



## EFFECT OF pH AND DISSOLVED OXYGEN ON ARSENIC RELEASE FROM ARSENOPYRITE SAMPLES

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### RESUMO

O estudo tem como objetivo a liberação de arsênio em solução aquosa a partir de três amostras ricas em As contendo teores de 85,7, 82,9 e 98,5% da fase arsenopirita (FeAsS). Os experimentos foram realizados em uma coluna de fluxo contínuo com amostras de tamanho de partículas ( $d_{50}$ ) entre 4-11 $\mu$ m, durante 24h, em diferentes condições de pH (5, 7 e 11) em soluções saturadas em O<sub>2</sub> ou N<sub>2</sub>, conforme esperado em disposição de rejeitos. Uma diferença de dez vezes ( $10^{-8,7}$ ,  $10^{-8,9}$  e  $10^{-10,0}$  mol.m<sup>-2</sup>.s<sup>-1</sup>) na taxa de liberação de arsênio em condições *steady-state* foi observada quando comparadas as três amostras. A taxa de liberação de arsênio em soluções saturadas com O<sub>2</sub> diminui à medida que o pH aumenta de 5 até 11. A quantidade de arsênio liberada e a taxa de liberação diminuem à medida que a concentração de oxigênio diminui, exceto para a amostra mais rica em arsenopirita (AM-03), para a qual o efeito dessa variável foi insignificante. Os resultados sugerem que as diferenças na mineralogia, embora ainda não completamente identificadas, podem implicar em diferenças significativas no arsênio liberado no meio ambiente.

**PALAVRAS-CHAVE:** Liberação de arsênio, arsenopirita, cinética, oxidação sulfetos.

### ABSTRACT

Arsenic release in aqueous solution from three As-rich samples containing arsenopyrite (FeAsS) 85.7, 82.9 and 98.5%, respectively. The experiments carried out in a jacketed, non-stirred continuous, flow column with solid samples of particles sizes ( $d_{50}$ ) within 7-11 $\mu$ m were carried out for 24h under different pH conditions (5, 7 and 11), in O<sub>2</sub>- or N<sub>2</sub>-saturated solutions, as expected in tailings disposal facilities. A tenfold difference ( $10^{-8,7}$ ,  $10^{-8,9}$ , and  $10^{-10,0}$  mol.m<sup>-2</sup>.s<sup>-1</sup>) on arsenic release rate under steady-state conditions was observed when comparing the three samples. The arsenic release rate in O<sub>2</sub>-saturated solutions decreases as pH increases from 5-7 to 11. Both the % arsenic release and the arsenic release rate decrease as oxygen concentration decreases, except the richest-FeAsS for which the effect was negligible. The results illustrate how differences in mineralogy features, though not fully identified, may imply in significant differences in the arsenic released into the environment.

**KEYWORDS:** Arsenic release, arsenopyrite, kinetics, sulfide oxidation.

## 1. INTRODUCTION

Arsenic is one of the ten primary toxic substances defined by the World Health Organization (WHO). As a group I carcinogen, its deleterious effects on human health include, in addition to cancer, dermal changes, respiratory problems, cardiovascular diseases, renal diseases, among others (Mandal and Suzuki, 2002; Bhattacharya *et al.*, 2007). Given these risks, WHO (2016) has set a provisional guideline value for the maximum concentration of As in drinking water of  $10\mu\text{g.L}^{-1}$  (ppb). Some European countries already adopt  $1\mu\text{g.L}^{-1}$  as the target concentration.

The main problems of human contamination by arsenic are associated with water intake by populations living in regions where groundwater contains high concentrations of the element, such as in Bangladesh, Taiwan, and Argentina. It is a natural occurrence, without anthropogenic action.

Nevertheless, arsenic minerals are often found in wastes and tailings generated from the processing of base metals, uranium and gold ores, thus creating potential sources for contamination. The main arsenic-bearing minerals are arsenopyrite ( $\text{FeAsS}$ ), arsenian pyrite ( $\text{Fe}(\text{As,S})_2$ ), scorodite ( $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ ), amorphous or crystalline ferric arsenates. The stability of the arsenic-bearing wastes should be well understood and controlled to prevent impacts from arsenic release into the environment (Smedley and Kinniburgh, 2002; Nordstrom, 2012; Ciminelli, 2014).

