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Arsenic release and transport during oxidative dissolution of spatially-distributed sulfide minerals

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Graphical Abstract
Abstract

The oxidative dissolution of sulfide minerals, naturally present in the subsurface, is one of the major pathways of arsenic mobilization. This study investigates the release and fate of arsenic from arsenopyrite and löllingite oxidation under dynamic redox conditions. We performed multidimensional flow-through experiments focusing on the impact of chemical heterogeneity on arsenic mobilization and reactive transport. In the experimental setups the As-bearing sulfide minerals were embedded, with different concentrations and spatial distributions, into a sandy matrix under anoxic conditions. Oxic water flushed in the flow-through setups triggered the oxidative dissolution of the reactive minerals, the release of arsenic, as well as changes in pore water chemistry, surface-solution interactions and mineral precipitation. We developed a reactive transport model to quantitatively interpret the experimental results. The simulation outcomes showed that 40% of the arsenic released was reincorporated into a freshly precipitated iron-arsenate phase that created a coating on the mineral surface limiting the dissolution reactions. The faster dissolution rate of löllingite compared to arsenopyrite was responsible for sustaining the continuous release of As-contaminated plumes. The model also allowed shedding light on the spatial distribution, temporal dynamics and interactions between arsenic sources (As-bearing minerals) and sinks (freshly formed secondary phases) in flow-through systems.
1 Introduction

Arsenic (As) contamination of groundwater is a problem of enormous relevance affecting the health of more than 100 million people worldwide (Podgorski and Berg, 2020; Ravenscroft et al., 2009). Long-term human intake of inorganic arsenic may have serious effects on human health, causing cancer and other skin, vascular and nervous systems disorders (WHO, 2011). High concentrations of arsenic in groundwater have been found in various parts of the world (Smedley, 2006), including South East Asia (e.g., Biswas et al., 2014; Charlet and Polya, 2006; Fendorf et al., 2010; Kocar et al., 2008; Postma et al., 2012), China (e.g., Guo et al., 2014; Pi et al., 2015; Stolze et al., 2019a), North and South America (e.g., Alarcón-Herrera et al., 2013; Ayotte et al., 2017; López et al., 2012; McClintock et al., 2012; Ormachea Muñoz et al., 2013; Welch et al., 2000), Europe (e.g., Battistel et al., 2020; Bundschuh et al., 2013; Kouras et al., 2007; Søgaard and Madsen, 2013), Africa (e.g., Bretzler et al., 2019; Mensah et al., 2020) and Australia (e.g., Fazle Bari et al., 2020). The complexity of dealing with arsenic contamination mainly stems from the geochemical and hydrogeological controls on arsenic release, fate and transport. Indeed, arsenic naturally occurs in As-rich iron (hydr)oxides and/or As-bearing sulfides minerals, which are the main geogenic sources of arsenic pollution (Smedley and Kinniburgh, 2002; Walker et al., 2006; Wallis et al., 2020).

Changes in hydrochemistry associated with the hydrological cycle, anthropic activities, and dynamic boundaries between different environmental compartments can trigger arsenic release in the subsurface (e.g., Appelo and Postma, 2005; Fendorf et al., 2010; LeMonte et al., 2017). The shifts in subsurface redox conditions represent one of the principal mechanisms responsible for the mobility of arsenic bound to sulfide minerals (Appelo and Postma, 2005; Jones and Pichler, 2007; Lazareva et al., 2015; Price and Pichler, 2006; Prommer and Stuyfzand, 2005; Schreiber et al., 2000; Shaheen et al., 2016; Wallis et al., 2010). The oxidative dissolution of As-bearing sulfide minerals is of primary importance in aquifer systems where conditions are typically dynamics and are subject to spatial and temporal changes. For instance, the fluctuation of groundwater level due to increased dryland water scarcity and/or aquifer overexploitation can expose lenses of reactive minerals to oxygen and promote
the mobilization of arsenic (Andersen et al., 2001; Kinniburgh et al., 1994; Larsen and Postma, 1997). Furthermore, the introduction of oxygenated recharge water into an aquifer during managed aquifer recharge, a common practice used in arid areas for improving the drinking water supply, can trigger the release of arsenic and cause the dissolution of As-bearing mineral lenses naturally present in the porous media (Descourvières et al., 2010a, 2010b; Fakhreddine et al., 2020; Prommer and Stuyfzand, 2005). The oxidation of As-bearing minerals upon contact with oxic water entails the consumption of oxygen as well as significant shifts in the water chemistry (Corkhill and Vaughan, 2009; Walker et al., 2006). Both the concentration and the spatial distribution of such minerals represent a primary control on the mobilization of oxidation products (Battistel et al., 2019; Fakhreddine et al., 2016). The dissolution of the As-bearing sulfide minerals causes the release of Fe, S, and As whose fate and transport depend on the local geochemical conditions. For example, under oxidizing conditions and at circumneutral pH, arsenic can precipitate with iron and/or bind to iron (hydr)oxides (Smedley and Kinniburgh, 2002; Smith et al., 1998), or can be reincorporated in secondary phase oxides (Asta et al., 2013; Filippi, 2004; Lengke et al., 2009; McKibben et al., 2008). The most common As-bearing mineral in the subsurface is arsenopyrite (FeAsS), that is often associated with other iron/sulfide minerals, such as orpiment (As$_2$S$_3$) and löllingite (FeAs$_2$) (Saintilan et al., 2017). Due to its predominance, arsenopyrite oxidation has been extensively studied under controlled laboratory conditions to quantify the reaction kinetics and the effects of temperature and pH (e.g., Asta et al., 2010; McKibben et al., 2008; Walker et al., 2006; Yu et al., 2007). In contrast, the oxidative dissolution of löllingite and other As sulfide minerals has received less attention (Filippi, 2004; Lengke et al., 2009; Williamson and Rimstidt, 1994). Most of the experiments investigating the oxidative dissolution of As-bearing sulfide minerals are conducted in batch and reactor setups (e.g., Asta and Acero, 2010; Lengke and Tempel, 2002; Yunmei et al., 2004), whereas literature studies based on flow-through porous media and focusing on the release and transport of arsenic from reactive sulfide minerals are still lacking.
The aim of this study is to assess the impact of arsenic-bearing reactive inclusions on groundwater quality through a combination of laboratory experiments and reactive transport modeling. We investigate the kinetic oxidative dissolution of arsenopyrite and löllingite under dynamic redox conditions obtained by flushing oxic water into an anoxic environment. We perform a detailed investigation of oxygen front propagation, its effect on mineral dissolution and arsenic release, as well as the spatial and temporal distribution of dissolved species and freshly formed secondary mineral phases. A number of experiments were performed in batch, 1-D columns and quasi 2-D setups. The flow-through experiments were conducted in physically homogeneous but chemically heterogeneous saturated porous media, where a natural As-bearing sulfide ore, composed of arsenopyrite and löllingite was embedded in a quartz sand matrix. The laboratory experiments allowed investigating the impact of the spatial distribution and concentration of the sulfide minerals on the release and transport of As, Fe, S and O₂ that were monitored at high spatial and temporal resolution. A reactive transport model was developed in order to quantitatively interpret the experimental observations and to shed light on the complex interplay between the dissolution of the As-bearing sulfide minerals and the precipitation of secondary iron oxide phases that controls the release and transport of arsenic.

