



The As behavior of natural arsenical-containing colloidal ferric oxyhydroxide reacted with sulfate reducing bacteria



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GRAPHICAL ABSTRACT

Collection of arsenical sediment from Shimen Realgar Mine, Changde City, Hunan province, China, September 2016.



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ABSTRACT

The extensive mining activities in Shimen realgar mine have generated large amounts of secondary arsenical ferric oxyhydroxides. The reductive dissolution of these tailing sediments at the soil/water interface influences the behavior of arsenic (As). Here, the dynamics of As in these flooded high arsenic tailing sediments at circumneutral pH conditions were investigated by employing a pure culture of a sulfate reducing bacteria (SRB). Changes in Eh, pH, aqueous Fe(II) and As speciation were monitored over 6 days in batch experiments. Our results demonstrated that SRB was able to reductively dissolve high levels of arsenical ferric oxyhydroxide. The results showed that reactions with aqueous As(III) and As(V) presented different trends, with As(III) (80–100% of total As) being the dominant arsenic species. Aqueous As behavior showed two distinct stages, firstly, the As (V) was released and immediately reduced to As(III) by biogenic sulfide. Next, the released As was removed from the solution by adsorption onto newly formed nano-Fe sulfides (e.g. FeS, FeS₂) or co-precipitation with S(-II) to produce nano arsenic sulfide (As₃S₂). In addition, the addition of sulfate, calcium and sodium lactate played different roles in the release of As. Addition of sulfate and sodium lactate can trigger the release of arsenic, while calcium caused the opposite effect.

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1. Introduction

Arsenic (As) pollution is an increasing worldwide concern because of the adverse impact of its toxic, carcinogenic and teratogenic properties have on human health [1–3]. The behavior and transport of As in tailing sediments are closely related to environmental conditions (e.g. Eh, pH, ionic competition) and microbial activities [4]. The predominant form of dissolved and adsorbed As in oxidizing conditions is arsenate [As(V) as H_2AsO_4^- and HAsO_4^{2-}], while arsenite [As(III) as H_3AsO_3^0 and H_2AsO_3^-] prevails under reducing conditions commonly found in anaerobic water-logged tailing sediments [5]. Microbes like anaerobic metal-reducing bacteria play an important role in controlling As geochemistry in these environments. For instance, As(V)-reducing bacteria like *Sulfurospirillum arsenophilum*, *Bacillus* sp., *Citrobacter* sp. are capable of reducing As(V) to the more mobile and toxic As(III) coupling the oxidization of organic carbon and enhancing As mobility in sediment-water systems [6–10]. In addition, iron (Fe) cycling is also an important process affecting arsenic transport. Reductive dissolution of iron (hydr)oxides (the main absorbents of As [11,12]) by dissimilatory Fe(III)-reducing bacteria (e.g. *Geobacter metallireducens*, *Shewanella oneidensis*) under anoxic conditions can also result in the release of sorbed As.

Dissimilatory sulfate-reducing bacteria (SRB) are ubiquitous in acid mine drainage (AMD) under anoxic conditions and profoundly affect biogeochemical cycling of As [13,14]. The fate of arsenic in anoxic sulfidic flooded soils (e.g. floodplain sediments, shallow and intermediate aquifer sediments, paddy soils, coastal wetlands, water/soil interface) has received a great deal of attention [10,15–18]. Many laboratory studies explored the correlation between sulfate reduction and As mobilization in these reducing conditions, which indicate that SRB plays an important role in the dynamic of As [13]. The reductive dissolution of As-bearing Fe(III) oxyhydroxysulfates and hydroxides (e.g. schwertmannite and ferrihydrite) may result in the release of structurally incorporated or surface adsorbed As [13,19,20]. Simultaneous, the sulfide produced by SRB can potentially promote the reduction of As(V) to As(III), which can precipitate as arsenic sulfide phases (realgar (AsS) and orpiment (As_2S_3)), or form soluble thio-As species when the As concentration at equilibrium, thus increasing or decreasing As mobilization and immobilization [21–23]. The formation of various secondary minerals (e.g. siderite, vivianite, green rust, magnetite or mackinawite), can also sequester As via precipitation, adsorption or structural incorporation into these newly formed minerals, and constrain As release, further complicating the system [14,24,25]. Therefore, sulfate reduction by SRB plays a key role in the biological cycling of As. Detailed investigations of the effect of sulfate addition on arsenic behavior are already reported elsewhere [13,26–28]. With seemingly contradictory observations reported in As mobilization under different sulfate levels, our study aims to help elucidate the effect of sulfate on the reductive dissolution of these high arsenic ferric tailings.

The Shimen Realgar Mine in China has been in operation for approximately 1500 years and was once one of the largest realgar supplier in Asia until its closure in 2011 [29,30]. The basic rock in the mine is composed of dolostone, limestone, while the main As-bearing minerals are orpiment and realgar formed by shallow low-temperature hydrothermal veins. Intensive mining and ore processing activities at this site has generated a large amount of As-rich wastes, which posed a great threat to local environment [31,32]. Poisoning from As in this region was reported as early as 1990s and once described as a “Disaster Village”. A previous investigation indicated different types of As-bearing secondary minerals were present in the mine tailings, including arsenic oxides, sulfur-bearing arsenates, As-gypsum, and As-Fe minerals [29]. Mobilization of As from these secondary As-bearing minerals is not yet fully understood. Some research have systematically investigated the biodiversity of Shimen realgar mine tailings, which indicated that this area had unique microbial communities that were different from other arsenic-contaminated sites [32,33]. *Proteobacteria*, *Actinobacteria*,

