerals originally present in the mine tailings (Fig. 3c). The

SEM observations demonstrated that both Fe^{2+} and Fe^{3+} ions were able to precipitate as new minerals (Fig. 3a and b), while the more stable minerals (e.g. goethite) were observed at the end of reaction (Fig. 3d).

3.2. Results from column reactor experiments

3.2.1. Release of Iron and arsenic into bulk fluid

Column reactor experiments were designed to investigate the mineral evolution and ion re-distribution throughout a column of solids when fluids were continuously pumped. The variation of Fe^{2+} , Fe^{3+}

Table 1
Kinetic parameters, rate expression and surface site densities used in the reactive transport model.

Parameter type	Unit	Value	Rate expression ^a	References ^b
Goethite, diss/precip, k	mol s^{-1}	2.78×10^{-10}	$r = k \times (1 - \Omega)$	1
Magnetite, diss/precip, k	s^{-1}	1.16×10^{-7}	$r = k \times C_{\text{Fe}^{2+}} \times (1 - \Omega)$	2
Jarosite, diss/precip, k_{H^+}	$\text{mol m}^{-2} \text{s}^{-1}$	3.26×10^{-7}	$r = (k_{\text{H}^+} \times \alpha_{\text{H}^+}^{0.899} + k_{\text{H}^+} \times \alpha_{\text{H}^+}^{0.899}) \times 3 \times S \times (1 - \Omega)$	3
Jarosite, diss/precip, k_{OH^-}	$\text{mol m}^{-2} \text{s}^{-1}$	1.09×10^{-11}		
Ferrihydrite, diss/precip, k	s^{-1}	3×10^{-5}	$r = k \times C_{\text{Fe}^{3+}} \times (1 - \Omega)$	4
Ferrihydrite, bio-reduction, k_{lactate}	s^{-1}	1.54×10^{-5}	$r = k \times C_{\text{lactate}}$	5
Arsenopyrite, oxidative dissolution, k	$\text{mol m}^{-2} \text{s}^{-1}$	9.33×10^{-8}	$r = k \times C_{\text{Fe}^{3+}}^{0.49} \times S \times (1 - \Omega)$	6
Pyrite, oxidative dissolution, k	s^{-1}	1×10^{-6}	$r = k \times C_{\text{Fe}^{3+}} \times (1 - \Omega)$	7
Ferrihydrite, site density, weak sites	Sites mol^{-1}	0.2	–	8
Ferrihydrite, site density, strong sites	Sites mol^{-1}	0.005	–	8
Ferrihydrite, specific surface area	m^2/mol	64,200	–	8

^a Variables used in rate expression: Ω - Saturation ratio of a mineral phase. C - Concentration of an aqueous species. α - Activity of an aqueous species. S - Initial surface area of a mineral (m^2/mol), $S_{\text{jarosite}} = 5000$, $S_{\text{arsenopyrite}} = 320$.

^b References: 1. Cheah et al., 2003; 2. White et al., 1994; 3. Elwood Madden et al., 2012; 4. Rose and Waite, 2003; 5. Sun et al., 2018; 6. Lengke et al., 2009; 7. Fowler et al., 2001; 8. Dzombak and Morel, 1990.