The kinetics of arsenopyrite oxidation has been extensively investigated, but the literature indicates significant discrepancies between the results. Differences in terms of the type of reactor, element analyzed (Fe, S or As), and reaction time may explain, at least in part, some of the discrepancies observed in the literature. It is essential to highlight that most studies focused on acidic conditions, and limited information is available on the rates and mechanisms of arsenopyrite oxidation under neutral or alkaline pH, conditions typically found in tailings disposal.

In their review paper, Corkhill and Vaughan (2009) discuss the divergences in the literature regarding arsenopyrite oxidation and highlight that additional research is necessary to address these discrepancies. Asta *et al.* (2010) pointed out that some differences, such as the type of reaction system, pH range, temperature, and oxidant concentration, may lead to divergences in the rate. It is also important to observe that only few studies (e.g., Walker *et al.*, 2006; Wang *et al.*, 2018) have focused on the reaction kinetics at circumneutral conditions.

The present work intends to compare the arsenic release from three different arsenopyrite mineral samples to evaluate the effect of sample mineralogy, another possible reason to explain the divergences observed in the literature. The effect of pH (varying from 5 to 11), and oxygen concentration (0-100% saturation) were also investigated.

## 2. EXPERIMENTAL

The three arsenopyrite samples used in this study were obtained from (i) Barroca Grande - Village of São Francisco de Assis, Portugal (AM-01), (ii) Paracatu – Minas Gerais, Brazil (AM-02), (iii) Yi Zhang - Hunan Province, China (AM-03). The samples were initially ground in a disc mill and sieved to size fractions below  $40\mu\text{m}$ . The particle size distribution

was measured by laser diffraction (CILAS, 1064L). Following sieving, the samples were rinsed with 75% v/v ethanol placed in an ultrasonic bath to remove ultrafine particles adhering to the surface of the mineral. The samples were then washed in 3 mol.L<sup>-1</sup> HCl (37% P. A., Química Moderna Ltda) solution to remove oxides and other acid-soluble phases. The samples were then vacuum-filtered on a nylon membrane, thoroughly washed with Milli-Q Water (Millipore Corporation), ethanol and stored in a desiccator.

The specific surface area analyses of the samples were measured (Quantachrome Nova-1200e), following the multipoint BET method through nitrogen adsorption, after degassing at 40°C for 72h under vacuum. The powdered samples were examined by X-ray diffraction (XRD) analyses (Philips, PW1710) using Cu(K $\alpha$ ) radiation over a 2 $\theta$  range from 3.03 to 89.94°, and a scan speed of 0.016°/s, tube voltage of 50kV and applied a current of 35mA. Samples prepared in polished sections were further subjected to quantitative mineralogy analysis using the Mineral Liberation Analyzer-MLA. Raman spectra of solid samples were obtained with a LabRam-HR 800 (Horiba Jobin Yvon,) spectrograph equipped with helium-neon laser ( $\lambda$  = 632.8nm), a microscope (Olympus BX-41, 100x), and an LN2 charged coupled device (CCD 3000 - Spectrum One). The spectra ranged within 100-1400cm<sup>-1</sup> with a step size of 1cm<sup>-1</sup>; a minimum of 30 scans of 30s each were recorded. The atomic composition of arsenopyrite was determined by electron microprobe analysis (Jeol, JXA-8900RL) using an average of 60 points measurements in each sample. The calibration was performed with pyrite (FeS<sub>2</sub>) for Fe and S elements, and löllingite (FeAs<sub>2</sub>) for As.

The chemical composition of the solid samples was determined after block digestion with aqua regia (HNO<sub>3</sub>/HCl - 3:1) (Correa *et al.*, 2002) and fusion digestion with lithium metaborate (Bartenfelder and Karathanasis, 1988), by inductively coupled plasma optical emission spectrometry (ICP-OES) (Perkin Elmer, Optima 7300DV). All reagents and experiments were prepared using Milli-Q water (18 M $\Omega$ .cm). The certified reference materials included Montana I Soil SRM NIST 2710a, TILL3 Soil CCRMP TILL3 (CANMET), Base Metals Ores CCRMP MP-1b and CCRMP KZK-1 (CANMET). Blanks prepared and included in each batch run of every ten samples returned values below the method detection limits (DL < 0.2mg.L<sup>-1</sup>). Total S was determined by combustion furnace (LECO).