Bacteroidetes, *Chloroflexi*, *Acidobacteria*, and *Planctomycetes* are the dominant microbial phyla; and this site also contains other microorganisms. Microbes such as metal-reducing bacteria, metal-oxidizing bacteria and sulfate reducing bacteria (SRB) are commonly found in this realgar tailing mine [33,34]. To date, knowledge about how microbial sulfidogenesis influences the coupled geochemistry of Fe and As of many synthetic As-bearing iron (hydr)oxide has come largely from laboratory-based soil/sediment incubations [13,17,35,36]. However, there are currently few (if any) corresponding studies examining the interaction of natural secondary arsenical sediments and microbial activities under sulfidic aerobic condition, especially regarding As speciation, which is of great importance to the distribution and geochemistry of the Shimen area. In this study, we have collected representative secondary As samples containing high concentrations of arsenic and sulfate from the Shimen realgar mine to study the fate of arsenic in flooding reducing conditions. As SRB coexists with these tailing sediments, as indicated by previous studies [32], microbial reduction of sulfate may naturally occur at the sampling site. We have also investigated this effect by simulation of indigenous sulfate reducing bacteria to give insight into the As distribution of these secondary As minerals.

The objectives of this work are to:

- 1) investigate the coupling release and reduction mechanism of As, Fe by pure SRB using batch incubation experiments;
- 2) determine the effect of additional sulfate, calcium (the main ion in the surface water of the tailing sediments) and sodium lactate on the release of arsenic at an abandoned tailing pond (Shimen Realgar Mine, Changde City, China).

2. Sample collection, preparation and experimental procedure

2.1. Sediment collection

The sediments were derived from an abandoned tailing pond (Fig. 1) at the Shimen Realgar Mine, Changde City, Hunan province, China, the Asian largest realgar deposit (Zhu et al., 2013). The sampling site was located at 29°38'52.3" N, 111°01'58.24" E. The rationale for choosing this particular sampling site was its close proximity to farmlands and springs, making the reductive dissolution tailing sediments pose a huge contamination. The tailing sediments were collected in December 2016. Sample collection involved careful transferring sediments directly from the pond by hand while wearing a plastic glove to sterile polyethylene plastic cans (1 L). The samples were transferred to the laboratory where sediments were kept at 4 °C for less than 2 days until the geochemical analysis were performed. The initial physico-chemical characteristics of the surface water of the tailing sediments



Fig. 1. Collection of arsenical sediment from Shimen Realgar Mine, Changde City, Hunan province, China, December 2016.

including pH, cation concentration and SO_4^{2-} were analyzed as described in section 2.4. The sediments were freeze-dried under vacuum environment (LABCONCO, FreeZone) and sieved to less than 100 mesh ($< 180 \mu\text{m}$). The main elemental compositions of the sieved tailing sediment were measured using X-ray fluorescence (XRF, PANalytical BV) analysis.

2.2. Bacterial culture

The SRB (*Desulfovibrio vulgaris miyazaki* SRB), used in this study, was isolated from abandoned mine tailings in Sichuan province, China. Prior to the bioreduction experiments, the bacteria were cultured in neutral liquid medium-63 of DSMZ containing per liter: 2.0 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 2.0 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 2.0 g DL-Na-lactate, 1.0 g Yeast extract, 1.0 g Na_2SO_4 , 1.0 g Resazurin, 0.5 g K_2HPO_4 [37]. The SRB were incubated for 7 days to logarithmic growth phase at 30°C in an anaerobic chamber.

2.3. Bioreduction experiment and sampling

50 mL SRB grown culture (biomass density $\sim 2 \times 10^7$ cfu/mL) was isolated by centrifugation (10,000 r/min, 10 min) for each trial. The supernatant at each step was removed. The residues were washed, and transferred to the amended buffer: 20 mM 1,4-piperazine-diethanesulfonic acid (PIPES), 1 L media of 1.0 g NH_4Cl , 5.0 g NaCl , 0.1 g CaCl_2 , 0.1 g KCl , and 10 mL each of modified Wolfe's vitamins and trace minerals [38,39]. The pH was adjusted to 7.0 using 1 M KOH . To simulate wet/flooding conditions, the washed cells were re-suspended in the amended buffer mixed with sample at a liquid/solid ratio of 10/1 (2.0 g sample, 20 mL amended buffer) in a series of 50 mL polypropylene vials. The biotic treatment was divided into four groups: the first group had 10 mM sodium lactate added; the second group had 4 mM sulfate, 10 mM sodium lactate added; the third group had 10 mM calcium and 10 mM sodium lactate, while 100 mM sodium lactate was added to the fourth group. The concentration of sulfate and calcium were determined by their concentrations in the surface water of the tailing sediments. Control samples that did not contain bacteria were also prepared and were herein termed abiotic treatments. All chemicals were of reagent grade and the buffer sterilized before use in the following experiments. All tests were conducted in triplicate with headspaces being flushed with N_2 prior to anaerobic incubation at 30°C for 144 h in a rotary shaker. The average result of the triplicate measurements was reported. Sampling of each system (2 mL each time) was collected at intervals of 0, 1.5, 24, 48, 96, 120, and 144 h. The supernatants were filtered ($0.22 \mu\text{m}$) for analysis of aqueous Fe(II) , As(V) and As(III) (see below). The redox potential (Eh) and pH were also monitored at each sample interval. Selected samples from reduction experiment (72 h, 144 h) were dried under O_2 -free conditions, finely ground, and stored within butyl-rubber sealed glass vials for further analysis.