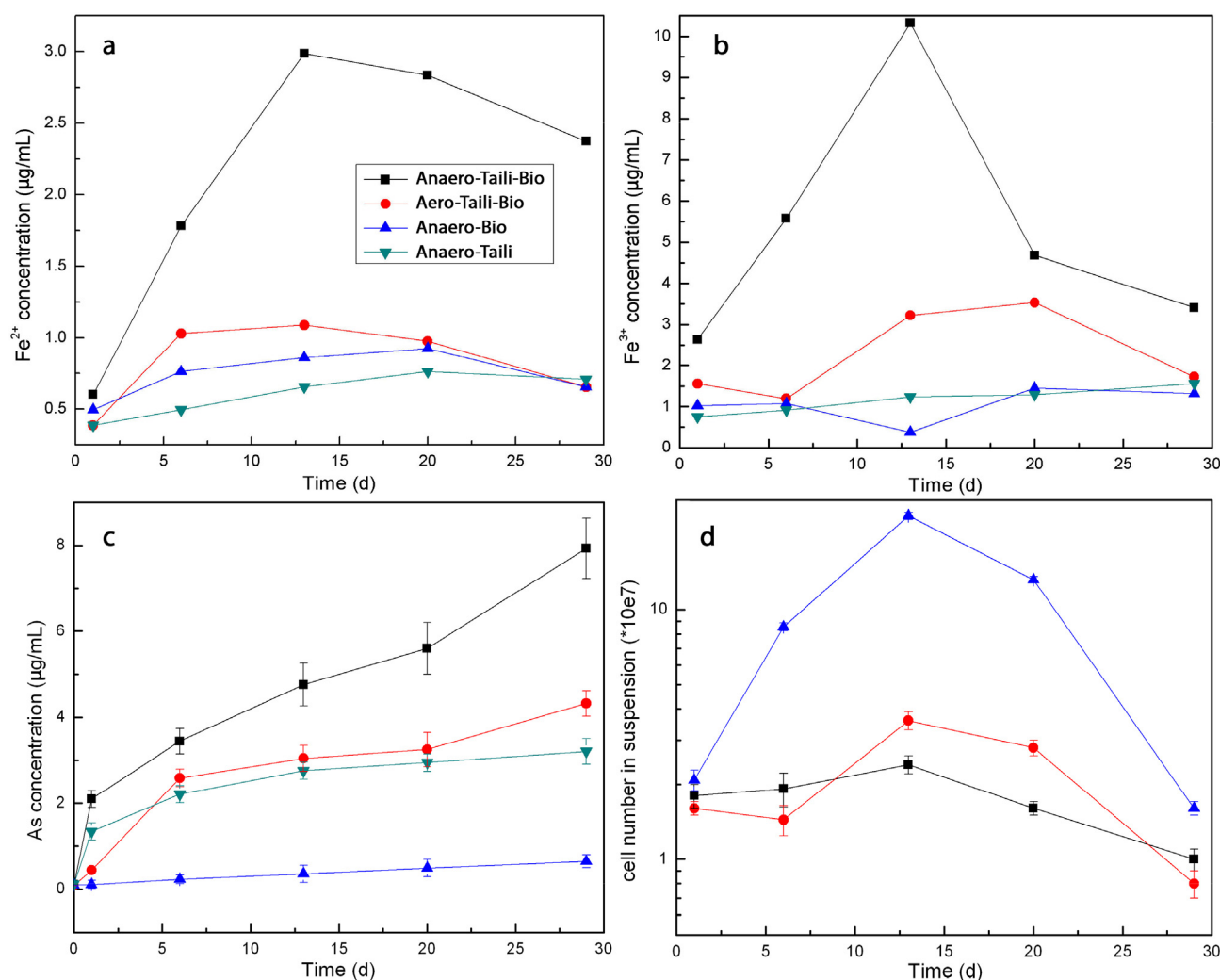


Fig. 2. Concentrations of (a) Fe^{2+} ions, (b) Fe^{3+} ions, (c) total As, and (d) bacterial cell counts in solution over the course of static reaction.

and arsenic in the bulk fluid collected at the end of the column reactor explained the dissolution of minerals over the reaction process. The concentrations of Fe^{2+} and Fe^{3+} in the bulk fluid peaked around the 8th–10th day of reaction, and then decreased over the rest of reaction days (Fig. 4a and b). The processes influencing Fe^{3+} concentration include release of Fe^{3+} from minerals, Fe^{3+} reduction, Fe(III) -mineral precipitation, and Fe^{3+} flush-out by pumping. The increase of Fe^{3+} in the bulk fluid before day 10 demonstrated that the rate of Fe^{3+} release overtook the sum of the other processes. After the peak day 8, Fe^{2+} decreased drastically signaling the start of reduced supply of Fe^{3+} in fluid, this signal was reflected in the decreased Fe^{3+} concentration two days later. Arsenic concentrations continued to increase throughout 12 days of reaction, suggesting that even though iron (hydro)oxides were able to remove arsenic from solution by adsorption, continuous input of fresh medium still rigorously flushed arsenic out from solid forms (Fig. 4c). After this process, arsenic left in the solid reduced significantly, resulting in the decreased arsenic concentration in the bulk fluid. By the 20th day, the majority of solid form iron and arsenic were removed from the column reactor system. This process simulated the accelerated reactive transport of iron and arsenic mediated by microbial activities in iron-rich environment.

3.2.2. Migration of Iron and arsenic in column reactor

Iron was continuously released to fluid and re-precipitated over the course of the flow reaction (Fig. 5). The concentration of Fe^{3+} in fluid increased along the column, indicating that the cumulative processes of

mineral dissolution and transport of Fe^{3+} overtook the rate of Fe^{3+} reduction and precipitation (Fig. 5a). On the other hand, the peak value of Fe^{2+} concentration in fluid shifted from the outlet of the column to near the inlet within 10 days of flow reaction (Fig. 5b). This observation implied that part of the released Fe^{3+} was reduced to Fe^{2+} in fluid, followed by transport and accumulation of Fe^{2+} , and formation of Fe(II) -containing minerals (e.g. magnetite and siderite, see details in Section 3.2.3). The formation of Fe(II) -containing minerals resulted in reduced Fe^{2+} concentration in fluid at the earlier sample-lets observed before day 10 (Fig. 5b). In contrast, control experiments without microbial activities showed minimal variation in Fe concentrations.

