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Arsenopyrite dissolution rates in O_2-bearing solutions

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ABSTRACT

Arsenopyrite dissolution was studied by means of long-term, stirred and non-stirred flow-through experiments in the pH range of 1 to 9 at 25, 50 and 70 °C and at different input dissolved-O_2 concentrations (from 0.2 to 8.7 mg L^{-1}).

At pH lower than 4, aqueous iron, which is mainly in the ferrous form, and arsenic are stoichiometrically released. Sulphur concentrations released were lower than stoichiometrically expected (S/As<1). X-ray Photoelectron Spectroscopy (XPS) and MicroRaman Spectroscopy surface analyses on reacted and unreacted samples showed an enrichment of the reacted arsenopyrite surface in sulphur and arsenic under acidic conditions.

In the light of these results, the steady-state dissolution rates were estimated by the release of arsenic at pH<4 and were used to derive an empirical dissolution rate law expressed as:

$$R_{\mathrm{arsenopyrite}}\left(\mathrm{mol\,m^{-2}\,s^{-1}}\right)_{25^{\circ}\mathrm{C}} = 10^{-7.41\pm0.47}\cdot a_{O_2}^{0.76\pm0.11}\cdot a_{H^+}^{-0.12\pm0.07}$$

where a_{O_2} and a_{H^+} are the activities of hydrogen ions and dissolved oxygen, respectively and their exponents were estimated from multiple linear regression of the dissolution rates. Temperature increase from 25 to 70 °C yields an apparent activation energy for the arsenopyrite oxidation by dissolved oxygen of 18.5 ± 1.6 kJ mol^{-1}.

At pH>6, aqueous iron is mainly in the ferric form and is depleted as it precipitates as Fe-oxyhydroxide onto arsenopyrite surfaces, yielding Fe/As and Fe/S less than one; between pHs 7 and 9, iron depletion is complete, and sulphur released is more abundant than arsenic released, which is precipitated as As–O phases, as confirmed by MicroRaman spectroscopy. At pHs 6–9, iron-oxyhydroxide phases and arsenic oxide phases upon the arsenopyrite surface provide an effective layer that reduces diffusion of dissolved oxygen and arsenopyrite dissolution. As coating on the arsenopyrite surface becomes the rate-limiting step, the Shrinking Core Model (SCM) allows quantification of the surface dissolution rate, especially from data obtained where the effect of coating was still negligible. The SCM also allowed us to calculate the effective coefficient for oxygen diffusion through the coating, which can vary from 10^{-17} to $1.5\cdot10^{-16}\,m^2\,s^{-1}$. The formation of such a coating produced a decrease in arsenic and sulphur release over time and a final surface passivation.

1. Introduction

Inorganic aqueous As release is an environmental and human health concern worldwide (Ferguson, 1990; Aposhian et al., 2004; Rosman et al., 2004; Bunnell et al., 2007).

The arsenic content in water (surficial or groundwater) has been attributed to two main processes: desorption of arsenic previously sorbed onto the structures of Fe or Mn oxy-hydroxides, and As release by oxidation of arsenopyrite and/or As-rich pyrites in mineralized areas (Casiot et al., 2003, 2005; Frau and Ardau, 2003; Lee et al., 2005; Lee and Chon, 2006; Pfeifer et al., 2007). The former process usually occurs in aquifers where redox conditions have been changed, e.g., the arsenic contamination in the Bangladesh delta (Bhattacharya et al., 1997, 2001, 2002, 2006; Nickson et al., 1998; Routh et al., 2000; McArthur et al., 2001; Dowling et al., 2002; Smedley and Kinniburgh, 2002; Anawar et al., 2003), whereas the latter process is mainly encountered in areas where As-bearing sulphides oxidize in acid mine drainage (AMD) or in near neutral to basic pH waters. In this study, we focus on the As release as arsenopyrite dissolution takes place. An important example of As mobilization is the Iberian Pyritic Belt (IPB) in the SW of Spain and S of Portugal, which is one of the most