2.4. Aqueous analysis

The cation (Ca, Fe, As, Al, Sb, Se, K, Mn, Mg, Si, U) and SO_4^{2-} on surface water of the tailing sediments were quantified using Inductive

Coupled Plasma Emission Spectrometry (ICP-AES, iCAP6500 Thermo Fisher) and Ion chromatography (IC, Metrohm, 881 Compact pro).

The quantification and specification of aqueous arsenic was performed via hydride generation-atomic fluorescence spectrometry coupled with high-performance liquid chromatography (HPLC-HG-AFS, Titan, China). The experimental conditions were as follows: an phosphate buffer solution (pH 6.0, $(\text{NH}_4)_2\text{HPO}_4$) was used as the mobile phase, anion separation column (Hamilton PRP-X100) to separate different arsenic species, KBH_4 in 3.5 % (m/v) KOH as reductant, highest purity Ar (0.3 Mpa) as gas carrier. Arsenic compounds were quantified by external calibration with standard solutions (0, 10, 25, 50, and $70 \mu\text{g/L}$) of As(III) , As(V) , DMA and MMA. The detection limit was $0.5 \mu\text{g/L}$, and concentrations of MMA and DMA were below this limit. Dissolved Fe(II) concentrations were determined using the ferrozine method using an Evolution 3000 UV-visible spectrophotometer at a wavelength of 510 nm [40]. Finally, the pH and Eh were measured inside the anaerobic chamber using a HACH440d meter with freshly calibrated platinum electrode (MTC 10103).

2.5. Solid-phase characterization

Mineralogical analysis of the dried tailings sediment samples was carried out using X-ray diffraction (XRD) analyses using a PANalytical X'Pert PRO X-ray diffractometer with a $\text{Cu-K}\alpha$ radiation at 15 kV, 40 mA, 2θ from 10° to 80° with scan and time step increments of 0.03° and 10.16 s, respectively.

The morphology and elemental composition in a selected area of solid particles were observed by EVO@18 Scanning Electron Microscopy associated with an energy-dispersive-X-ray-spectroscopy (SEM-EDX). The samples were mounted on pin stubs by use of double-sided carbon tape and sputter-coated with gold, and imaged at 15 kV.

The chemical analysis of species of As and Fe were analyzed by X-ray photoelectron spectroscopy (XPS, VG-ScientaR 3000). The XPS spectra were obtained with a monochromated $\text{Al-K}\alpha$ X-ray source, with an analyzer pass energy of 30 eV and a step size of 0.05 eV.

Attenuated total reflection (ATR) Fourier transform infrared spectroscopy analysis of the dried tailing sediment and post-reduction sediment were performed using with a Perkin-Elmer Fourier Transform Infrared Spectrometer (FTIR) coupled with a diamond attenuated total reflection (ATR) accessory. Spectra were collected in a range of $400\text{--}4000 \text{ cm}^{-1}$ with a spectral resolution of 1 cm^{-1} and 64 scans per sample.

3. Results and discussion

3.1. Characterization of the sediment

The tailing sediments sampled at the Shimen Realgar Mine were reddish brown in appearance. The surface water was slightly acidic (pH = 6.58), and As, Ca, Mg, K, Si and SO_4^{2-} concentrations were 0.4, 411, 14, 3.8, 2 and 402 mg/L , whereas Al, Sb, Se and U concentrations were less than 0.01 mg/L . The main elemental properties of the sediments as determined by XRF analysis were summarized in Table 1, it can be seen that the tailing sediments contained high concentrations of Fe (292 mg/g), S (101 mg/g), Ca (159 mg/g), As (36.6 mg/g). The

Table 1
The XRF results of the tailing sediment.

Elements	Concentration (wt%)	Elements	Concentration (wt%)	Elements	Concentration (wt%)
Fe_2O_3	41.78	SiO_2	1.8	BaO	0.04
SO_3	25.32	TiO_2	0.78	P_2O_5	0.02
CaO	22.28	MnO	0.29	K_2O	0.02
As_2O_3	4.83	Al_2O_3	0.27	ZnO	0.02
MgO	2.48	SrO	0.05	Cl	0.02