2 Material and Methods

2.1 Experimental setups

We performed a series of batch and flow-through experiments with a natural ore material containing arsenopyrite and löllingite as As-bearing sulfide minerals. A schematic overview of the flow-through setups used in this study is given in Fig. 1. The flow-through experiments were run in 1-D columns and a quasi 2-D flow-through chamber filled with saturated porous media. Both in the one-dimensional and in the quasi two-dimensional setups the reactive minerals were embedded as inclusions in the sandy porous media and the experiments were performed varying the mineral content and spatial distribution. The flow-through experiments were physically homogeneous, with the same
grain size of the quartz sand and the reactive sulfide minerals, but chemically heterogeneous. The oxygen consumption due to the kinetic oxidative dissolution of arsenopyrite and löllingite was preliminary assessed in a series of batch experiments, and a detailed overview of the batch setup is given in the Supplementary Material.

Figure 1. Experimental laboratory flow-through setups for the investigation of pyrite oxidation (a) 1-D columns and (b) 2-D flow-through chamber. The inset shows the characterization of the mineral composition of the As-bearing sulfide ore by using spectroscopy techniques.

2.1.1 Preparation of the porous media

Both the sand and the As-sulfide ore (Ward’s Science) were dry sieved to obtain a 125-250 μm grain fraction and then cleaned to remove impurities that may be attached to the surface of the grains. The sand was sequentially washed with pH 4, pH 10 and pH 2 solutions, rinsed with milli Q water and completely dried in an oven. The reactive As-bearing sulfide minerals were prepared and cleaned with the method described by Walker et al. (2006). After the washing process, the cleaned ore was dried with nitrogen gas and immediately used in the experiment. The mineral composition of the As-bearing sulfide minerals was determined by X-ray diffraction (XRD, Rigaku MiniFlex 600 Benchtop) in a Bragg-Brentano Theta-Theta geometry and compared and validated by performing X-ray fluorescence analyses (XRF, Spectro XRF-XEPOS) of the mineral ore. The As-bearing sulfide ore considered in this work consists of 45 w% arsenopyrite (FeAsS) and 55 w% of löllingite (FeAs₂).
Iron K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy was conducted at Stanford Synchrotron Radiation Lightsource, (SSRL) and revealed that the cleaning method does not impact the mineralogy of the ore and that Fe exists entirely linked to sulfide minerals. Further details regarding the mineral analyses are provided in section S1 of the Supplementary Material.

2.1.2 Flow-through experiments

The experiments were performed in 1-D columns and in a quasi 2-D flow-through chamber. In both setups, high resolution spatially distributed measurements of oxygen were taken using oxygen sensitive strips (SP-PS\textsuperscript{3}-NAU, PreSens GmbH, accuracy ±0.4% O\textsubscript{2}) glued onto the inner walls of the setups. This allowed for measurements to be taken non-invasively using a polymer optical fibre cables (Haberer et al., 2011). Conventional sampling of dissolved species in the effluent was performed in the column setups and from the multiple outlet ports of the quasi 2-D flow-through chamber.

In the 1-D flow-through experiments we used three glass columns (length: 11.7/14.5 cm; inner diameter: 1.7 cm), equipped with a 10 cm × 0.5 cm O\textsubscript{2} sensor strip glued onto the inner wall. The columns were wet packed with the cleaned media to minimize air entrapment (Haberer et al., 2012).