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important massive sulphide provinces in the world. This area contains a large number of abandoned sulphide mines, open pits, galleries, tailings and sulphide-sludge ponds that generate creeks with acidic water with high levels of arsenic (Sánchez-Rodas et al., 2005; Sarmiento et al., 2005, 2007; Acero et al., 2006; Asta et al., 2010a). Dissolved oxygen promotes dissolution of arsenopyrite (AsFeS) and arsenical pyrite ($Fe(As,S)_2$) with the consequent As release into runoff water (Williams, 2001; Lazareva et al., 2002; Smedley and Kinniburgh, 2002; Casiot et al., 2003; Frau and Ardau, 2003; Welch and Stollenwerk, 2003; Lee et al., 2005; Pfeifer et al., 2007). Other examples of arsenic contaminated groundwaters have been attributed to oxidation of arsenopyrite and As-bearing sulphides in non acidic waters at pH ranging from 7 to 9 in the Madrid Tertiary detrital aquifer (central Spain) (Hernández-García and Custodio, 2004) or in groundwater with near neutral pH at Ester dome (Fairbanks, Alaska), where dissolved arsenic concentration appears to be controlled by oxidation of arsenopyrite in the near-surface environment (Verplanck et al., 2008). Smedley et al. (2007) have recently reported arsenic contamination in circumneutral-pH groundwaters in Proterozoic basement rocks in Burkina Faso. There are also other scenarios where higher pH (neutral or alkaline) is common. For example, acid generation may be artificially attenuated by adding alkaline substances to the AMD producing materials (Pérez-López et al., 2007), which results in acid neutralization. Similarly, hydrometallurgical techniques such as cyanidation have been conducted at high pH producing alkaline waters in contact with mine residues (Salzsauler et al., 2005).

The effects of different factors on the oxidative dissolution of arsenopyrite, such as temperature, Fe(III) concentration, the presence of bacteria (*Acidithiobacillus ferrooxidans*), pH and particle size have been reported in the literature, either related to aqueous chemistry studies (Breed et al., 1997; Ruitenberg et al., 1999; McGuire et al., 2001a; Craw et al., 2003; Yu et al., 2004, 2007; Tallant and McKibben, 2005; Walker et al., 2006; McKibben et al., 2008) or to arsenopyrite surface spectroscopy research, mainly by X-ray Photoelectron Spectroscopy (XPS) (Buckley and Walker, 1988; Richardson and Vaughan, 1989; Nesbitt et al., 1995; Nesbitt and Muir, 1998; Hacquard et al., 1999; Mikhlin et al., 2006). This extensive literature is indicative of the important role of arsenopyrite oxidative dissolution in different geochemical environments, from AMD to metallurgical processes, and groundwater contamination.

Recently, two thorough reviews on arsenopyrite oxidative dissolution that take into account the aforementioned studies have been published (Corkhill and Vaughan, 2009; Lengke et al., 2009). These authors indicate that discrepancies in the kinetics of arsenopyrite dissolution still exist, being induced by different experimental parameters and limited datasets. It is pointed out that there is no consensus in fundamental processes that are involved in the overall reaction, such as: (1) formation of S layers on arsenopyrite surface, (2) dissolution stoichiometry, (3) variability in dissolution rate, (4) dissolution rate-DO dependence and (5) anomalous rate-Arrhenius behaviour.

The aim of this paper is to describe the kinetics of arsenopyrite oxidative dissolution at different oxidizing conditions by assessing the effects of environmental factors, such as pH, dissolved oxygen, sulphate content, and temperature. The main innovation of this study is that oxidation kinetic data were obtained at a long-term steady state (hundreds of hours) and a wide range of pH values, dissolved oxygen concentrations and temperature, combining the analysis of the reacted solutions with an exhaustive examination of arsenopyrite surface by means of Scanning Electron Microscopy (SEM), X-ray Photoelectron Spectroscopy (XPS) and MicroRaman Spectroscopy. In addition, the effect of iron coatings formed at high pH on arsenopyrite surface and its implication on arsenic release has been contemplated using the Shrinking Core Model (Wen, 1968). Therefore, the results from this study should be useful to improve the applicability of the empirical rate laws for As-bearing sulphide dissolution.