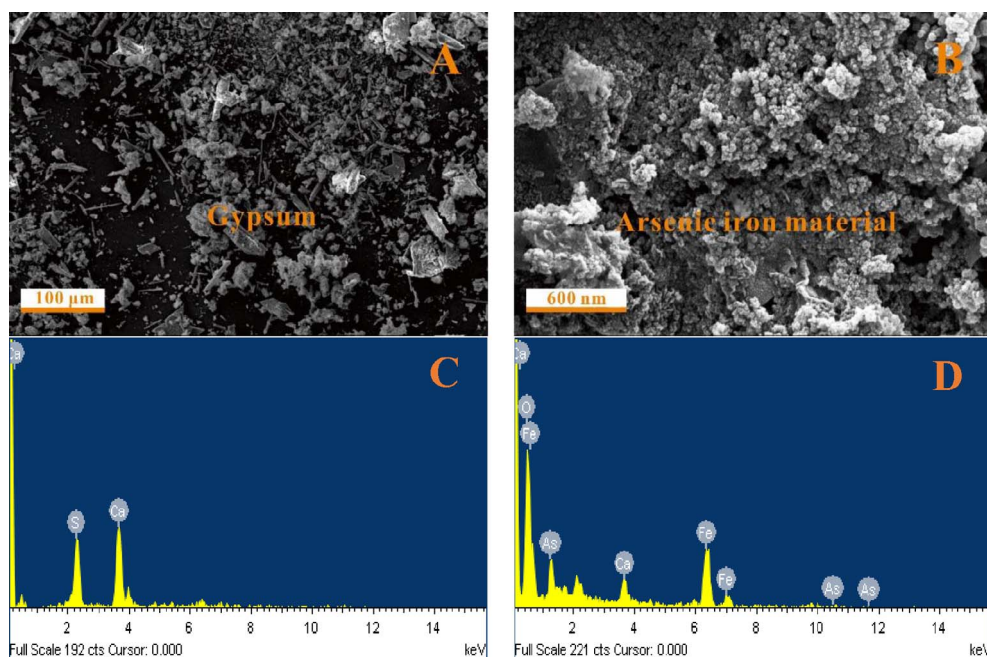


Fig. 2. SEM (A, B) and EDX (C, D) analyses of the tailing sediments in Shimen realgar mine.

sediments were confirmed as mostly gypsum and some amorphous arsenical iron materials by XRD (no data were shown) and SEM-EDX results (Fig. 2). The XPS results showed that the valence of Fe and As of dried tailing sediments were Fe(III) and As(V), respectively (no data were shown).

3.2. FTIR analysis

The infrared spectra of the products obtained from the reaction of the sediment (72 h, 144 h) with SRB in anaerobic condition were compared with the primary sediment in Fig. 3. The stretching and bending vibration regions of As–O ($730\text{--}930\text{ cm}^{-1}$), S–O bonds ($500\text{--}1250\text{ cm}^{-1}$), and water HOH/OH vibration region ($1000\text{--}4000\text{ cm}^{-1}$) are displayed. The FTIR spectra of the reaction product after 72 h and 144 h showed new broad bands at 2205 cm^{-1} and 2146 cm^{-1} , which were similar position to the Fe–S stretching vibration of a mackinaitite reference sample [41]. The bands at 790 cm^{-1} and 872 cm^{-1} of primary tailing sediment were assigned to the symmetric stretching vibration of As–O. After treatment of the sediment by SRB, the band position of the As(V) at 790 cm^{-1} shifted to 780 cm^{-1} by 144 h. This weaker band was assigned to As(III), which confirmed the existence of As reduction [42]. A band localized at 464 cm^{-1} was assigned to the C–N–C deformation mode of organic matter, possibly derived from bacteria residues, representing metabolic products formed by the cells [43].

3.3. Dynamics of pH and redox potential

The change of Eh and pH over the 6-day reaction period was shown in Fig. 4, similar evolutions were observed in all systems. The pH in biotic systems increased from the initial value of about 7.0 in first 1.5 h along with a corresponding decrease in Eh, which was attributed to the generation of alkalinity (HCO_3^-) as a by-product of sulfate reduction [44]. The pH and Eh values fluctuated during the following incubation. These pH fluctuations were attributed to the accumulation of biogenic H_2S due to SRB activity, or the above reason [44]. In the abiotic control, the pH continuously increased, while the Eh presented an upward trend.

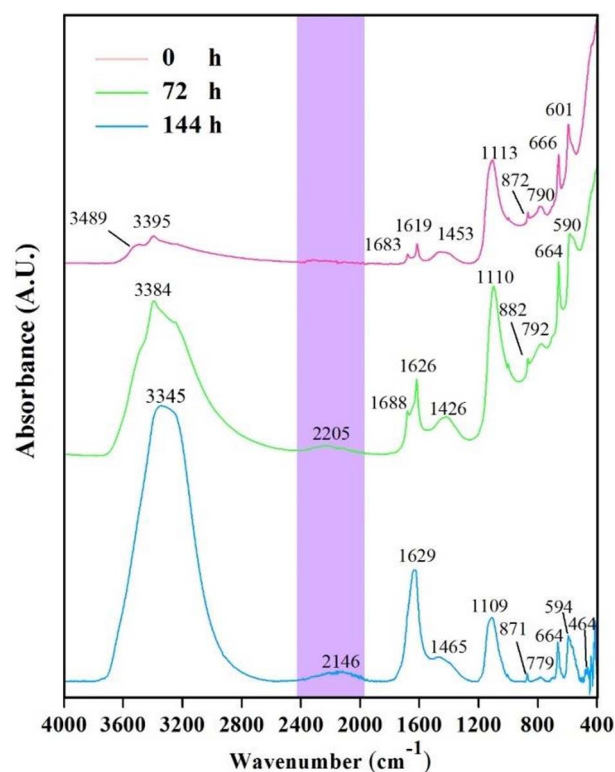


Fig. 3. ATR-FTIR spectra of the reaction products by 0 h, 72 h, 144 h in the effect of SRB. The pale pink area presented the stretching vibration of mackinaitite. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.4. The effect of SRB on the dissolution of the sediment

As the tailing sediments contained abundant gypsum, the SRB in this experiment can directly utilize it as a source of sulfate to produce a sulfidic reducing environment. The key reaction was the oxidation of lactate (electron donor) coupled to the reduction of sulfate in the sediment (electron acceptor) [45]. Sulfate was reduced by SRB to hydrogen sulfide, accompanying alkalinity generation and acidity as