Arsenic migration followed the release and precipitation pattern of iron (Fig. 5c and d). On the 3rd and 5th day of reaction, arsenic concentration initially increased along the column and then reduced at the latter sample-lets. This phenomenon is in accordance with the results for solids (see details in Section 3.2.3), newly formed goethite and ferrihydrite at the latter sample-lets provided great surface areas to adsorb arsenic and thus reduce arsenic concentration in fluid. Interestingly, arsenic concentration continued to increase till the end of the column on the 10th day of reaction, which is suggestive of reduced adsorption capacity of the iron minerals for arsenic ions. Note that as flow continues, the un-precipitated Fe^{2+} and Fe^{3+} in fluid were flushed out of the column reactor system (Fig. 4), resulting in decreased total iron minerals. Less iron minerals and continuous flow together led to the increased arsenic concentration on the latter half of column reaction.

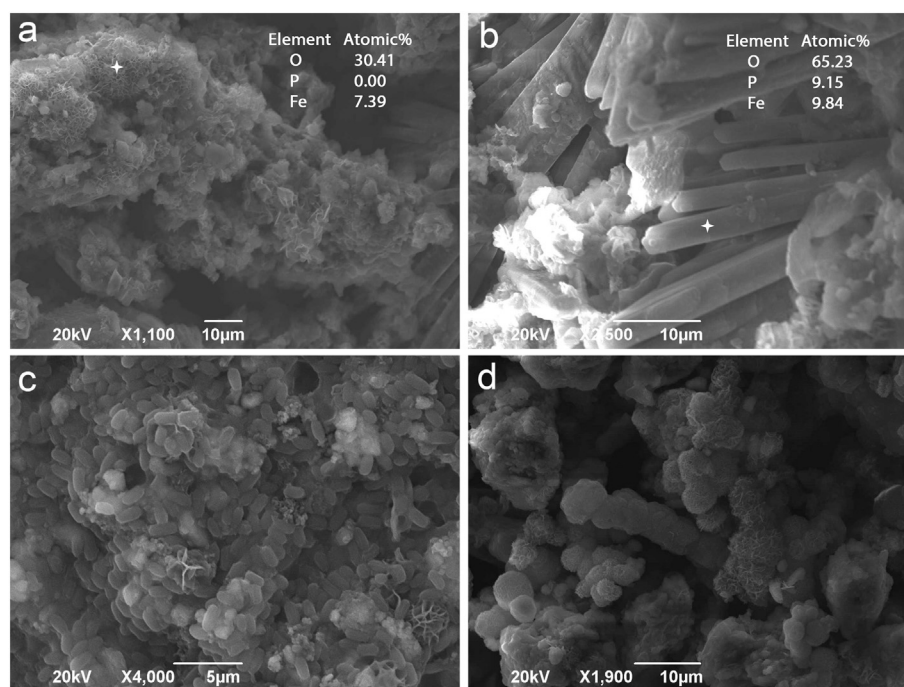


Fig. 3. SEM images of Anaero-Taili-Bio static experiment showing (a) goethite and (b) vivianite formed after reaction for 20 days, (c) original Fe(III) minerals almost completely covered with bacteria cells (short rod particles) and (d) newly crystallized goethite after reaction for 30 days. + indicate locations conducted EDS measurements, elemental compositions were given at the top-right corner of corresponding images.

3.2.3. Variation of solid composition across the column reactor

Compositions of major iron minerals varied across the column after reaction for 20 days in Flow-Taili-Bio experiments. Mineral transformation across the profile at sample-lets 1–5 was summarized in Fig. 6a. The total weight percentages of major minerals in the solids were calculated using MAUD software (Lutterotti et al., 1999). The weight percentages of jarosite in the solid decreased from ~19% at the beginning of the column (sample-let-1) to ~16% at the end (sample-let-5). This suggested that although jarosite was initially present in the mine tailings as a Fe (III) source, it was not reduced by bacteria at the start of the flow. Jarosite weight percentage at sample-let-5 being close to that of pristine mine tailings further supported this argument. Instead, goethite was suspected to be preferentially dissolved and transported at the location close to inlet. As the flow transport from the inlet to the outlet, bacterial iron-reducing capability declined along the column. Goethite weight percentage at latter sample-lets (e.g. sample-let-4) therefore remained

higher than sample-let-1, whereas jarosite weight percentage at latter sample-lets was smaller than sample-let-1. Notice that goethite weight percentage at sample-let-4 is even higher than that of pristine mine tailing sample, which indicated that goethite was precipitated in the flow process. Similarly, ferrihydrite was formed at the latter phase of the flow process. Due to the large specific surface area of goethite and ferrihydrite, their formation provided large quantity of adsorption sites to sequester heavy metals as described in 3.3 and 4.2.

