



Bioremediation of arsenic-contaminated groundwater by sequestration of arsenic in biogenic pyrite

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ARTICLE INFO

Editorial handling by Dr T Pichler

Keywords:

Arsenic
Sulfate reducing bacteria
Bioremediation
Arsenian pyrite

ABSTRACT

Pyrite (FeS₂) is the most common sulfide mineral in the Earth's crust, and it commonly contains minor amounts of arsenic. Here we show that authigenic pyrite can remove arsenic from contaminated groundwater and this can be used as a new and relatively inexpensive remediation process. Laboratory batch experiments presented show that fine-grain natural pyrite is an effective sorber of dissolved arsenic. Arsenic sorption onto pyrite is shown to increase with increasing pH, particularly at pH > 5 and at elevated dissolved arsenic concentration. We also present results from a field experiment at an arsenic-contaminated industrial site, which demonstrates the results of stimulation of natural sulfate-reducing bacteria in groundwater by injection of a labile organic carbon source, iron, and sulfate. Within a week, bacterial sulfate reduction triggered the formation of biogenic pyrite nanoparticles, which sequestered arsenic by adsorption and co-precipitation. Microscopic and X-ray diffraction analyses confirmed that pyrite was the only iron-sulfide formed, and that no arsenic-only sulfide phase precipitated (e.g. orpiment or realgar). Pyrite occurs as either 1–10 μm euhedral crystals or similar-sized framboids both of which contain 500–4000 mg/kg arsenic. As a result, dissolved arsenic decreased from its initial concentration of 0.3–0.5 mg/L to below the regulatory clean-up standard for the site of 0.05 mg/L in a matter of weeks. In addition to the potential of this technique to remediate anthropogenic arsenic contamination, it is possible that it can be modified to inexpensively treat individual small drinking-water wells contaminated by natural sources of arsenic in many developing nations.

1. Introduction

The concept of stimulating sulfate-reducing bacteria (SRB) to produce biogenic pyrite as a potential groundwater remediation approach for arsenic and metals was first proposed by Saunders et al. (1996), based on research that showed that arsenic and other trace elements were common in recent marine sediments (Huerta-Diaz and Morse, 1992) and also in terrestrial systems, such as in Holocene stream floodplain deposits (Saunders et al., 1997). This proposed approach was evaluated in laboratory experiments by Keimowitz et al. (2005, 2007). Keimowitz et al. (2007) also proposed that a technology based on stimulating SRB metabolism might prove useful in bioremediating groundwater contaminated by arsenic, similar to the approach of Saunders et al. (2005a), who demonstrated in a field study that indigenous SRB could be stimulated to bioremediate lead, zinc, and cadmium in contaminated groundwater. Kirk et al. (2004) observed

that where natural SRB activity occurs in groundwater aquifer systems, low concentrations of arsenic are typically observed. Wolthers et al. (2005a) tracked iron-sulfide formation and its effect on dissolved arsenic in laboratory experiments, and showed that arsenian pyrite efficiently sequesters arsenic from solution. Saunders et al. (2008) reported on reconnaissance experiments designed to stimulate biogenic sulfate reduction in a shallow “tube” well installed in a naturally arsenic-contaminated aquifer in Bangladesh, and showed that SRB metabolism lowered groundwater arsenic concentrations. A number of recent laboratory experiments were conducted to evaluate the effects of anaerobic bacterial sulfate reduction and subsequent iron-sulfide biomineralization on dissolved arsenic (Kirk et al., 2010; Onstott et al., 2011; Omeregie et al., 2013; and Sun et al., 2016). In addition, a laboratory investigation by Xie et al. (2016) showed that inorganically formed pyrite, which coated quartz grains during their experiments, was effective in removing As(III) for solution. Finally, Pi et al. (2017)

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conducted a short (~1 month-long) field demonstration of stimulating SRB to remove arsenic from groundwater.