The arsenic release from samples of different mineralogical compositions was evaluated in a flow-through column system, containing 1g of solid in solutions saturated with O<sub>2</sub> or N<sub>2</sub> (99.99% O<sub>2</sub> and 99.999% N<sub>2</sub>, Air Products). The experiments were carried out in a jacketed, non-stirred continuous, flow column, 25mm of diameter, and 150mm high, similar to that described by Asta *et al.* (2010). The temperature (25 $\pm$ 2°C), was controlled by circulating external water flow. Aliquots of the column effluent were collected by an automatic sampler device (Fraction Collector SuperFrac, Amersham Pharmacia Biotech Inc). The solution pH and Eh were measured (Digimed, model DM-23) using a combined pH electrode and a redox electrode with platinum ring and Ag/AgCl reference electrolyte, after calibration. At the end of the experiment, the solid sample was removed from the column, vacuum filtered, washed with ethanol, and stored in a desiccator for further characterization. During the oxidation experiments, As and Fe concentrations in the aqueous phase were also determined by ICP-OES (detection limit, DL, of 0.1mg.L<sup>-1</sup>) and by Hydride Generation Inductively Coupled Plasma Optical Emission Spectrometry (HG-ICP-OES) (DL 1.0 $\mu$ g.L<sup>-1</sup>).

### 3. RESULTS AND DISCUSSION

The XRD patterns (not shown) of the As-received samples indicated arsenopyrite as the main constituent, with minor amounts of (i) sphalerite (ZnS) and muscovite ( $KAl_2(AlSi_3O_{10})(OH, F)_2$ ) in sample AM-01, (ii) quartz ( $SiO_2$ ) in sample AM-02 and (iii) galena (PbS) in sample AM-03. Quantitative mineralogy by MLA (Table 1) of acid-cleaned samples indicated arsenopyrite content within 82.9 and 98.5% in the studied samples. Arsenic, Fe, and S are the major elements in all samples according to chemical analysis. The minor elements identified were Zn (2.82%) in sample AM-01, Si (2.98%) in sample AM-02, Pb (2.12%) in sample AM-03. The average chemical formula of arsenopyrite in the studied samples was determined as  $Fe_{0.98}As_{1.04}S_{0.97}$  (AM-01),  $Fe_{0.98}As_{1.04}S_{0.98}$  (AM-02),  $Fe_{1.03}As_{0.92}S_{1.4}$  (AM-03), based on electron microprobe analysis.

**Table 1: Mineralogical composition (MLA) and BET surface area of the mineral samples**

	AM-01	AM-02	AM-03
<b>Mineral phases</b>			
Arsenopyrite	82.9	85.7	98.5
Pyrite	--	2.7	--
Quartz	--	9.5	--
Muscovite	6.3	1.0	--
Sphalerite	6.6	--	--
Others (<1%)	4.2	1.1	1.5
<i>Total</i>	<i>100.0</i>	<i>100.0</i>	<i>100.0</i>
<b>BET SSA (<math>m^2.g^{-1}</math>)</b>			
BET SSA ( $m^2.g^{-1}$ )	0.432	0.430	0.533
$d_{50}(\mu m)$	11	7	4

Figure 1 (a) shows the cumulative arsenic release from sample AM-01 at initial pH of 5, 7 and 11, and in the presence and absence of  $O_2$ . In all cases, a drop in pH was observed in the first hours. After 5h, the pH stabilizes at about 5.0,  $5.0 \pm 0.5$  and  $10.5 \pm 0.5$ , respectively. It can also be observed that the amount of arsenic released increased with pH. Some authors reported the increase of arsenic release with increasing pH at  $pH > 8$  (Koslides and Ciminelli, 1992; Yu *et al.*, 2007; Asta *et al.*, 2010). The As/S molar ratio was equal to 1 and  $Fe/As < 1$  in the aqueous phase, the latter is consistent with the precipitation of iron oxyhydroxides.

The rate of arsenic release, shown in Figure 1 (b), decreased with time and stabilized after 10-15h in the oxygen saturated solutions. The rates steady-state conditions were  $10^{-8.8} mol.m^{-2}.s^{-1}$  at pH 5 and 7, and  $10^{-9.3} mol.m^{-2}.s^{-1}$  at pH 11. It may be seen that the initial release rate of As (the slope at of the curve % As release vs. time at the time close to zero) is favored at pH 11 compared to the lower pH conditions, but becomes relatively lower at longer times. This behavior may be associated with the favorable formation of a product layer at higher pH, which may hinder the oxidation reaction, as suggested by the onset of a plateau at pH 11 in Figure 1 (a). The pH effect also demonstrates how conclusions based on initial reaction rates may be different from those obtained at longer reaction times, under steady-state conditions.