Three different configurations of mineral inclusions, obtained by mixing the quartz sand and the reactive minerals were embedded in the sandy matrix: column 1 had one single inclusion of 3.5 cm length, with a bulk concentration of As-bearing minerals of 50% v/v, column 2 had two inclusions of 2 cm each, with a bulk concentration of As-bearing minerals of 50% v/v, and column 3 had one inclusion of 2 cm, with a bulk concentration of As-bearing minerals of 10% v/v. Both ends of the columns were sealed with a cap and a septum that prevented the intrusion of atmospheric oxygen.

Steady-state flow-through conditions were established in the three columns with a high-precision multi-channel peristaltic pump (IPC-N24, ColeParmer, Vernon Hills, United States). Additionally, a 1-D flow-through experiment in the absence of reactive sulfide minerals was performed to characterize the conservative transport of oxygen in the column setup.
The 2-D experiment was performed in a flow-through chamber filled with a physically homogeneous but chemically heterogeneous porous medium. The setup has inner dimensions of 80 cm × 40 cm × 0.5 cm (length × height × width) and the walls are made of transparent acrylic glass and equipped with four O₂ sensitive strips with dimensions of 20 cm × 1 cm, glued in the inner-side of the chamber wall. The sensor strips were located at 16, 32, 48 and 64 cm from the inlet, perpendicular to the flow direction. The chamber was filled with a wet-packing procedure and two lenses of sand mixed with the minerals were included (Fig. 1b). One of these reactive inclusions had a length of 23.5 cm and a height of 1.8 cm and was placed at 10.5 cm from the inlet and at 14 cm from the bottom of the flow-through chamber. The other inclusion had a length of 17 cm and a height of 2.2 cm and was placed at 47 cm from the inlet and at 6 cm from the bottom of the flow-through chamber. Two high-precision multichannel peristaltic pumps (IPC-N24, ColeParmer, Vernon Hills, United States) connected to 19 ports (1.2 cm spacing) at the inlet and at the outlet of the chamber were used to create steady flow conditions throughout the duration of the experiment.

The columns and the quasi 2-D flow-through systems were initially maintained under anoxic conditions (background O₂ concentration < 0.5 mg/L, 1-5 mM NaCl) by injecting a deoxygenated water bubbled with nitrogen gas. At the beginning of the experiment, a continuous flow of oxic solution (equilibrated with the atmosphere and with 1-5 mM NaCl) was injected into the setups at a seepage velocity of 1.5 m/day. The propagation of the oxygen fronts in the different porous media was monitored by measuring high-resolution spatial profiles (0.5 mm spacing) along the strips at different times and the breakthrough of oxygen at different spatial locations was measured with a 5 minute interval. The outflow of the setups was sampled at different times and acidified with 3% HNO₃ to determine total As, Fe and S. The analyses were performed using ICP-MS (Agilent Technologies 7700x) for arsenic and iron and ICP-OES (PerkinElmer Avio 200 in radial mode) for sulfur, following a procedure based on triplicate measurements and certified reference materials. Part of the sample was used to determine the arsenic speciation: As(III) was measured by filtering the sample through
an arsenic speciation cartridge contained 0.8 g aluminosilicate adsorbent that selectively adsorbs As(V) but not As(III) (Jessen et al., 2012; Meng and Wang, 1998).

In column 1, 2 and in the flow-through chamber also S was analyzed using inductively-coupled-plasma optical emission spectrometry (ICP-OES, PerkinElmer Avio 200 in radial mode).

A detailed overview of the physical properties of the columns and the flow-through chamber, as well as the mineral concentrations in each inclusion, and the aqueous concentrations of the solutions used in the different laboratory experiments are given in Table 1.

**Table 1. Overview of the laboratory experiments performed in the 1-D columns and quasi 2-D flow-through chamber.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1-D columns</th>
<th>2-D chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Physical properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experiment duration [hours]</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>Seeage velocity [m/day]</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Grain size [mm]</td>
<td>0.125-0.250</td>
<td>0.125-0.250</td>
</tr>
<tr>
<td><strong>Initial aqueous concentrations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5.1</td>
<td>5.2</td>
</tr>
<tr>
<td>O$_2$ [mol/L]</td>
<td>2.8×10$^{-4}$</td>
<td>2.8×10$^{-4}$</td>
</tr>
<tr>
<td>Na$^+$ [mol/L]</td>
<td>5.0×10$^{-3}$</td>
<td>5.0×10$^{-3}$</td>
</tr>
<tr>
<td>Cl$^-$ [mol/L]</td>
<td>5.0×10$^{-3}$</td>
<td>5.0×10$^{-3}$</td>
</tr>
<tr>
<td><strong>Solid phase</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk concentration of the As-sulfide ore [% v/v]</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td><strong>Inlet aqueous concentrations</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>O$_2$ [mol/L]</td>
<td>2.8×10$^{-4}$</td>
<td>2.8×10$^{-4}$</td>
</tr>
<tr>
<td>Na$^+$ [mol/L]</td>
<td>5.0×10$^{-3}$</td>
<td>5.0×10$^{-3}$</td>
</tr>
<tr>
<td>Cl$^-$ [mol/L]</td>
<td>5.0×10$^{-3}$</td>
<td>5.0×10$^{-3}$</td>
</tr>
</tbody>
</table>

### 2.2 Modeling approach

A reactive transport model was developed to simulate the continuous supply of oxic water into the anoxic system, the subsequent oxidative dissolution of the As-bearing sulfide minerals, and the impact on aqueous and solid geochemical reactions in the 1-D and 2-D flow-through setups.