Relative abundance of Fe(II) and Fe(III) species along the column of reacted solid were determined by XPS analysis (Fig. S2) and summarized in Fig. 6b, in order to overcome the drawback of Fe(II) minerals being non-detectable by XRD when crystalline structures were not clearly-defined or concentrations were too low. In the pristine mine tailings, approximately 99% of iron minerals are composed of Fe(III) forms (Fig. 6b). As flow continues, the relative quantity of Fe(III) minerals decreased with the increase of Fe(II) minerals (Fig. 6b). Note that although

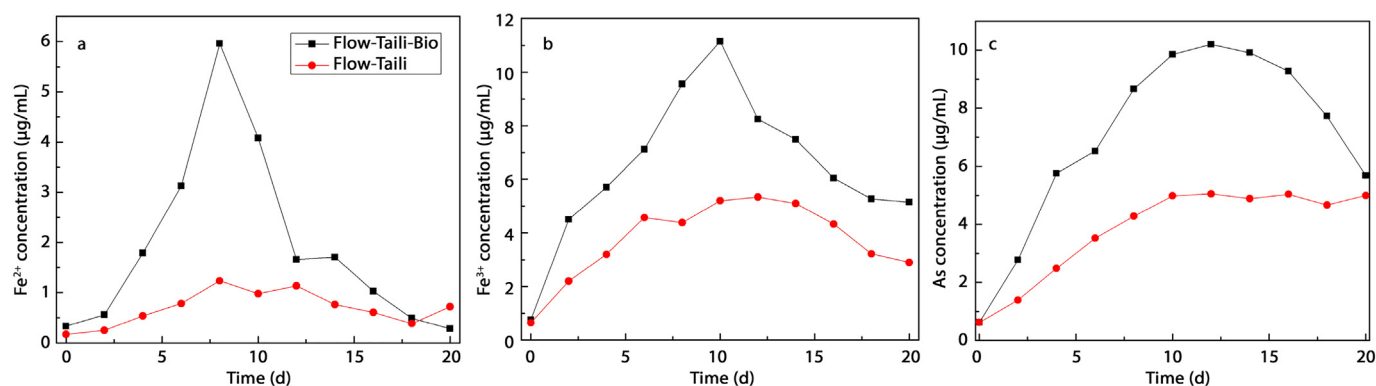


Fig. 4. Concentrations of (a) Fe²⁺, (b) Fe³⁺, and (c) total arsenic in bulk fluid collected at the end of the column reactors.