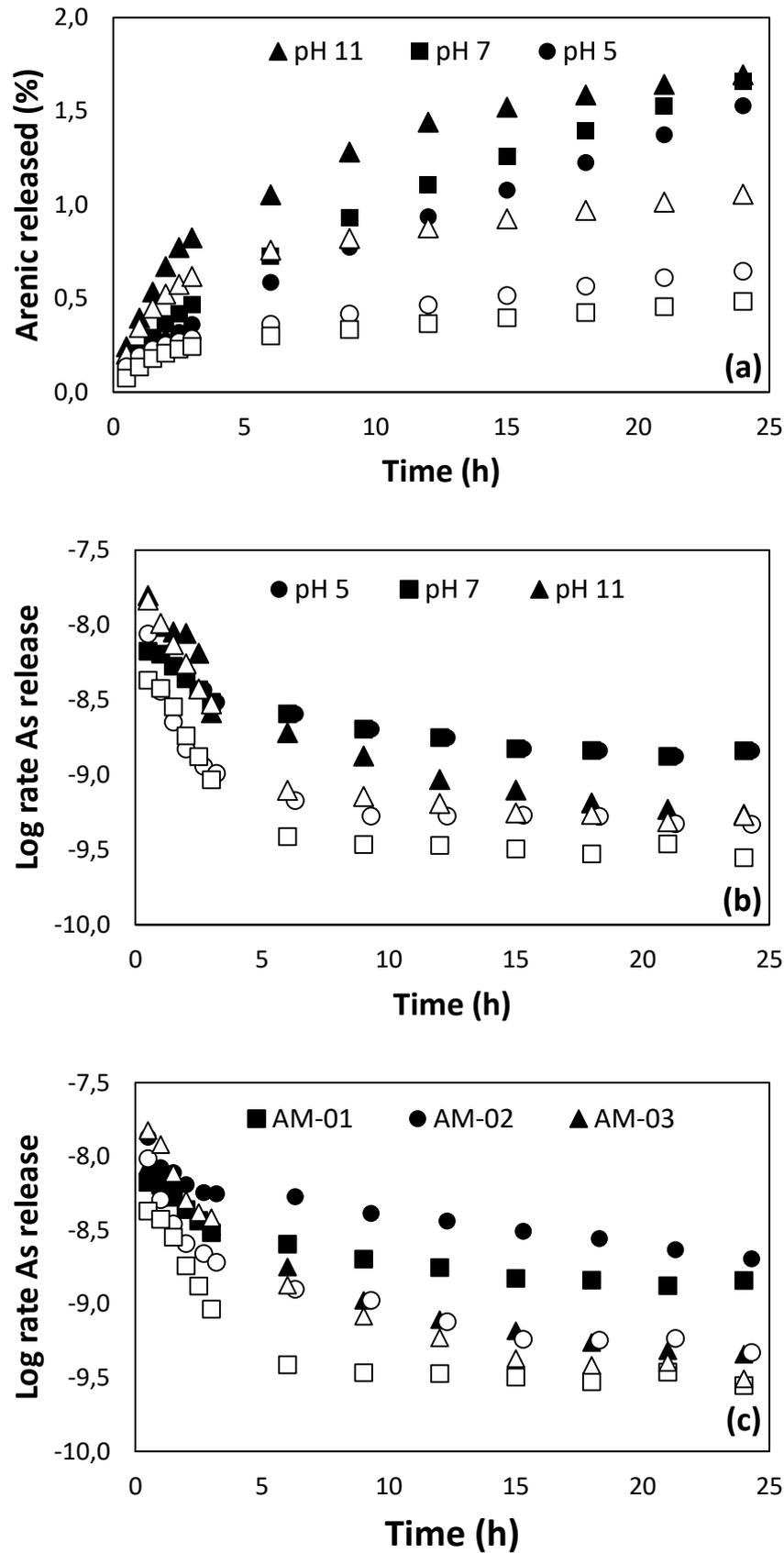


Figure 1: Effect of pH and oxygen on % As release AM-01 (a) and Log rate of arsenic release (in mol.m<sup>-2</sup>.s<sup>-1</sup>) in column tests, sample AM-01 (b) and samples AM-01, AM-02, AM-03, pH 7 (c). Closed symbols 100% O<sub>2</sub>; open symbols 100% N<sub>2</sub>.