#### 2.2.1 Chemical reaction network

The conceptual model for the geochemical reactions includes (i) the oxidative dissolution of arsenopyrite and löllingite, (ii) the precipitation of iron oxides and ferric arsenate phases, (iii) the
surface passivation of the As-bearing sulfide minerals induced by the formation of new mineral phases, as well as (iv) the sorption of arsenic onto freshly precipitated iron oxides. A sketch of the conceptual model for the reaction network of the experimental setups is shown in Fig. 2.

Figure 2. Conceptual model of the As-bearing sulfide minerals oxidative dissolution inducing the release of As, Fe, and S and the precipitation of secondary mineral phases causing As sequestration and surface passivation.

The oxidative dissolution of arsenopyrite (FeAsS) and löllingite (FeAs₂) leads to oxygen consumption and to the release of ferrous iron, arsenite and sulfate and are expressed, respectively, as:

\[
\text{FeAsS} + 2.75\text{O}_2 + 1.5\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{H}_3\text{AsO}_3 + \text{SO}_4^{2-}
\]

(1)

and

\[
\text{FeAs}_2 + 2\text{O}_2 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{H}_2\text{AsO}_3^{-}
\]

(2)

In presence of O₂, ferrous iron and arsenite are oxidized following the reactions:

\[
\text{H}_3\text{AsO}_3 + 0.5\text{O}_2 \rightarrow \text{HAsO}_4^{2-} + 2\text{H}^+
\]

(3)

and

\[
\text{Fe}^{2+} + 0.25\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + 0.5\text{H}_2\text{O}
\]

(4)

The formation of a ferric arsenate/scorodite phase, which is commonly observed during the oxidation of As-sulfide minerals by oxygen (Asta et al., 2010; Dove and Rimstidt, 1985; Filippi, 2004), was described with the general expression:
\[
\text{Fe}^{3+} + 0.5\text{O}_2 + \text{H}_3\text{AsO}_3 + 2\text{H}_2\text{O} \rightarrow \text{FeAsO}_4\cdot 2\text{H}_2\text{O} + 3\text{H}^+ \quad (5)
\]

Furthermore, the precipitation of iron (hydr)oxide was expressed as:

\[
\text{Fe}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{FeOOH} + 3\text{H}^+ \quad (6)
\]

The reactions were controlled by kinetic rate expressions defined based on thermodynamic constraints as well as hydrochemical and mineral composition. The dissolution rates of arsenopyrite and löllingite were expressed as a function of oxygen, proton concentrations and surface area of the mineral following the empirical rate formulation developed for pyrite (Battistel et al., 2019; Fakhreddine et al., 2016; Williamson and Rimstidt, 1994) and widely applied to describe the dissolution of sulfide minerals including arsenopyrite (Asta et al., 2013, 2010; McKibben et al., 2008; Walker et al., 2006). An additional term was added to account for the passivation of the reactive sulfide mineral surfaces due to coatings formed by the precipitation of iron (hydr)oxide and ferric arsenate phases (Asta et al., 2013, 2010; Corkhill and Vaughan, 2009; Lengke et al., 2009). Thus, the kinetic rate \( R_m \) controlling the dissolution of the sulfide mineral \( m \) (FeAsS, FeAs\(_2\)) was expressed as:

\[
R_m = k_m \times [\text{O}_2]^{x_1,m} \times [\text{H}]^{x_2,m} \times (A_m \times \{m\}) \times \frac{1}{1 + \frac{\{\text{FeOOH}\} + \{\text{FeAsO}_4\}}{\{m\} \times K_{\text{ox},m}}} \quad (7)
\]

where \( k_m \) is the rate constant, \( x_{1,m} \) and \( x_{2,m} \) are calibrated exponents, \( A_m \times \{m\} \) is the total exposed surface area of the sulfide mineral relative to the volume of solution [m\(^2\) L\(^{-1}\)], \( K_{\text{ox},m} \) is a calibrated constant. Quantities in brackets and braces, [ ] and { }, represent the molar concentration of the dissolved and mineral species, respectively.

The precipitation of a ferric arsenate phase and iron (hydr)oxide were assumed to depend on the degree of oversaturation and were expressed by the following kinetic rate expressions (Pallud et al., 2010; Tufano et al., 2009):

\[
R_{\text{FeAsO}_4} = k_{\text{FeAsO}_4\cdot \text{ppm}} (\Omega_{\text{FeAsO}_4}^{-1}) \delta_{\Omega>1} \quad (8)
\]

\[
R_{\text{FeOOH}} = k_{\text{FeOOH\cdot ppm}} (\Omega_{\text{FeOOH}}^{-1}) \delta_{\Omega>1} \quad (9)
\]
where \( k_{\text{FeAsO}_4} \) and \( k_{\text{FeOOH}} \) are the rate constants and \( \Omega_m \) is the saturation ratio of the mineral \( m \).

\[
\Omega_m = \frac{IAP_m}{K_{sp,m}}
\]

where \( IAP_m \) and \( K_{sp,m} \) are the ion activity product and the solubility product of the mineral \( m \), respectively, with \( \delta=1 \) if \( \Omega_m > 1 \). \( K_{sp,\text{FeAsO}_4} = 10^{22.252} \) (Chukhlantsev, 1956), \( K_{sp,\text{FeOOH}} = 10^{-2.5} \) (Battistel et al., 2019). The kinetic rate parameters of Eq. 7 controlling the dissolution of sulfide minerals were optimized within calibration ranges established based on previous studies (Table S4).

