



# Coupling effect of $\text{Fe}^{3+}_{(\text{aq})}$ and biological, nano-sized FeS-coated limestone on the removal of redox-sensitive contaminants (As, Sb and Cr): Implications for *in situ* passive treatment of acid mine drainage<sup>☆</sup>



Lei Zhou<sup>a</sup>, Faqin Dong<sup>a</sup>, Jing Liu<sup>a</sup>, Karen A. Hudson-Edwards<sup>b, \*</sup>

<sup>a</sup> The Key Laboratory of Solid Waste Treatment and Resource Recycle, Ministry of Education, Southwest University of Science and Technology, Mianyang 621010, China

<sup>b</sup> Department of Earth and Planetary Sciences, Birkbeck, University of London, Malet St., London WC1E 7HX, UK

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## ABSTRACT

Nano-sized FeS particles have been shown to improve the adsorption performance in permeable reactive barrier (PRB) technologies that are used to treat acid mine drainage. To investigate the coupling effect of  $\text{Fe}^{3+}$  and biological nano-sized FeS on removal of redox-sensitive contaminants and the permeability of a limestone system, Fe-reducing bacteria (FRB) and sulfate-reducing bacteria (SRB) were used to form nano-sized FeS coatings on limestone grains. For initial acidic solutions containing 0.5 mg/L As(V), Cr(VI) and Sb(V), retardation factors increase from 26, 5 and 7, respectively, in a limestone-only (pristine) system to »367, 89 and 9, respectively, in an FeS-coated limestone system, and to 345, 367 and 308, respectively, in an FeS- $\text{Fe}^{3+}_{(\text{aq})}$  system. The permeability coefficient of the FeS-coated limestone system is better than that of the pristine limestone system, but declines to two-thirds of the pristine limestone system in the presence of  $\text{Fe}^{3+}_{(\text{aq})}$ , possibly due to the formation of secondary ferric hydroxides. XPS analysis suggests that the FeS particles are effective at reducing As(V), Sb(V) and Cr(VI) and removing them from solution. These results demonstrate that FeS particles improve retention of redox-sensitive contaminants with and without  $\text{Fe}^{3+}_{(\text{aq})}$ . These new findings give new insights on the coupling effect of redox systems used in PRBs.

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## 1. Introduction

Permeable Reactive Barrier (PRB) technologies are used to remediate acid mine drainage (AMD) by passing the AMD through a wall filled with reactive material that removes metal and metalloid elements by chemical adsorption, precipitation and/or biomineralization (Gibert et al., 2011; Liu et al., 2014b, 2016). Limestone is the most common PRB filling material due to its low cost and ability to neutralise acidic solutions, and it has, as a result, been widely used for AMD treatment (Hedin et al., 1994; Liu et al., 2013; Lottermoser, 2010). The contaminant removal ability and permeability of the limestone filling are important factors determining the performance and service life of PRB systems. For example, the maximum adsorption capacity of limestone for As(V) is only 0.01 mg/g (Davis et al., 2007), but this can be improved significantly

if the limestone is coated with reactive materials such as iron and manganese oxides (Han et al., 2011a; Liu et al., 2016). In practice, smaller limestone particles are desirable for increasing neutralization rates and adsorption performance, but these can be clogged by secondary precipitates, reducing the permeability of the system.  $\text{Fe}^{3+}_{(\text{aq})}$ , derived mainly from the oxidation of pyrite ( $\text{FeS}_2$ ), is the most common cation in AMD.  $\text{Fe}^{3+}_{(\text{aq})}$  can help to remove AMD contaminants by adsorption and uptake in precipitates such as ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) and schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ ) (Boi, 2010; Soler et al., 2008; Dou et al., 2013). However,  $\text{Fe}^{3+}_{(\text{aq})}$  can negatively affect the permeability of the limestone-filled PRB due to the occlusion of pore spaces by these secondary precipitates (Boi, 2010; Soler et al., 2008). For example, Liu et al. (2013) showed that the formation of schwertmannite during treatment of AMD by zero-valent iron rapidly decreased the permeability of the PRB. To improve permeability, 'reductive walls' are often built in front of the limestone-filled PRBs to maintain a reducing environment to decrease the production of these secondary Fe(III) precipitates (Luptakova and Kusnierova, 2005; Wang et al., 2014; Zagury et al.,

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\* Corresponding author.