It may also be noticed that arsenic release is lower in a nitrogen atmosphere ( $10^{-9,5}\text{mol.m}^{-2}.\text{s}^{-1}$  in pH 7 and  $10^{-9,3}\text{mol.m}^{-2}.\text{s}^{-1}$  at pH 5 and 11), being the difference at pH 11 lower than those observed at pH 5 and 7. Similar trends were seen with sample AM-02, the reaction rates decrease with time and the lowest rates at longer times are observed at pH 11, and in the absence of oxygen. Figure 1 (c) compares the As release rate from the three studied samples at pH 7. The rates were similar for the samples AM-01 and AM-02 in the presence of oxygen, but ten times higher than the rate for the sample AM-03. Both the % arsenic release (not shown) and the arsenic release rate decrease as oxygen concentration decreases for all samples, except the richest-FeAsS (AM-03) for which the effect was negligible. The results reiterate how differences in mineralogy features may imply in significant differences in the arsenic released into the environment.

The reacted particles were analyzed by micro Raman spectroscopy (Figure 2). The analyses of the oxidation products, obtained at pH 5 and 7 and  $\text{O}_2$  saturation, showed the presence of iron oxyhydroxides ( $\sim 680\text{-}700\text{cm}^{-1}$ ) and associated arsenate/arsenite phases ( $\sim 860\text{cm}^{-1}$ ) (Muller et al., 2010). At pH 11, multiple bands at 150 and  $400\text{-}650\text{cm}^{-1}$  region (Tonizazzo et al., 1999) may indicate a presence of a mixture of polysulfide ( $\text{S}_n^{2-}$ ) and elemental sulfur ( $\text{S}_8$ ) at the arsenopyrite surface. Iron oxyhydroxides phases were observed around  $680\text{-}700\text{cm}^{-1}$ . Others shifts (198, 227,  $301\text{cm}^{-1}$ ) can indicate iron lattice modes, common in both Fe-Ox and Fe-S (polysulfides/sulfates) phases (pH 11). In the region of  $980\text{-}1200\text{cm}^{-1}$ , the bands are characteristic of sulfate species. At the start of the oxidation, the reacted surfaces showed a yellowish color, which was modified to a more intense reddish-brown color, characteristic of the regions where the formation of amorphous iron oxides has been detected. A broadband in the region of  $650\text{-}700\text{cm}^{-1}$ , typical of iron oxyhydroxides such as ferrihydrite, were observed in all the studied conditions. Even in the absence of  $\text{O}_2$ , the early formation of iron oxides on the surface of arsenopyrite was observed.

Other authors studied the effect of pH on the rate of arsenic release. The majority of the results, including ours, are concentrated in the range rates from  $10^{-8,5}$  to  $10^{-9,5}\text{mol.m}^{-2}.\text{s}^{-1}$ . Samples (AM-01 and AM-02) show rates in the range from  $10^{-8,5}$  to  $10^{-9,5}\text{mol.m}^{-2}.\text{s}^{-1}$  in the runs conducted at pH 5 to 11. The relatively low rates obtained by Walker *et al.* (2006)  $10^{-10,0}\text{mol.m}^{-2}.\text{s}^{-1}$  and Asta *et al.* (2010)  $10^{-9,4}\text{mol.m}^{-2}.\text{s}^{-1}$  were ascribed by the latter authors to the longest reaction times (30h and 4500h, respectively) adopted in both investigations. The explanation would imply that the other works did not achieve a steady state. The higher values reported by McKibben *et al.* (2008) ( $10^{-7,6}\text{mol.m}^{-2}.\text{s}^{-1}$ ) may be related to the fact that the authors reported initial reaction rates (in experiments approximately 6h long) and not steady-state rates. This is not the case of the work by Yu et al. (2007), where experimental results indicated the achievement of steady state, rate  $10^{-8,9}\text{mol.m}^{-2}.\text{s}^{-1}$ . We hypothesize, based on the behavior of sample AM-03 (pH 7), that the differences may be somewhat related to mineralogical features, not fully understood at this point.