In addition to the co-precipitation of arsenic and iron into a ferric arsenate phase, the sorption of arsenic onto the surface of iron oxides (FeOOH) was considered in the model. The complexation reactions were considered instantaneous and modeled with the diffuse double layer (DDL) model using the set of reactions and affinity constants developed for ferrihydrite (Appelo et al., 2002; Dixit and Hering, 2003; Dzombak and Morel, 1990). Table S5 shows the surface reactions and the corresponding affinity constants considered in the model. The mineral surface was represented with a surface area of 600 m\(^2\)·g\(^{-1}\) and with weak and strong adsorption sites and the total site density [mol sites / mol FeOOH] was calibrated within the range of literature values available for iron oxides.

The proposed chemical reaction network for the oxidative dissolution of arsenopyrite and löllingite was preliminary tested in the batch experiments (details are provided in section 2 of the supplementary material and in Fig. S2) and successively applied to the flow-through setups.
Table 2. Geometry of the flow-through domains and parameters used in the reactive transport simulations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>1-D columns</th>
<th>2-D setup</th>
</tr>
</thead>
<tbody>
<tr>
<td>Domain size ($L \times H$)</td>
<td>[cm]</td>
<td>14.4</td>
<td>14.4</td>
</tr>
<tr>
<td>Discretization ($\Delta x \times \Delta z$)</td>
<td>[cm]</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Time step, $\Delta t$</td>
<td>[s]</td>
<td>84</td>
<td>84</td>
</tr>
<tr>
<td>Porosity, $\theta$</td>
<td>[-]</td>
<td>0.38</td>
<td>0.38</td>
</tr>
<tr>
<td>Volumetric water content, $\theta_w$</td>
<td>[-]</td>
<td>0.368</td>
<td>0.37</td>
</tr>
<tr>
<td>Volumetric gas content, $\theta_g$</td>
<td>[-]</td>
<td>0.012</td>
<td>0.012</td>
</tr>
<tr>
<td>Kinetic water-gas mass transfer coefficient, $\lambda$</td>
<td>[s⁻¹]</td>
<td>7.55×10⁻⁶</td>
<td>7.55×10⁻⁶</td>
</tr>
<tr>
<td>Henry's law coefficient for oxygen, $H$</td>
<td>[-]</td>
<td>31.25</td>
<td>31.25</td>
</tr>
</tbody>
</table>

**Arsenopyrite** ($\text{FeAsS}$)

- Concentration of arsenopyrite in inclusion [mol L⁻¹ bulk⁻¹]: 4.84 4.84 0.91 4.84
- FeAsS dissolution effective rate constant, $k_{\text{FeAsS}}$ [mol⁻² L⁻³ m⁻² s⁻¹]: 1.34×10⁻⁷ 1.34×10⁻⁷ 1.34×10⁻⁷ 1.34×10⁻⁷
- $x_1$, $\text{FeAsS}$ [-]: 0.45 0.45 0.45 0.45
- $x_2$, $\text{FeAsS}$ [-]: 0.26 0.26 0.26 0.26
- FeAsS surface area, $A_{\text{FeAsS}}$ [m² mol⁻¹]: 47.64 47.64 47.64 47.64
- $K_{\text{ox,FeAsS}}$ [-]: 0.12 0.12 0.12 0.12

**Löllingite** ($\text{FeAs}_2$)

- Concentration of löllingite in inclusion [mol L⁻¹ bulk⁻¹]: 4.68 4.68 0.88 4.68
- FeAs₂ dissolution effective rate constant $k_{\text{FeAs}_2}$ [mol⁻² L⁻³ m⁻² s⁻¹]: 1.94×10⁻⁷ 1.94×10⁻⁷ 1.94×10⁻⁷ 1.94×10⁻⁷
- $x_1$, $\text{FeAs}_2$ [-]: 0.65 0.65 0.65 0.65
- $x_2$, $\text{FeAs}_2$ [-]: 0.0023 0.0023 0.0023 0.0023
- FeAs₂ surface area, $A_{\text{FeAs}_2}$ [m² mol⁻¹]: 88.93 88.93 88.93 88.93
- $K_{\text{ox,FeAs}_2}$ [-]: 0.0052 0.0052 0.0052 0.0052

**Secondary phase products**

- FeOOH precipitation effective rate constant, $k_{\text{FeOOH}}$ [mol s⁻¹]: 7.48×10⁻¹⁴ 7.48×10⁻¹⁴ 7.48×10⁻¹⁴ 7.48×10⁻¹⁴
- FeAsO₄ precipitation effective rate constant, $k_{\text{FeAsO}_4}$ [mol s⁻¹]: 1.23×10⁻¹¹ 1.23×10⁻¹¹ 1.23×10⁻¹¹ 1.23×10⁻¹¹