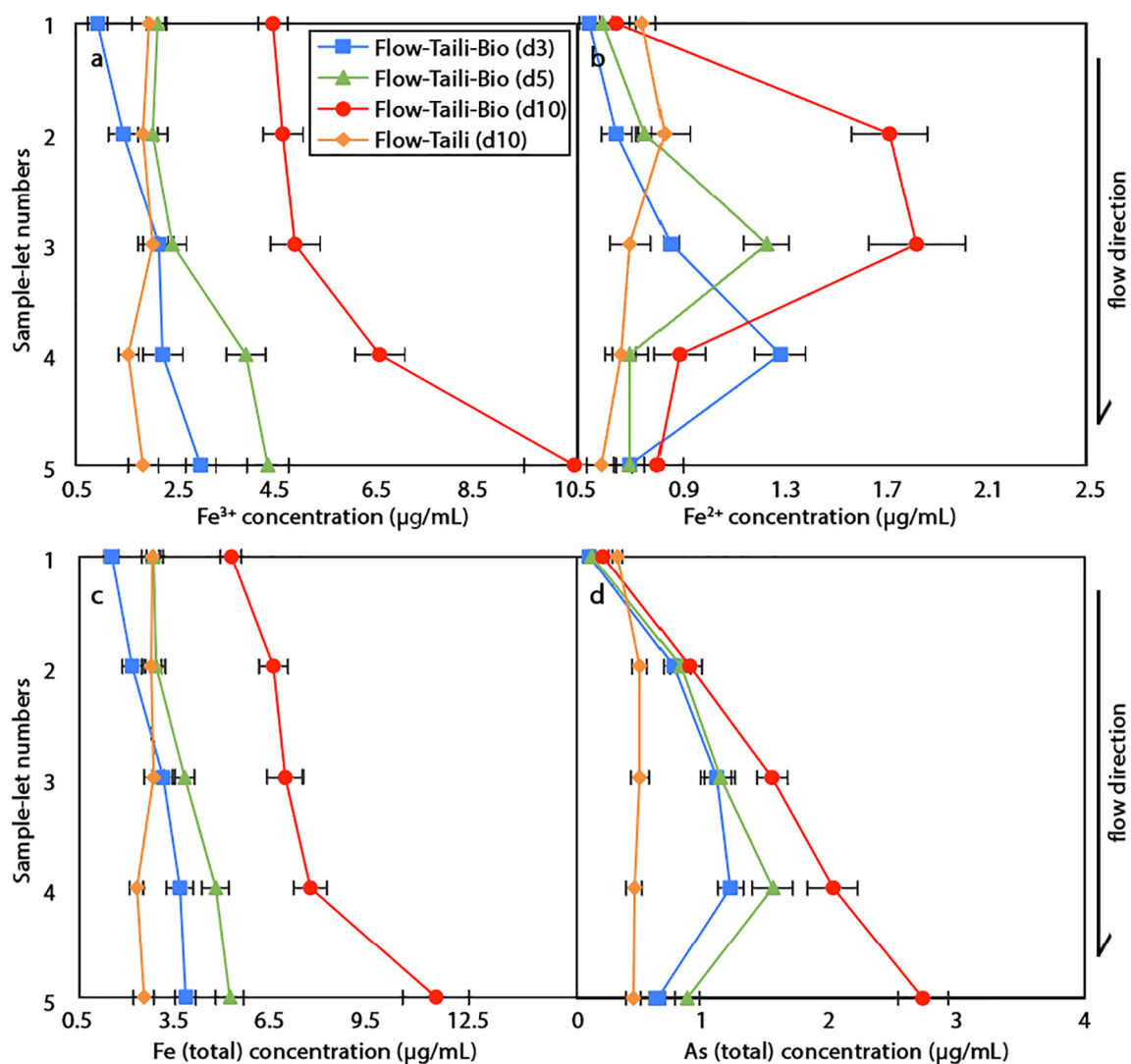


Fig. 5. Profiles describing variation of (a) Fe^{3+} , (b) Fe^{2+} , (c) total Fe, and (d) total arsenic concentrations in fluid across the column.

the consumption rates of Fe(III) minerals are high close to the inlet (e.g. sample-let-1 in Fig. 6), the Fe(III) minerals are still relatively abundant. This is because new Fe(III) minerals such as ferrihydrite likely formed

immediately after generation of Fe^{3+} ion. Closer to the outlet (e.g. sample-let-5 in Fig. 6), the proportions of Fe(III) and Fe(II) species changed to 91.20% and 8.80% respectively, which suggested formation

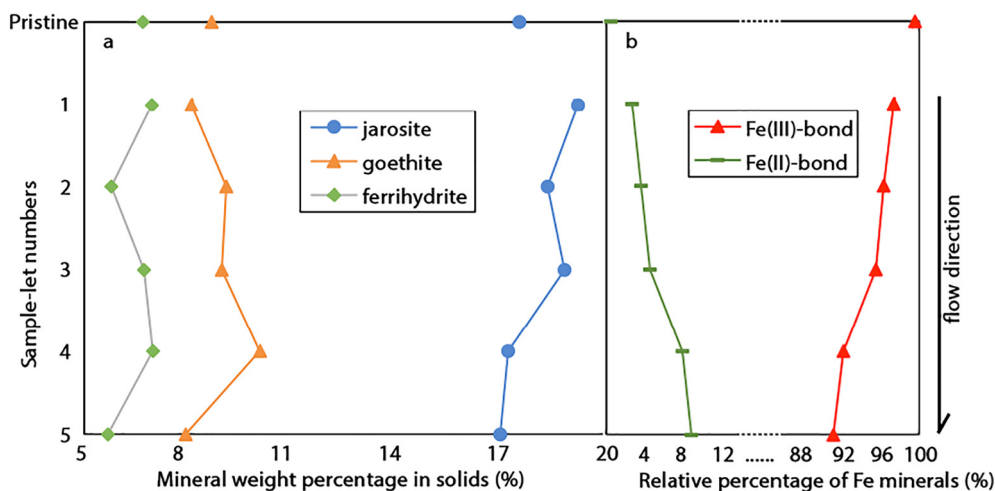


Fig. 6. Profiles describing variation of (a) major Fe(III) minerals and (b) relative percentages of Fe(II)/Fe(III) bonding across the column of solid samples for Flow-Taili-Bio experiment at the end of 20-day reaction.

of Fe(II) minerals there. This profile of iron minerals indicated that large quantities of dissolved Fe(III) and Fe(II) were transported along the column and probably partly precipitated at a distance from the inlet.