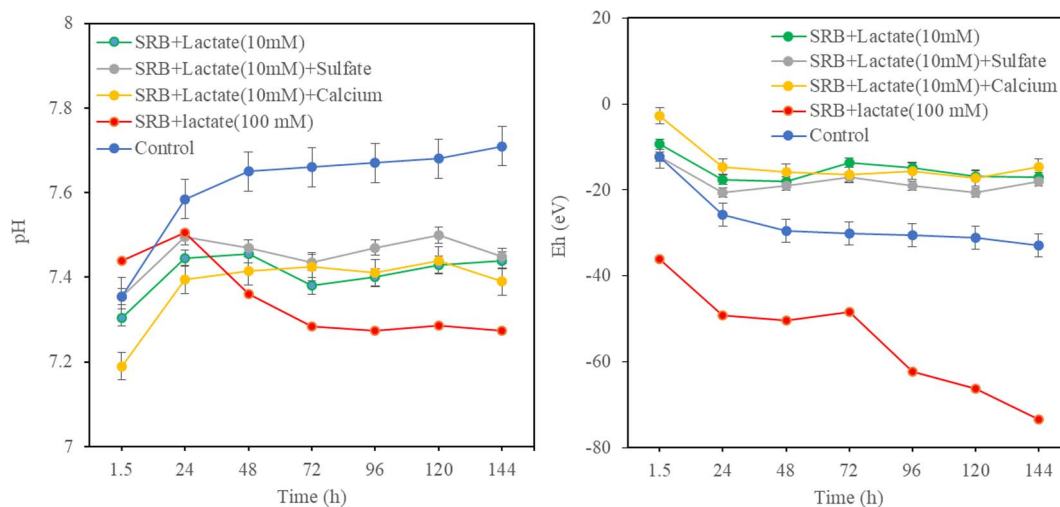
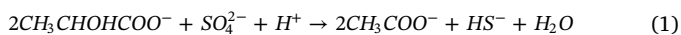


Fig. 4. Change of pH and Eh during the incubation time.

described in Eqs. (1) and (2) [46]:



The kinetics of the release of As by SRB was shown in Fig. 5A. It was obvious that the trend consisted of two stages: first, the concentration of As accumulated rapidly, then diminished. In the presence of SRB, arsenic was released into solution within hours of incubation (first 1.5 h). However, the release of As(III) and As(V) exhibited different trends. The concentration of As(T) reached a maximum of 1200 µg/L by 72 h, which greatly exceeded the Environmental Protection Agency's maximum concentration level of arsenic (10 µg/L). Arsenic leaching from the control group was mostly in the form of As(V) and remained stable at ~200 µg/L. While in the biotic incubation As(V) was dominant at start (1.5 h), As(III) gradually became the dominant species (80–100% of total As). The As(V) was released within the first 1.5 h of incubation, after that As(V) began to decrease quickly from aqueous phase, while dissolved As(III) exhibited opposite trend peaking at 72 h. These results indicated that SRB were effective in releasing arsenic, and the reason for the different release behavior of As(III) and As(V) were ascribed to the sulfide produced by SRB. The As(V) (the main arsenic species in primary tailing sediment as identified by XPS results) released during the experiment was rapidly reduced to As(III) due to the effect of the HS^- generated by microbial sulfate reduction by the SRB. The band position of the As(V) at 790 cm^{-1} shifted to As(III) at 780 cm^{-1} by 144 h, thus confirming the existence of As reduction. Many literature

studies have previously confirmed that biogenic sulfide was capable of reducing As(V) to As(III) [10,36,47]. During the first phase (0–72 h), reductive dissolution of these tailing sediments enhanced As mobilization at the water/sediment interface due to the reduction of As(V). The dissolved colloidal iron might also increase As release due to colloidal transport.

Detectable aqueous Fe(II) was recorded throughout the experiment. Fe(II) concentrations increased and peaked at 24 h to a maximum of 10 mg/L (Fig. 5B) before decreasing over the 24 h to 144 h period with some fluctuations. The maximum measured concentration of dissolved Fe(II) was significantly higher than the concentrations of dissolved As(III) in a ratio of about 8:1. The high concentration of dissolved Fe(II) is likely due to the high proportion of Fe(III) compared to As(V) in the primary sample, as determined by the XRF result. The accumulation of Fe(II) was faster than that of As. The rate of Fe(III) was faster than that of As(V) in the presence of HS^- , the Fe(III) reduction increased the release of arsenic. Some research have provided important information on the concurrent reduction of sulfate and Fe(III) by SRB [45]. There was also evidence that microbial iron (Fe) reduction, which reduced Fe(III) to Fe(II), can enhance the mobilization of As by reductive dissolution of Fe (oxy)hydroxide [48]. After 72 h, the arsenic concentration started to decrease, while the Fe(II) concentration started to decrease by 24 h. The attenuation of As and Fe were assigned to the production of secondary minerals. The Fe(II) solution concentration began to decrease before the As(III) decreased, which indicated that in an Fe(II)-As(III)-S(-II) system, Fe(II) and As(III) competed each other for