2.2.2 Reactive transport

The reactive transport of aqueous solutes and oxygen in the chemically heterogeneous flow-through setups was described with a modeling approach accounting for (i) advection and dispersion, (ii) multicomponent ionic transport formulation including compound-specific diffusive/dispersive properties and Coulombic interactions between charged species (Appelo and Wersin, 2007; Muniruzzaman et al., 2014; Rolle et al., 2013b), and (iii) kinetic partitioning of oxygen between the aqueous and an entrapped gas phase (Donaldson et al., 1998, 1997; Fry et al., 1997). The latter process was found to significantly delay the oxygen fronts propagation in the 1-D and 2-D flow-through experiments despite the care taken during preparation of the experimental setup in order to minimize
air entrapment. The partitioning of oxygen between the aqueous and gas phases, thus, influenced the
overall transient behavior of the mineral dissolution and precipitation and the generated aqueous
species. The model includes 32 species (see Table S6) and the governing mass conservation equations
for reactive transport of species $i$ within the mobile aqueous phase and the partitioning of oxygen are
expressed as:

$$
\theta_w \frac{\partial C_{w,i}}{\partial t} + (1 - \theta_w - \theta_g) \rho_s \frac{\partial S_i}{\partial t} + \theta_g \frac{\partial C_{g,i}}{\partial t} + q \left( \nabla C_{w,i} \right) - \nabla \left( \theta_w D_{ij} \nabla C_{w,i} \right) = - \sum_{k=1}^{N_k} v_{ik} R_k 
$$

with the mass transfer of O$_2$ between the aqueous and gas phases defined as:

$$
\theta_g \frac{\partial C_{g,O_2}}{\partial t} = \lambda (H C_{w,O_2} - C_{g,O_2})
$$

where $C_{w,i}$, $C_{g,i}$ [mol·L$^{-1}$] and $S_i$ [mol·kg$^{-1}$] are the aqueous, gas phase and surface concentrations of
species $i$ and $\theta_w$ and $\theta_g$ [-] are the volumetric water and gas content, respectively. $R_k$ [mol·L$^{-1}$·s$^{-1}$] and
$v_{ik}$ [-] represent the reaction rate and the corresponding stoichiometric coefficient of species $i$ for the
$k^{th}$ reaction, $\lambda$ [s$^{-1}$] is the kinetic water-gas mass transfer coefficient; $H$ [-] is the Henry’s law
coefficient, and $t$ [s] is the time. $\lambda$ was determined based on the O$_2$ transport behavior in the
conservative flow-through experiments whereas $\theta_g$ was considered as a fitting parameter for each
flow-through setups.

Regarding transport in the aqueous phase, $q$ [m·s$^{-1}$] denotes the specific discharge vector and $D_{ij}$ [m$^2$·s$^{-1}$]
is the dispersion tensor. In a two-dimensional coordinate system, oriented along the principal flow
directions, the dispersion tensor is diagonal:

$$
D_{ij} = \begin{bmatrix} D_{ij}^L & 0 \\ 0 & D_{ij}^T \end{bmatrix}
$$

where $D_{ij}^L$ and $D_{ij}^T$ are the longitudinal and transverse cross-coupled dispersion coefficients
(Muniruzzaman and Rolle, 2017):

$$
D_{ij}^L = \delta_{ij} D_{ij}^T \frac{z_i z_j D_{ij}^T D_{ji}^T C_i}{\sum_{k=1}^{N} (z_k^2 D_{kj}^T C_k)}
$$
\[ D_{ij}^T = \delta_{ij} D_i^T \frac{z_i z_j D_i^T D_j^T C_i}{\sum_{k=1}^{N} (z_k^2 D_k^T C_k)} \]  

(14)

where \( D_i^L \) and \( D_i^T \) are the longitudinal and transverse components of the hydrodynamic self-dispersion coefficients of species \( i \), \( \delta_{ij} \) is the Kronecker delta which is equal to 1 when \( i=j \) and 0 when \( i \neq j \), \( z_i \) is the charge of species \( i \), \( N \) is the number of mobile species. For each specie \( i \), \( D_i^L \) was calculated with a linear parameterization determined empirically from detailed experimental studies (De Carvalho and Delgado, 2005; Kurotori et al., 2019):

\[ D_i^L = D_i^P + 0.5dv \]  

(15)

whereas \( D_i^T \) was calculated with a non-linear, compound-specific parameterization for transverse dispersion derived in previous experimental and pore-scale modeling investigations (Hochstetler et al., 2013; Rolle et al., 2012):

\[ D_i^T = D_i^P + D_i^{aq} \left( \frac{Pe_i^2}{Pe_i + 2 + 4 \delta^2} \right)^\beta \]  

(16)

where \( D_i^{aq} \) [m²/s] is the aqueous diffusion coefficient and \( D_i^P \) [m²/s] is the pore diffusion coefficient of species \( i \), respectively with \( D_i^P = vd/D_i^{aq} \) where \( v \) and \( d \) are the seepage velocity and the grain size diameter; \( Pe \) is the Péclet number; \( \delta [-] \) is the ratio between the length of the pore channel to its hydraulic radius, and \( \beta [-] \) is an empirical exponent that accounts for the effects of incomplete mixing in the pore channels. In this study, we adopted values of \( \delta = 5.37 \) and \( \beta = 0.5 \), determined in laboratory experiments performed with different grain sizes and seepage velocities in both 2-D and fully 3-D porous media (Ye et al., 2015a).