E-mail address: [k.hudson-edwards@bbk.ac.uk](mailto:k.hudson-edwards@bbk.ac.uk) (K.A. Hudson-Edwards).

2006). The reductive walls are filled with materials such as organic waste (Lee et al., 2010) and animal manure (Khan Eusuf Zai et al., 2010).

Nano-sized FeS particles are used as PRB filling materials, and they have been shown to have better adsorption performance than common mineral adsorbents such as zero-valent iron and other iron-bearing minerals (Zhang et al., 2010; Yanyan et al., 2012; Xiong et al., 2009; Han et al., 2011b) and to reduce contaminants such as uranium (Lee et al., 2013). In view of these properties, it is hypothesised that nano-sized FeS could improve limestone-filled PRB systems by acting as coatings on the limestone. Ferric reducing bacteria (FRB) and sulfate reducing bacteria (SRB) are ubiquitous bacteria in AMD, and they can be isolated and cultured in the laboratory (Bowell et al., 2014). They can reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  and  $\text{SO}_4^{2-}$  to  $\text{S}^{2-}$ , and the resultant ions can then form  $\text{Fe}_n\text{S}_m$  (Sen and Johnson, 1999). These bacteria could therefore be used to form *in situ* FeS that could coat limestone particles in PRB systems. The FeS could also potentially reduce redox-sensitive contaminants in AMD, such as arsenic (As), antimony (Sb) and chromium (Cr) (Robinson, 2010), and incorporate them via adsorption or secondary precipitation. To date, however, these hypotheses have not been tested.

In this manuscript we describe the results of an innovative study in which nano-sized FeS precipitates were formed on limestone using FRB (*Acidiphilium cryptum* JF-5) and SRB (*Desulfovibrio vulgaris miyazaki* SRB). The efficiency and mechanism of removal of elements As(V), Sb(V) and Cr(VI) from synthetic AMD, and the effects on the permeability of the system in the presence of  $\text{Fe}^{3+}_{(\text{aq})}$  were investigated. The results of the study will help to design more efficient PRB systems to remediate AMD, the most significant global issue facing the mining industry (Hudson-Edwards et al., 2011).

## 2. Materials and methods

### 2.1. Culturing of microorganisms, limestone collection and preparation of FeS-coated limestone

*A. cryptum* JF-5 was very kindly supplied by Friedrich Schiller of the University of Jena. To culture an acidophilic Fe(III)-reducing bacteria, an acidic Fe-tryptone soya broth (Fe-TSB) medium was prepared according to the methods described by Küsel et al. (1999). The culture medium contained 0.025% TSB-basal salts at a pH of 2.5 and was supplemented with 5 mM glucose. The medium was autoclaved at 121 °C for 15 min, cooled and dispensed under  $\text{N}_2$ . Ferric sulfate was added from an anoxic 500 mM stock solution (pH = 1.7, sterilized by passing through a 0.22  $\mu\text{m}$  pore size membrane) to a concentration of 35 mM  $\text{Fe}^{3+}$ . The final solution pH was approximately 2.3. In an acidic Fe-TSB medium, *A. cryptum* JF-5 bacteria can completely reduce 35 mM of Fe (III) in about 7 days, resulting in the culture medium turning colorless (Fig. S1 left).

SRB was isolated from abandoned mine tailings from the Sichuan province of China. SRB was cultured in neutral liquid medium-63 of DSMZ containing per litre: 2 g  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ , 2 g  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ , 2 g DL-Na-lactate, 1 g yeast extract, 1 g  $\text{Na}_2\text{SO}_4$ , 1 g resazurin, 0.5 g  $\text{K}_2\text{HPO}_4$  and 0.5 g  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . Both *A. cryptum* JF-5 and SRB (without ferrous sulfate in culture) were pre-incubated in an anaerobic chamber for 6 days prior to formation of the coating.