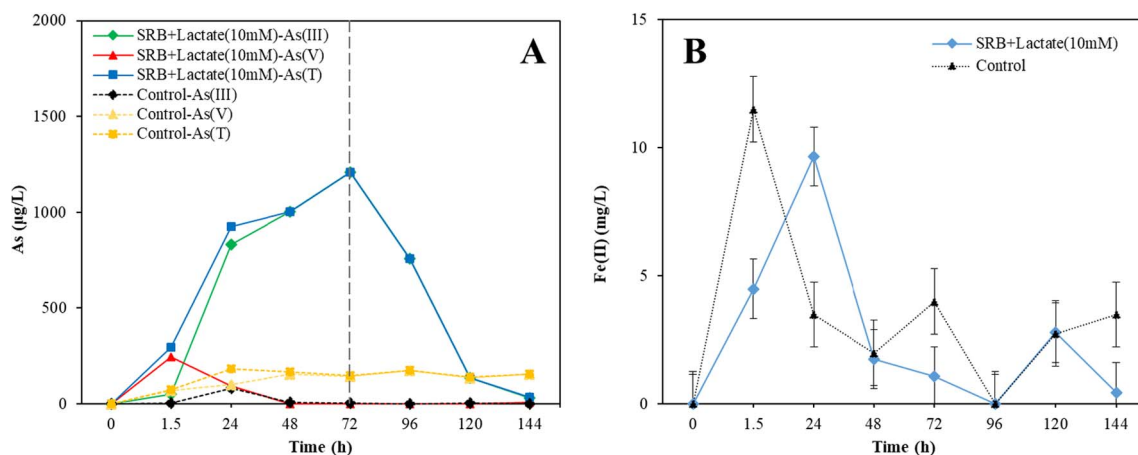


Fig. 5. Change of dissolved As (A) and Fe (B) concentrations with incubation time in the effect of SRB.

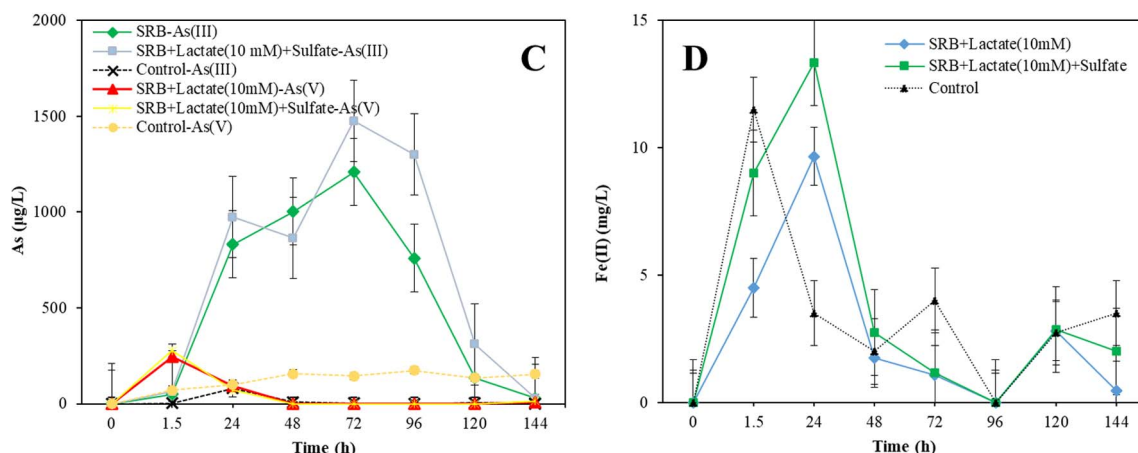


Fig. 6. Change of dissolved As (C), Fe (D) concentrations during the incubation time with the addition of sulfate (As(III):arsenite; As(V):arsenate; Fe(II):ferrous).

a limited supply of microbially mediated dissolved S(-II) to precipitate. S(-II) reacted preferentially with Fe(II) forming nano Fe sulfides (i.e. FeS, FeS₂) as the initial precipitates. The decrease of aqueous Fe(II) was faster than that of aqueous As(III). Once all aqueous Fe(II) has precipitated, the As can be removed by adsorption or co-precipitation with newly formed Fe sulfides or As(III) and S(-II) interact to produce nano arsenic sulfides. A black precipitate was observed, which was attributable to the formation of nano FeS and FeS₂, and its presence was confirmed by the FTIR analysis. Eqs. (3) and (4) described the formation of these nano FeS and FeS₂ materials. Similar trends of attenuated mobility of As have been reported in several previous studies [10,41].



3.5. The effect of coexisting sulfate

As shown in Fig. 6, the impact of sulfate on the release of arsenic was explored. Over the full incubation, the variations of the As(III), As(V) and Fe(II) concentrations were consistent across both sulfate concentrations. Over the first 24 h, the extent of As released under the effect of SRB was very similar with additional sulfate concentrations (4 mM/L) and no added sulfate experiments. All these treatments displayed aqueous As(III) concentrations at 24 h that were close to 800–900 µg/L. However, as the experiment progressed, dissolved As(III) concentration began to differ in these two sulfate treatments. The addition of extra sulfate can trigger the release of As. When sulfate was amended, the accumulation of Fe(II) was also increased, and the reductive dissolution of the sediment was greatly enhanced by biogenic HS⁻. A large amount of aqueous Fe(II) was observed in accordance with the increasing sulfate concentration. The S(-II) produced by microbial sulfate reduction can accelerate the release of Fe(II). This indicated that the addition of sulfate promoted reductive dissolution of the sediment, which agreed with the results of Song and Burton's experiments [17,36]. However, in contrast to their observations, several batch studies have demonstrated that high sulfate addition is a feasible way to immobilize As [35].