### 2.2.3 Model implementation and calibration strategy

The column experiments were simulated with the geochemical code PHREEQC-3 (Parkhurst and Appelo, 2013) considering the chemical reaction network presented above, including the dissolution of arsenopyrite and löllingite caused by the presence of \( O_2 \), the precipitation of iron (hydr)oxide and ferric arsenate phases and the subsequent sorption of arsenic onto the freshly precipitated iron (hydr)oxide. The multicomponent ionic transport capabilities of PHREEQC were used to consider...
the species-specific diffusive-dispersive properties (i.e., diffusion coefficients are shown in Table S6) and the electrostatic coupling of the hydrodynamic dispersive fluxes (Rolle et al., 2013a). The thermodynamic database WATEQ4f, amended with the aqueous speciation reactions of arsenic from Dixit and Hering (2003), was used to calculate the aqueous speciation and reactions between dissolved species.

The dataset collected in the 1-D flow-through experiments, which consisted in the concentrations time series of reaction products (i.e., As, Fe, S) measured at the outlet of the columns and the O₂ breakthrough curves determined at different spatial locations (i.e., 5.8 and 9.6 cm from the inlet of the columns) was used to calibrate the kinetic model parameters controlling the dissolution of the As-sulfide minerals and the precipitation of secondary mineral phases as well as the site density of iron oxide used in the surface complexation model. Therefore, simulations of the column experiments and calibration of a single set of model parameters capable of reproducing all experimental observations were performed simultaneously by parallelizing the reactive transport simulations of the three column experiments (Stolze et al., 2020). Parameters optimization was conducted by coupling PHREEQC-3 with Matlab® with the IPhreeqc module (Charlton and Parkhurst, 2011), to combine the transport and geochemical calculations of PHREEQC with the calibration and data analysis capabilities of Matlab (Muniruzzaman and Rolle, 2016; Stolze et al., 2019b). The global search particle swarm algorithm was employed to minimize the objective function which was expressed as the sum of normalized root mean squared errors (NRMSEᵢ). The latter were calculated between the simulated and measured concentrations of species at the considered locations of the columns:

\[
NRMSEᵢ = \frac{1}{n} \sum_{l=1}^{n} \frac{O_{l,m} - P_{l,m}}{O_{l,m}}
\]

where \(O_{l,m}\) is the \(l^{th}\) observation of the \(m^{th}\) dataset referring to a species at a specific location in a given column, \(P_{l,m}\) is the corresponding variable predicted by the numerical simulation and \(n\) is the number of observations in this dataset.
Reactive transport in the flow-through chamber was simulated with a 2-D multicomponent ionic transport model implemented in Matlab® and coupled with the geochemical solver PHREEQC based on a sequential non-iterative operator splitting approach (Muniruzzaman and Rolle, 2016). The PhreeqcRM module was used to couple the geochemical and transport simulators (Muniruzzaman and Rolle, 2019; Parkhurst and Wissmeier, 2015; Rolle et al., 2018; Sprocati et al., 2019). We used a finite element method to solve the water flow in the two-dimensional flow-through setup and to obtain the flow velocity field, which was used as input to the multicomponent reactive transport model. The latter was solved with a finite volume method on the streamline-oriented grids, which were generated based on the results of the flow simulation (e.g., Cirpka et al., 1999). In this step, we adopted an upwind differentiation scheme for the spatial discretization, the explicit Euler method for the advection (with Courant number, $C_r \leq 1$) and kinetic gas partitioning, and the implicit Euler method for the computation of the coupled multicomponent ionic dispersion fluxes. The system of discretized algebraic transport equations was solved with the direct matrix solver UMFPACK (Davis and Duff, 1997) in connection with the Picard iterative scheme. For a given time step, the physical transport processes (i.e., advection, dispersion, and Coulombic interactions) are simulated and, subsequently, the updated vector of aqueous species concentrations is passed to PhreeqcRM for the geochemical calculations. The latter involves the computation of all the aqueous and mineral reactions by considering a batch reactor in each cell of the simulation domain and by using the model parameters determined from the 1-D simulations. The simulations considered a constant flux boundary at the inlet of the domain, whereas the locations and shapes of the inclusions were inserted in the 2-D numerical grid by superimposing and digitizing the graphic image of the experimental setup. Further details regarding the coupling between the 2-D multicomponent ionic transport model and PhreeqcRM can be found in Muniruzzaman and Rolle (2019) and Muniruzzaman et al. (2020).
3 Results and Discussion

3.1 1-D Column experiments

The oxygen front propagation, the sulfide mineral dissolution and the dynamics of arsenic release and transport observed in the column experiments during the injection of oxic water in the 1-D column setups are quantitatively interpreted with the reactive transport model described above.

Oxygen front propagation

The propagation of the oxygen fronts in the porous media were temporally and spatially monitored using the non-invasive optode technique (section 2.1.2). In the column where no reactive minerals were included, the oxygen in the setup increases over time until it reaches the saturated concentration of the inlet solution. In columns 1 and 2, where one or two inclusions with a mineral bulk density of 50% v/v were embedded, no oxygen is detected at the outlet of the flow-through setups during the experiments, since the oxygen provided by the inlet solution is completely consumed by the oxidation of the sulfide minerals. Conversely, in column 3, with one inclusion of 2 cm length and with smaller amount of As-bearing sulfide minerals (10% v/v) part of oxygen flows through the inclusion and is not completely consumed by the oxidation and precipitation reactions.