3.3. Reactive transport model

The trends of solution variations simulated using PHREEQC program were in line with observations of the column reactor experiments (Figs. 7 and 8). For clarity in presentation, this section only shows simulation results for experiments inoculated with bacteria. Results for control experiments are provided in SI, in which the values of Fe and As release are significantly lower than those of the experiments with microbial activities (Fig. S3), but the general trends are similar for microbial and control experiments (Fig. S3 and S4). In experiments with microbial activities, the peaks of total Fe and total As concentrations shifted from the beginning to the end of the reaction column (Fig. 7), supporting the aforementioned progressive mineral dissolution pattern with increasing depth of reaction column (Fig. 5). At the latter stage of the simulated reactive transport, e.g. day 10 to day 40, total released Fe notably reduced compared to day 8, indicating the dissolution rates of iron minerals were overtaken by the rate of Fe transport and precipitation (Fig. 7a). Consequently, large quantities of arsenic was released to fluid (Fig. 7b). The weight percentages of goethite and ferrihydrite remained unchanged with reaction time before day 10, which is supportive of the coupled dissolution and re-precipitation process. Jarosite demonstrated continuous decrease in weight percentage across the column and along the reaction period. In the end, the relative weight percentages of jarosite and ferrihydrite decreased drastically, whereas the decline in goethite weight percentage is minimal. These observations suggested that jarosite and ferrihydrite were the major net Fe providers in reactive transport.

4. Discussion

4.1. Evolution of iron minerals

Evolution of iron minerals was dictated by the types and rates of different processes in experiments. The static experiments are closed reaction systems, where the major processes include mineral dissolution, precipitation and bio-reduction. The column reactor experiments happened in open systems, where the losses of both pristine and secondary minerals should be considered. In the closed static systems, the secondary minerals include iron oxides and trace amount of vivianite (Fig. 3). Similar minerals are found in secondary products in the column system (Fig. S1). The major difference between the static and column experiments is that the static system represents long-term reactions (e.g. dissolution, reduction, and precipitation) in closed systems while these reactions were controlled by flow dynamics in the initial stage of column system.

In a column of iron-rich natural solids, the dissolution and precipitation of major iron minerals varied at three stages of flow reaction. At the first stage from day 0 to day 10, Fe(III) minerals such as jarosite, ferrihydrite and goethite were dissolved rapidly due to chemical and microbial activities (Fig. 8). The initial dissolution of these minerals accumulated high concentrations of Fe^{3+} . Meanwhile, part of the released Fe^{3+} was reduced by iron-reducing bacteria to generate Fe^{2+} (Gescher et al., 2008; Ouyang et al., 2014, 2013) and by oxidative dissolution of As-containing minerals (e.g. arsenopyrite, arsenite) to generate arsenic ions (Corkhill et al., 2008). With the continuously flowing fluid, the released Fe and As ions were transported further away from the inlet by continuously flowing fluid as shown in Fig. 5. At this point, the reaction proceeded to the second stage by precipitating intermediate ferrihydrite and goethite minerals at where with high Fe^{3+} concentrations (Cheah et al., 2003; Dzombak and Morel, 1990; Hansel et al., 2003; Ouyang et al., 2014). Because forming goethite, magnetite and ferrihydrite were relatively fast processes (from seconds to weeks), and immediately precipitated crystals were unstable and required aging processes to stabilize and grow the minerals (Hiemstra, 2018; Sun et al., 2018; Vodyanitskii, 2010; Yee et al., 2006), they are relatively easy to dissolve and to adsorb Fe and As ions. Compared with jarosite and arsenopyrite, these minerals can be referred to as relatively unstable minerals. At this stage, amount of ferrihydrite remained unchanged due to its balanced dissolution and precipitation rates. At the third stage of flow reaction, extent of jarosite and arsenopyrite dissolution were enhanced due to their increased specific surface area and continuous transport of dissolved iron from near inlet to near outlet. Such transport accumulated dissolved ions and triggered the precipitation of the relatively unstable minerals (e.g. ferrihydrite, goethite) at different locations across the column as demonstrated in Fig. 6. Although both dissolution and precipitation still occurred in this stage, precipitation rates declined and dissolution started to dominate. As reaction continues, the relative abundance of jarosite noticeably decreased at the inlet compared to goethite and ferrihydrite. In the end, large quantities of aqueous Fe and As were transported outside of the column system, and mineral amounts continued diminishing. In addition to the previously described processes, other bacteria (e.g. *Acidithiobacillus ferrooxidans*) (Li et al., 2016; Lu and Wang, 2012) might also exist in the original tailings, taking part in reactions and influencing the behavior of ions throughout these stages.