Arsenic sorption onto natural and synthetic pyrite has been examined by some researchers (Zouboulis et al., 1993; Han and Fyfe, 2000; Farquhar et al., 2002; Kim and Bachelor, 2009; Han et al., 2013; Bulut et al., 2014) and all the previous research has shown pyrite to be an effective sorber of dissolved arsenic. As a result, Zouboulis et al. (1993), Han and Fyfe (2000), and Bulut et al. (2014) have all proposed that pyrite could prove useful in treating arsenic-contaminated waste waters (e.g. as an above-ground engineering process). The previous research has typically focused on the use of synthetic pyrite to sorb arsenic, with the exception of Bulut et al. (2014). Here we investigate the sorptive capacity of natural pyrite of varying grain sizes and over a wider range of pH than was investigated by Bulut et al. (2014). Our intent is to use these experimental results as a very conservative assessment of the capacity of natural pyrite surfaces to sorb arsenic, which we interpret below as the first step in the incorporation of arsenic into the growing pyrite crystals that form during bioremediation.

Here we present some of the initial results of an ongoing, long-term field demonstration of groundwater arsenic bioremediation. The process has been specifically designed to stimulate SRB to make biogenic pyrite, which removes arsenic from contaminated groundwater at an industrial site in northern Florida, USA. For this paper, we focus on the geochemistry and mineralogy of iron sulfides produced in the experiment, and the efficacy of using pyrite to remove arsenic from groundwater, similar to the approach that was demonstrated for lead, zinc, and cadmium removal (Lee and Saunders, 2003; Saunders et al., 2005a, 2008).

1.1. Arsenic geochemistry and mineralogy

The general geochemistry and mineralogy of arsenic has been discussed in detail previously (e.g., Smedley and Kinniburgh, 2002; Nordstrom and Archer, 2003; O'Day et al., 2004; Ford et al., 2007; Saunders et al., 2008; and Howell et al., 2014), and thus we present only a brief summary here. Common arsenic minerals include scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), which forms under oxidizing conditions, and realgar (AsS), orpiment (As_2S_3), and arsenopyrite (FeAsS) that form under reducing conditions. Aqueous arsenic occurs in two oxidation states, As(V) (arsenate) and As(III) (arsenite) and the distribution of the important species are shown in Fig. 1 in Eh–pH space for the As–S–H₂O system. In iron-deficient systems, and taking into account thermodynamic data for thioarsenite complexes (e.g. Wilkin et al., 2003), the restricted stability fields for orpiment and realgar are shown in Fig. 1. Addition of iron to the system leads to displacement of the stability fields of orpiment and realgar by either arsenopyrite (e.g. Langner et al., 2013, Supporting information) or arsenian pyrite (Saunders et al., 2008). Orpiment, realgar, and arsenopyrite are typically formed under hydrothermal conditions and can be associated with more valuable minerals in ores, and thus can be important mineral phases (and sources of arsenic) found in some mine tailings. Realgar and “amorphous” orpiment (Le Pape et al., 2017) and arsenopyrite (Rittle et al., 1995; Onstott et al., 2011) have reportedly been synthesized in low-temperature laboratory experiments utilizing SRB consortia, although only realgar has been confirmed by XRD. Secondary (authigenic) realgar has been reported (with no XRD confirmation) from mine tailings (Walker et al., 2009; DeSisto et al., 2016), in an anthropogenically arsenic-contaminated shallow aquifer (O'Day et al., 2004), and in lignite (Langner et al., 2012, 2013). Langner et al. (2013) also report arsenopyrite in lignite (also with no XRD confirmation). Crystalline and/or amorphous realgar and orpiment have also been reported from cooled hydrothermal discharges (e.g., Webster, 1990; Godelitsas et al., 2015). However, based on a number of investigations, it is apparent that under most natural reducing groundwater conditions (pH in range of 5–8) that arsenian pyrite is the most important mineral host for arsenic (Saunders et al., 1996, 2008, 1997; Price and Pichler, 2006; Lowers et al., 2007;