3.6. The effect of coexisting calcium ion

The impact of calcium on the release of arsenic was also explored (Fig. 7). Over the full incubation the As(III), As(V) and Fe(II) changing trend were consistent with sulfate groups. However, the addition of calcium to the sediment resulted in lower dissolved arsenic concentrations than group treated only with SRB. The maximum accumulation of As(III) and As(V) decreased with the addition of calcium ion,

which restrained the release of As. The accumulation of dissolved As did not maintain consistency along with the quantity of calcium ion. Added calcium can lead to the lower volume of sediment dissolution and mobilization of a portion of As that would have otherwise been released into solution. These results might provide insight into the effects of both calcium and microbial sulfate reduction on coupling of As mobility. It appeared that calcium can help to mitigate As mobility in the sediment in the effect of SRB under anaerobic environment, which was consistent with the decrease of calcium in the later stage (no data was shown). Dissolved As(V) in the form of H₂AsO₄ or HAsO₄⁻ can form complexes with Ca²⁺ (CaH₂AsO₄⁺, CaHAsO₄, or CaAsO₄) at circumneutral pH range [49]. Jia et al. (2005) and Guan et al. (2009) also proposed that the introduction of calcium can result in a positively charged surface to adsorb anionic species. Calcium ion was found to decrease arsenic removal by co-precipitation with iron(III) [50,51], which in a certain aspect identified the reason for the lower volume of sediment dissolution with additional calcium.

3.7. The effect of sodium lactate

Sodium lactate is the sodium salt of lactic acid, which represents organic matters and electron donor in this bacterial environment [52]. The results of the gradient sodium lactate (10 mM, 100 mM) level supplementation and its effects on the reductive dissolution of As/Fe from high arsenic ferric tailing sediments under anaerobic conditions was shown in Fig. 8. Over the full incubation, the variations of the As(III) concentration were basically consistent across both sodium lactate concentrations, while As(V) presented a different trend. It was obvious that dissolved As(III) and As(V) concentrations increased significantly as the sodium lactate concentration increased. Tailing sediments supplemented with 100 mM sodium lactate exhibited the most superior and the concentration of As(III) was approximately 2500 µg/L compared to 10 mM sodium lactate (1200 µg/L). The increase of sodium lactate can remarkably trigger the release of As, and the concentrations of sodium lactate were correlated to release of dissolved arsenic. Dissimilatory metal-reducing bacteria have been demonstrated to oxidize sodium lactate, enhancing electron transfer and Fe(III)/As(V) reductive dissolution in some laboratory experiments, consistent with this phenomenon [33,53]. The activity of SRB was enhanced by increasing the carbon source, which can accelerate the release of As(V) and the reduction of As(V) to As(III) by biogenic sulfide. The accumulation of aqueous Fe(II) did not present an obvious increase, which was might ascribed to that more sulfide co-precipitate with iron, thus leaving less Fe(II) in solution. A notable change in Eh and pH (Fig. 4) were observed during the experiment compared to other groups. This indicated considerable SRB activity during the dissolution process, and the rate of tailing sediments dissolution was accelerated as the level of sodium

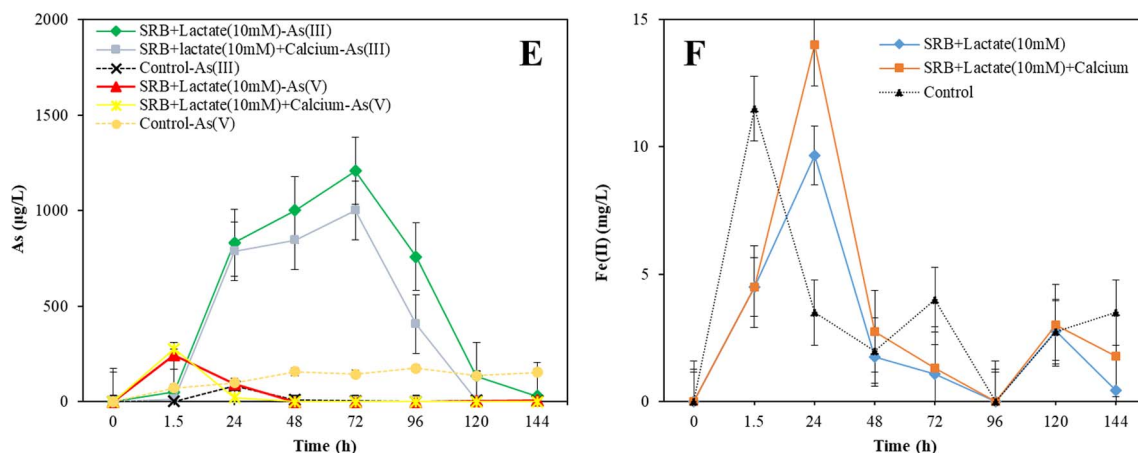


Fig. 7. Change of dissolved As (E), Fe (F) concentration during the incubation time with the addition of calcium.

lactate (carbon source) increased, and the rate of change in pH and Eh were greater. The results indicated that an enhancement in sodium lactate led to more high arsenic ferric tailing sediments being reductively dissolved, resulting more arsenic transformation and migration.

3.8. The As dynamic

The As contamination in Shimen region has become a hot research topic in recent years. Although this realgar mine had been closed since 2011, the interactions between microbial bacteria and quantities of secondary arsenic ferric sediments might pose a potable threat to local area due to As contamination. Many natural seasonal flooding, rainfall can introduce an anoxic-sulfidic environment in flooded tailing sediments. These newly flooded areas will see obvious geochemical changes which significantly influence the behavior of As in the local environment.