4.2. Mobilization and transport of arsenic

Two major processes dominated the transport of arsenic: dissolution of arsenic-containing minerals and arsenic surface complexation. Dissolution of arsenic-containing minerals (i.e. As-containing oxides and sulfates, amorphous Fe-As (hydr)oxides, and arsenopyrite) was directly related to the rate of Fe^{3+} accumulation in fluid, which was controlled by 1) dissolution and 2) precipitation rate of Fe(III)-minerals, as well

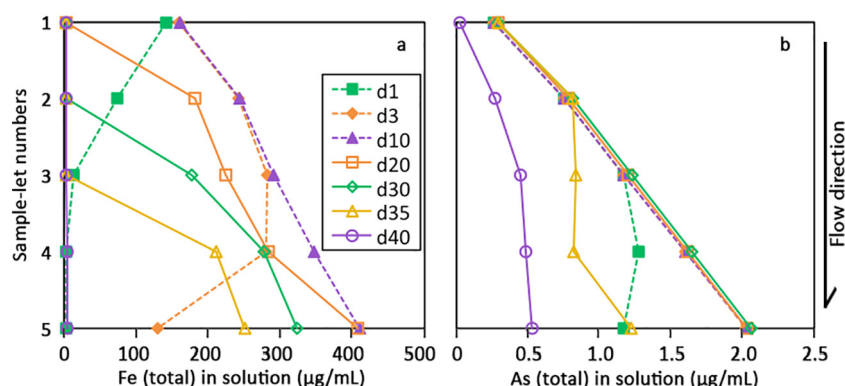


Fig. 7. Simulated profiles of released concentrations for (a) total iron and (b) total arsenic in fluid across column reactions for experiments with bio-reduction.

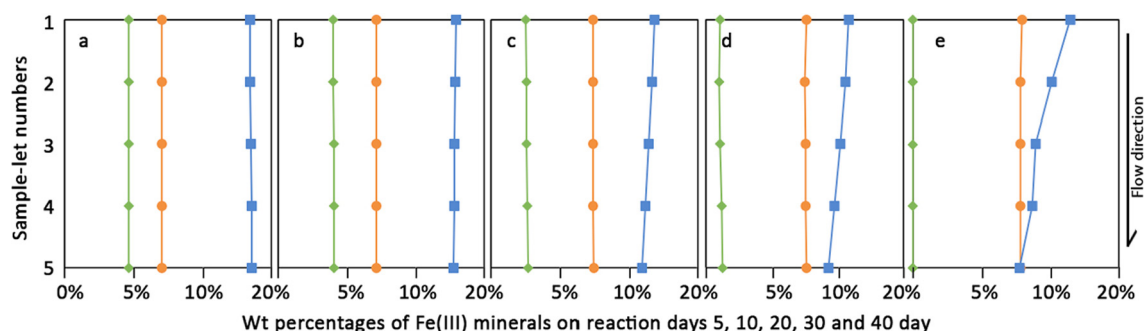


Fig. 8. Simulated profiles of relative percentages of major Fe(III) minerals on a) day 5, b) day 10, c) day 20, d) day 30, and e) day 40 across the column of solids for experiments with bio-reduction. ♦ represents ferrihydrite, ● represents goethite, and ■ represents jarosite.

as 3) Fe^{3+} bio-reduction rate. Because current understanding on As quantification in oxides, sulfates, and amorphous minerals are limited, only dissolution kinetics of arsenopyrite and small amount of iron hydr(oxides) are calculated in the reactive transport model. The dissolved arsenic is therefore biased to a lower value compared to lab experiments. Arsenic surface complexation was influenced by the available binding-sites in hydrous ferric oxides (HFO). The common HFO includes ferrihydrite, pre-mature goethite and magnetite (Sun et al., 2018). In this experiment, ferrihydrite is considered as the dominant HFO. The HFO surfaces also have great tendency to complex with Fe^{2+} and Fe^{3+} ions (Benjamin, 1983; Hiemstra and van Riemsdijk, 2007; Tanwar et al., 2009, 2008). Therefore, arsenic surface complexation was controlled by 1) dissolution and 2) precipitation rate of ferrihydrite, and 3) the un-occupied binding-site from earlier stages.

These major processes dominated arsenic re-distribution across the column. Arsenic was removed from minerals that were close to the inlet of a column, and was re-distributed to minerals that were near the outlet. Since the major As-source (e.g. arsenopyrite and As-containing oxides/sulfates) was dissolved, part of the arsenic in fluid was immediately adsorbed to HFO (e.g. ferrihydrite) surfaces. When the dissolved arsenic was accumulated and the majority of the HFO sites were occupied, arsenic was carried along the flow and adsorbed by HFO beneath the saturated layer. This process continued and resulted in the re-location of arsenic from near the surface to further depth (e.g. sample-let-4). Until all available HFO sites were bound with arsenic, mobile arsenic would stay in flowing fluid and be removed from the column system.