2. Materials and methods

2.1. Characterization of arsenopyrite

The arsenopyrite samples used in this study were obtained from Martinet skarn mineralization (East Pyrenees range). Some arsenopyrite fragments were crushed in an agate mortar and sieved to a size fraction below 100 μm. The powdered sample was examined by X-ray diffraction (XRD) using Cu Kα radiation over a 2θ range from 0 to 60° and using a scan speed of 0.025°/18 s. The XRD patterns obtained showed that the sample consisted of arsenopyrite as the main phase and a minor amount of quartz (approx. 5%). BSE image of the raw sample by Cameca SX-50 electron microprobe showed that arsenopyrite (AsFeS) was the dominant phase with minor amounts of quartz (SiO_2) (<3%), pyrite (FeS_2) and native Bi (<1%). The electron microprobe analysis (EMP) of the arsenopyrite atomic composition (%) was Fe 33.5 ± 0.1, As 32.1 ± 0.4 and S 34.4 ± 0.4 based on 18 points, yielding an average chemical formula of $Fe_{1.0}As_{0.94}S_{1.05}$. Geometric areas were estimated from particle size distributions, determined for powdered reacted and unreacted arsenopyrite samples by using a laser diffraction size analyser (Malver, mastersize E) after ultrasonic disaggregation in ethanol. The obtained geometric areas ranged from 0.04 to 0.1 $m^2 g^{-1}$.

BET surface areas in the same types of samples were measured using 5-point N_2 adsorption isotherms with a Micromeritics ASAP 2000 surface area analyzer and the obtained values were used for normalizing the experiments at $pH < 6$. The final BET-determined specific surface area in those experiments varied from 0.3 to 0.7 $m^2 g^{-1}$. These values are generally five to ten times larger than the corresponding estimated geometric areas, which is a very common finding in kinetic studies and has also been described in earlier works (White and Peterson, 1990; White and Brantley, 2003 and references therein). Unreacted and reacted powders were examined by Scanning Electron Microscopy (SEM) using a JEOL JSM-840 microscope and a field-emission scanning microscope Hitachi H-4100FE.

XPS surface examination of the initial and reacted powdered samples mounted on carbon conductive tabs was carried out with a Physical Electronics (PHI) 5500 spectrometer using a monochromatic X-ray source (with an Al Kα line of 1486.6 eV energy and 350 W) placed perpendicular to the analyzer axis and calibrated using the 3d5/2 line of Ag with a width of 0.8 eV and a binding energy of 368.3 eV. All these measurements were made in an ultra high vacuum (UHV) chamber (pressure between $6.6 \cdot 10^{-11}$ and $6.6 \cdot 10^{-12}$ atm). The analyser pass energy was 23 eV. An electron flood gun at low energies (below 25 eV) was used for charge compensation. Comparison of the relative positions of the different peaks in all the studied spectra indicated that charge shifting could be considered uniform. Spectra are shown as raw data corrected by adjusting the C1s peak (corresponding to adventitious carbon, to a binding energy of 284.6 eV) because of the charge of the sample. Given the lack of sample cooling while acquiring the measurements, loss of elemental sulphur could occur. Therefore, the presence or absence of elemental sulphur is discussed below. Atomic concentrations of arsenic, iron and sulphur were determined from the XPS peak areas divided by atomic sensitivity factors following the Shirley background substraction. A deconvolution of the spectra into different components was carried out. Each spectrum was fitted by means of an iterative least-squares procedure with Gaussian bands. The proportion of each surface species was then determined as a function of the areas covered by each band. However, a systematic quantification of the different iron species present in the samples is not presented here because of the low signal-to-noise ratio in most of the XPS spectra for these peaks. Only the approximate position of the observed sulphur species will be described below.

Surfaces of raw arsenopyrite powder and some powders retrieved at the end of the runs at different pH were examined by MicroRaman spectroscopy, revealing traces of quartz and pyrite at the surface.