The As contaminated tailing sediment (arsenic iron-oxyhydroxide) can undergo reductive dissolution in the effect of SRB, which greatly influences the probable arsenic transformation pathway (Fig. 9). Firstly, the ferric arsenic material was destroyed by SRB, with As(V) and Fe(III) were released from the sediment. Subsequently, a notable increase in As(III) was observed. As(V) and Fe(III) reduction occurred in the effect of biogenic HS^- generated by SRB activities. Decreases in As and Fe concentrations happened in the later stage. The reductive dissolution of Fe(III)/As(V) minerals initially increased the aqueous Fe(II), As(III) concentrations. Then Fe(II) concentration decreased via formation of FeS_n and As(III) decreased via formation of As_3S_2 or adsorbed on the

surface of FeS_n , which influenced the dynamic of arsenic. The results from this study might enhance our understanding of coupling Fe and As dynamic by SRB in flooded tailing sediments.

4. Conclusions

- (1) During the reductive dissolution of the sediment by sulfate-reducing bacteria, the changing trend of As(III) and As(T) were different, As(III) was the dominant arsenic species in sulfidogenic sediment/water interface and determined the change of total As.
- (2) The change of aqueous As concentration showed two stages, firstly, the reductive dissolution of arsenic iron(hydr)oxide resulted in the release of As and immediately reduced to As(III) by biogenic sulfide. Next, the released As removed from the solution by adsorption with newly formed nano Fe sulfides (e.g. FeS , FeS_2) or co-precipitation with S(-II) to produce nano arsenic sulfide.
- (3) The additional sulfate and calcium played different roles in the release of As, additional sulfate can trigger the release of arsenic, while calcium had the opposite effect. The level of sodium lactate significantly influenced the As behavior, and the release of As increased as the sodium lactate increased.

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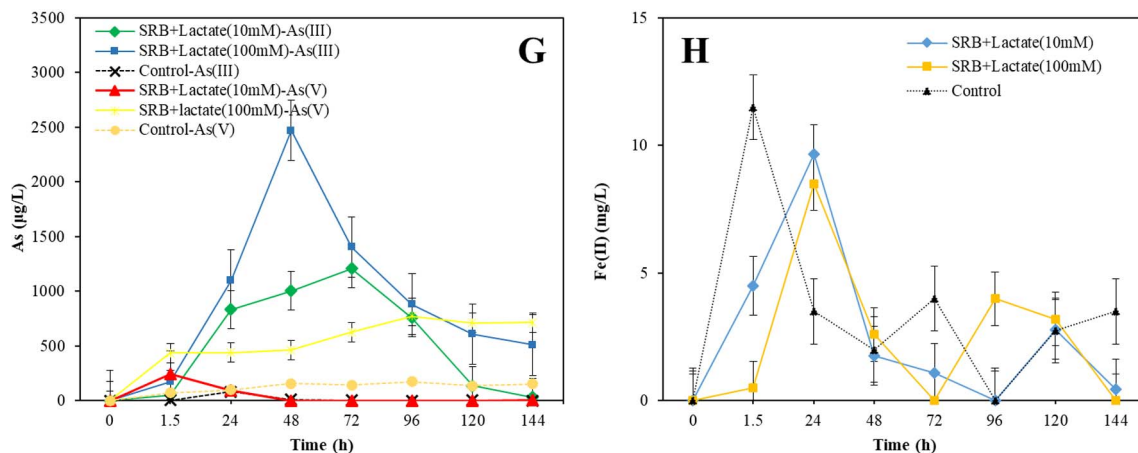


Fig. 8. Change of dissolved As (G), Fe (H) concentration during the incubation time in different sodium lactate concentrations (10 mM, 100 mM), respectively.

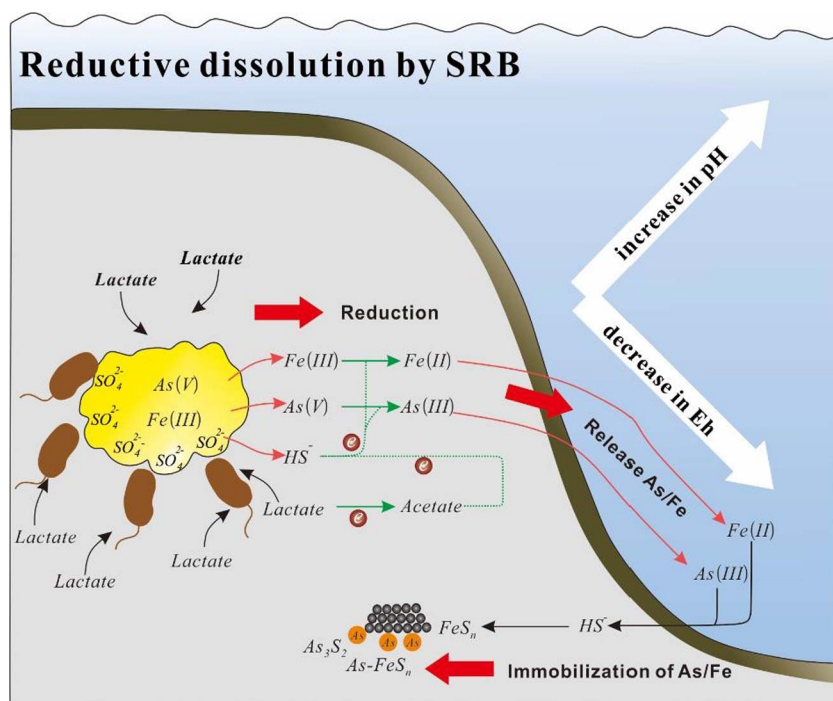


Fig. 9. The schematic map of the behavior of As/Fe in sediment/water interface by SRB.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cej.2017.09.078>.

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