Limestone was collected from the strata of the Permian Jialingjiang Formation in Sichuan Province, China. The limestone is uniform and micritic. Limestone particles were ground and passed through a 425–850  $\mu\text{m}$  (20–40 mesh) sieve. 0.5 g of prepared limestone was taken into 20 mL sample bottles and subsequently, 1 mL of *A. cryptum* JF-5 culture solution and 19 mL of SRB culture solution (without ferrous sulfate in culture) were added. The suspensions were then shaken, covered with sealing films and kept

static for two days.

After two days, the supernatant was transferred into 50 mL centrifuge tubes. The coated limestone was rinsed three times using 5 mL of Milli-Q water and then dried inside the anaerobic chamber. The washing waters were transferred into the same 50 mL centrifuge tubes to determine residual Fe with 0.1 M HCl digestion.

### 2.2. Batch As(V), Sb(V) and Cr(VI) sorption experiments on FeS-coated limestone

The isothermal adsorption of As(V), Sb(V) and Cr(VI) was evaluated using batch experiments. For these, approximately 0.0124 g of FeS-coated limestone was added to clean sample bottles. Subsequently, 20 mL of As(V), Sb(V) and Cr(VI) solutions with different concentrations (0.1, 0.5, 2.5, 10, 25, 50 mg/L) were respectively added in each sample bottle and sealed. These solutions were prepared by diluting stock solutions of  $\approx 1$  g/L As(V), Sb(V) and Cr(VI), which in turn were prepared by dissolving appropriate amounts of 4.1646 g  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ , 1.5823 g  $\text{NaSbO}_3$  and 2.8287 g  $\text{K}_2\text{Cr}_2\text{O}_7$  per batch, respectively (Alfa Aesar company). The sample bottles were oscillated 24 h at 150 rpm and 25 °C to achieve equilibration sorption. The time of 24 h was based on kinetic adsorption experiments for arsenate on FeS particles, for which equilibration was achieved after 4 h. We assumed that similar times would be needed for Sb and Cr sorption, but greatly exceeded them to 24 h to ensure complete equilibration. The samples were subsequently passed through a 0.22  $\mu\text{m}$  filter and analyzed for As, Sb and Cr by Inductive Coupled Plasma Emission Spectrometry (ICP-AES, iCAP6500 ThermoFisher). Each batch of adsorption experiments was done in duplicate and contained blank controls.

### 2.3. X-ray photoelectron spectroscopy (XPS) characterization of As(V), Sb(V) and Cr(VI)-sorbed FeS particles

To understand the effect of the FeS particles on the contaminants, XPS was used to analyse the As, Sb and Cr-sorbed nano-FeS samples prepared in the batch experiments. We did not do XPS on the column experiment materials due to the rapid oxidation of the Fe-bearing phases within them (see below) and to the difficulty in sampling the columns during the experiments. For these samples, the initial concentrations of As(V), Sb(V) and Cr(VI) were 0.5 mg/L, similar to those found in synthetic AMD solutions (Yin et al., 2008). We term these the 'contaminant-sorbed samples', although we acknowledge that other removal mechanisms such as surface precipitation may have occurred. These samples were prepared using the FeS formation method described in section 2.1, and by adding 2 mL of 10 mg/L As(V), Sb(V) and Cr(VI) which was diluted from 1 g/L stock solution into the initial bacterial culture mixtures to ensure the initial concentrations were 0.5 mg/L. The concentrations of As(V), Sb(V) and Cr(VI) are therefore the same as those used in the column experiments described below. These samples were collected in an anaerobic glove box and transferred using an airtight container filled with  $\text{N}_2/\text{H}_2$  gas to minimize exposure of the sample surfaces to atmospheric oxygen. The Al-K $\alpha$  line was used as radiation source. Survey spectra were obtained with a VG-ScientaR3000 analyzer pass energy of 70 eV. Narrow XPS scan peaks were obtained for the model compounds with a pass energy of 30 eV. Raw spectra were smoothed before being fitted using software XPSpeak software using a Shirley base line and a Gaussian-Lorentzian peak shape.

### 2.4. Column experiments

#### 2.4.1. Column design and solution preparation

Column experiments were built using Perspex with a diameter

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