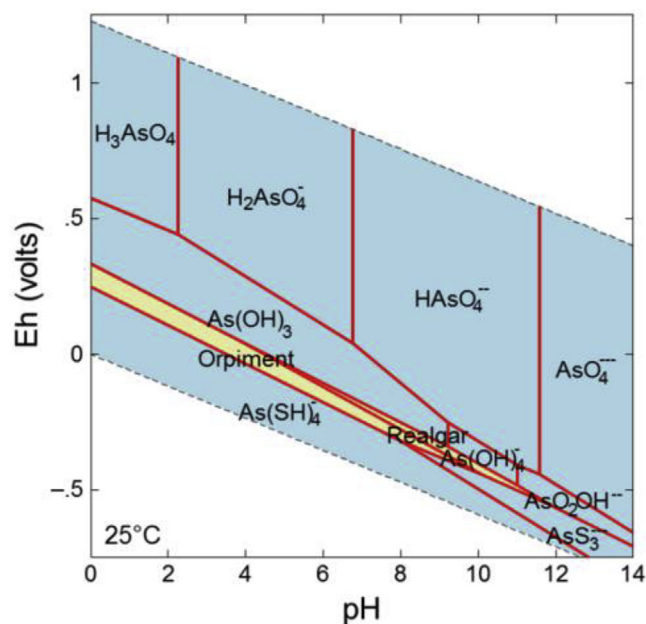


Fig. 1. Eh–pH diagram calculated for As–S–H₂O system at 25 °C and fixed arsenic and sulfate activities of 10^{-6} and 10^{-5} , respectively. The results show the stability field of different arsenic species under different geochemical conditions. Plot was constructed using Geochemist's Workbench including thermodynamic data listed in the Appendix.

Mango and Ryan, 2015; Pi et al., 2016; Houben et al., 2017). Further, arsenian pyrite is common in recent marine and lacustrine sediments as well (Huerta-Diaz and Morse, 1992; Neumann et al., 2013), in recent peat deposits (Langner et al., 2012; Stuckey et al., 2015), and also in coal seams (Kolker et al., 2001).

Aqueous systems containing dissolved sulfide species, which are necessary to form iron (arsenic)-sulfide minerals, also form stable aqueous thioarsenite complexes that can significantly enhance arsenic mobility under reducing conditions (Wilkin et al., 2003; Bostick et al., 2005). However, these thioarsenite aqueous complexes become less important if iron is present in the system, as it removes aqueous sulfide species by forming solid iron sulfide phases (Wilkin et al., 2003; Burton et al., 2014). Finally, another important control on aqueous arsenic geochemistry is the sorption of arsenic onto common aquifer minerals such as iron oxides and oxyhydroxides (e.g. Farquhar et al., 2002; Dixit and Hering, 2003; Giménez et al., 2007) and iron sulfides (Farquhar et al., 2002; Bostick and Fendorf, 2003; Wolthers et al., 2005b; Han et al., 2013; Bulut et al., 2014; this study). The stability of minerals (oxide or sulfide) capable of sorbing arsenic has important implications for arsenic release to the hydrosphere. For example, the reductive dissolution of iron oxyhydroxides that had previously sorbed arsenic by Fe(III)-reducing anaerobic bacteria, is apparently the major cause of natural arsenic contamination of groundwater in Holocene aquifers of SE Asia and elsewhere (Nickson et al., 2000, 2005; McArthur et al., 2004; Saunders et al., 2005c; Fendorf et al., 2010). Conversely, oxidation of arsenic-bearing pyrite in aquifers is also a major source of groundwater contamination (Smedley and Kinniburgh, 2002; Price and Pichler, 2006; Howell et al., 2014; Mango and Ryan, 2015; Houben et al., 2017). The fact that pyrite can be both a sink and a source for arsenic in groundwater system has led to some confusion about the in environmental geochemistry or arsenic (Saunders et al., 2008).

1.2. Pyrite and arsenian pyrite occurrence and geochemistry

Pyrite is by far the most common iron sulfide phase formed in nature and definitely the most commonly preserved iron sulfide phase in the geologic record (Rickard and Luther, 2007). Other less-common

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