4.3. Comparison of the laboratory, simulated and natural systems

The laboratory and simulated results are based on simplified systems with extremely favorable conditions. Compared with natural systems, the major differences in conditions include three aspects. First, the fluid flowed in only one direction at a constant rate in the laboratory and simulated experiments; but in natural systems, the fluid flows at multi-dimensions and at varying rates (Pei et al., 2010; Warrick, 1991), which slow down the rates of reaction along the depth of a natural system. Second, the laboratory and simulated experiments only investigated the activity of one bacteria strain in mineral bio-reduction processes, however, there usually exist a variety of bacteria species in natural systems (Cluff et al., 2014; Dopson and Johnson, 2012; Kim, 2003; Ouyang et al., 2017). As a result, the presence of different bacteria species may compete for nutrients with and reduce the effectiveness of iron reducing and/or oxidizing bacteria, and the most effective bacteria may not be concentrated to achieve the optimum extent of reaction. Third, the laboratory and simulated experiments were conducted as open systems with loss of Fe and As continued throughout the reaction period, whereas natural systems can vary from closed to semi-open conditions where dissolved ions are partly trapped in the systems and do not dissipate for a long period. Thus, dissolution of minerals in closed

to semi-open natural systems is not as sufficient as in open experimental systems. Instead, the laboratory and simulation results are comparable to the long-term weathering results for natural systems. In addition, the parameters used in simulations are empirical results retrieved from past studies (Cheah et al., 2003; Dzombak and Morel, 1990; Elwood Madden et al., 2012; Fowler et al., 2001; Lengke et al., 2009; Rose and Waite, 2003; Sun et al., 2018; White et al., 1994), whose conditions (e.g. ionic strength, crystallinity) may differ greatly from this work, resulting in unforeseen bias and uncertainties. Therefore, the results for laboratory and simulated systems are conducted at favorable conditions and achieved with errors.

4.4. Environmental implications

This study revealed the heavy metal transport pathways during leaching of iron-rich mine tailings under buried conditions. In mining environment, mine tailings are often incompletely oxidized (Lu and Wang, 2012). In the burial of these incompletely oxidized mine tailings, iron minerals transformed from oxidized to relatively reduced states. Transformation of iron minerals results in release and re-immobilization of heavy metals. During transformation of iron minerals, dissolution and dissimilatory iron reduction release large amounts of Fe^{3+} and Fe^{2+} , which participate in oxidative dissolution of minerals with low valence state elements (e.g. pyrite, arsenopyrite, and chalcopyrite) and formation of intermediate and/or new iron minerals. Examples of intermediate and new minerals include ferrihydrite, goethite, magnetite, siderite, and vivianite, and so on. Heavy metals that are released during mineral dissolution are partly adsorbed to HFOs (e.g. ferrihydrite, goethite, and magnetite). As natural water penetrates through depth of iron-rich mine tailings, more released Fe^{3+} and Fe^{2+} will promote HFO precipitation, allowing for more heavy metal adsorption and aging to mature/stable minerals (Meng et al., 2014). At this point, the mining environment has the capacity to maintain a steady circulation that heavy metals are released from near surface minerals, but then adsorbed and/or fixed to HFOs precipitated at further deep locations. In this relatively closed reducing environment, heavy metals are released due to transformation and redox processes. The released heavy metals are immobilized via adsorption onto HFOs, which maintains stable net concentrations of metal ions and therefore does not severely affect the environment. However, once the balanced system is disrupted and starts to lose iron minerals, the environment will inevitably become contaminated by continuous release of heavy metals. Therefore, preservation of iron-rich solids is a lasting strategy for environmental protection.

5. Conclusion

In this study, iron mineral transformation coupled transport of dissolved Fe and As species under the influence of microbial activities was investigated using static, column reactor experiments and a PHREEQC reactive transport model. Both experimental and numerical

modeling results show the release and then decrease of aqueous Fe and As, the consumption of original Fe(III)-minerals, and formation of secondary minerals.

The changes in aqueous ions and mineralogy are summarized in both spatial and temporal aspects. Spatial-wise, most of the dissolution happen near the start of a reactive transport. The released aqueous Fe and As are transported and accumulated at the latter part of the transport, where precipitation of secondary minerals (HFOs such as magnetite, goethite, and ferrihydrite) and aqueous As adsorb to HFOs. Temporal-wise, major Fe(III)-minerals – jarosite, ferrihydrite and goethite – are dissolved in the first place, and intensive dissimilatory iron reduction happens afterwards. Later, accumulated aqueous Fe precipitate to form secondary minerals (HFOs), which then enhance the adsorption of As to HFOs. In the end when continuous flow removed large quantities of Fe^{3+} and Fe^{2+} from the system, HFOs are no longer sufficient for As adsorption, and As become released and transported out of the system. Throughout the reaction, changes in flow rates and reaction time will influence the extent of mineral dissolution and transformation. These experiments showed microbial-mediated iron mineral transformation processes and contaminant transport pathways under buried conditions, and the results provided scientific basis for environmental protection and restoration.

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Appendix A. Supplementary data

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