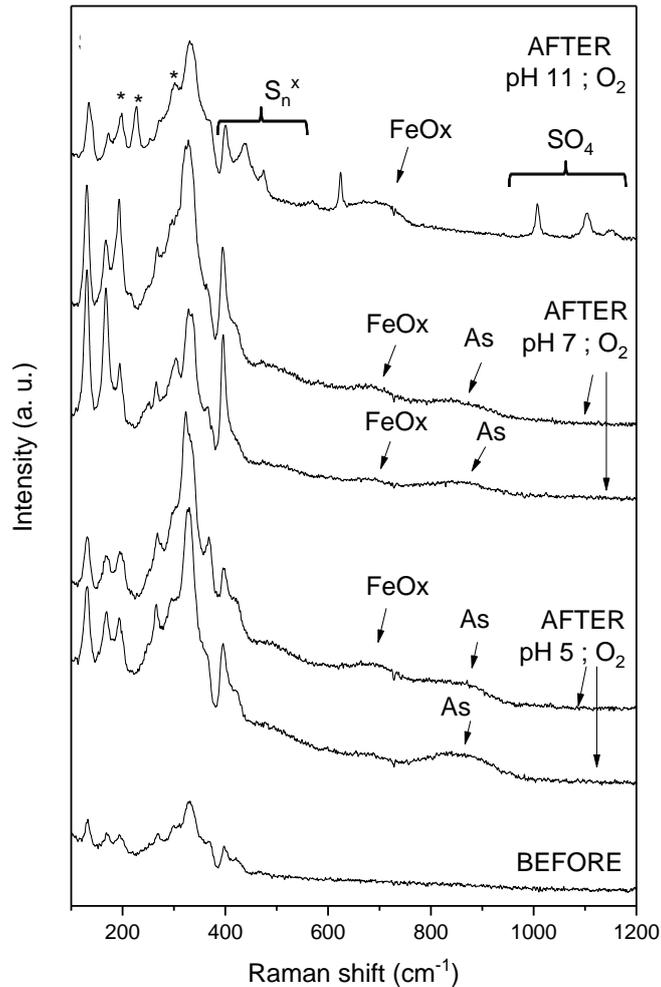


Figure 2: Raman spectra obtained from solid products formed on sample AM-01 ( $d_{50} \sim 11 \mu\text{m}$ ) oxidation at pH; 5, 7 and 11, 100%  $\text{O}_2$  and  $T=25 \pm 2^\circ\text{C}$ . FeOx: Fe-oxides  $680\text{-}700\text{cm}^{-1}$ ; As: arsenate/arsenite species at  $860\text{cm}^{-1}$ ;  $\text{S}_n^x$  (441, 474, 623);  $\text{SO}_4^{2-}$  sulfate species ( $1008, 1130$  and  $1150\text{cm}^{-1}$ ).

#### 4. CONCLUSIONS

A ten times difference in the rate of arsenic release was observed among the three studied FeAsS samples. At pH 7 and 100%  $\text{O}_2$  the rates were  $10^{-8,8}\text{mol.m}^{-2}.\text{s}^{-1}$  (AM-01),  $10^{-8,7}\text{mol.m}^{-2}.\text{s}^{-1}$  (AM-02) and  $10^{-9,3}\text{mol.m}^{-2}.\text{s}^{-1}$  (AM-03). The effect of oxygen also varied as the three samples are compared. The rate of arsenic release is reduced as  $\text{O}_2$  concentration is reduced (by saturating with  $\text{N}_2$ ) for the samples AM-01 and AM-02 but not for the richest FeAsS sample (AM-03), for which the rates were not affected by the presence or absence of the oxidant. The pH increase (5 to 11) led to the increase of the initial amount of arsenic release but the reduction of the steady state rate of arsenic release from  $10^{-8,8}$  to  $10^{-9,3}\text{mol.m}^{-2}.\text{s}^{-1}$  (AM-01) and from  $10^{-8,8}$  to  $10^{-9,1}\text{mol.m}^{-2}.\text{s}^{-1}$  (AM-02). Reaction products such as iron oxides, arsenates, and sulfates were identified on the arsenopyrite surface.

The results demonstrate how conclusions based on initial reaction rates may be different from those obtained at longer times, steady-state conditions. The results also corroborate the need for a careful examination of the mineralogy features of arsenic-containing tailings, since these differences may imply significant differences in the arsenic released into the environment.

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