In Fig. 3, the O$_2$ breakthrough curves of column 3 measured in the middle of the inclusion (at 5.8 cm from the inlet) and close to the outlet (at 9.6 cm from the inlet) are compared to the oxygen concentrations measured at the same locations during the conservative experiment.
Figure 3. Experimental (symbols) and simulated (lines) $O_2$ breakthrough curves for the conservative (green) and the reactive (red) column (Column 3) at two different locations: $x=5.8$ cm (a) and $x=9.6$ cm (b) from the column inlet.

The reactive column has considerably lower oxygen levels than its conservative counterpart. Whereas in the conservative column the oxygen reaches the fully saturated values at both measurement locations, in column 3 $O_2$ is consumed by the oxidation reaction and reaches approximately 40% of the saturation at 5.8 cm (Fig. 3a) and 10% at 9.6 cm (Fig. 3b) from the inlet after flushing 10 pore volumes of oxic solution. The conservative breakthrough curves show the effect of oxygen partitioning between the aqueous phase and the entrapped air, resulting in a gradual and mass-transfer limited increase of oxygen concentration towards the saturation value that is reached after flushing at least 5 pore volumes. The propagation of the oxygen front in the reactive column is also impacted by
kinetic mass transfer and is further retarded by the presence of the reactive inclusions. The O$_2$ concentrations do not reach a steady value at the end of the experiment, after flushing 10 pore volumes of the inlet solution.

The measured breakthrough curves in the conservative and reactive flow-through experiments were captured very well by the numerical transport model implementing a kinetic linear mass transfer of oxygen between the aqueous solution and the entrapped air (Eq. [10-11]). The values of $\theta_w$ and $\theta_g$ (Table 2) used in the simulations were obtained by fitting the experimental data and a small value of the volumetric gas content is consistent with the presence of small gas bubbles entrapped in the porous media. Minor variations of $\theta_g$ between the columns can be attributed to the unpredictable entrapped gas content, which depends on the packing of the porous medium in each experiment.

The oxygen spatial profiles were measured at different times in both the conservative and the reactive setups and Fig. 4 shows a selection of spatial profiles taken during the experiments in the conservative column and in column 3.

Figure 4. Experimental (symbols) and simulated (lines) spatial profiles of oxygen concentrations at different times during the conservative and reactive 1-D flow-through experiments: conservative column (a) and reactive column 3 (b). The grey area shows the position of the reactive As-sulfide minerals inclusion in the reactive column.

In the conservative column the O$_2$ concentrations progressively increase over time due to the input of the oxic solution flowing through the porous medium (Fig. 4a). The final spatial profile was taken after 5.25 hours of experiment and it flattens approaching the value of the inlet concentration. Similar to the conservative experiment, the spatial profiles in the first part of the reactive column (Fig. 4b)
show a rapid increase of the $O_2$ concentration within the first hours, but as soon as the $O_2$ front propagates through the mineral inclusions, the oxidation of the sulfide minerals is triggered and causes oxygen depletion as shown by the sharp decrease of the $O_2$ concentrations in the spatial profiles. At late times, the oxygen that reaches the reactive inclusion attains the values of the inflow solution where it is substantially consumed to reach approximately 40% of the initial concentration. The $O_2$ spatial profiles appear to stabilize and reach a pseudo steady-state condition, which reflects the dynamic balance between the dissolved oxygen provided by the inflow solution and the oxygen consumed by the oxidation of the As-sulfide minerals. The simulations also capture the shape of the oxygen spatial profiles measured during the 1-D column experiments and the progressive evolution of both the conservative and reactive systems upon the injection of the oxic solution in the initially anoxic setups.
Arsenic mobility

The injection of the oxic solution in the anoxic porous media in the reactive columns triggers the oxidation of the arsenopyrite and löllingite embedded as reactive mineral inclusions. As described in section 2.2.1 and shown in Fig.2, the oxidation reactions of these minerals lead to the release of arsenic iron and sulfur (Eq. [1-2]). Approximately 100% of the total arsenic sampled at the outlet of the setups was found to be As(III) for all the experiments and in both text and figures we will refer to the measured total arsenic concentration.

Figure 5. Measured (symbols) and simulated (lines) breakthrough of As, Fe and S in the three columns (a, b, c) and simulated As spatial profiles of column 1 (panel d), 2 (panel e) and 3 (panel f).

The maximum elemental concentrations achieved during the experiment are comparable in all the three reactive experiments; however, remarkable differences in the patterns of arsenic breakthrough are observed in column 3. The analyses of the dissolved species at the outlet showed that in both column 1 and 2 the maximum As concentration reaches ~11 mg/L, while in column 3 the As concentration peaks at 7.77 mg/L. Despite the large difference in the mineral content between the setups, being the bulk minerals concentration 50%v/v in columns 1 and 2 and 10% v/v in column 3, the oxidative reaction is stoichiometrically limited by the inlet oxygen concentration and yields a
maximum As concentration at the outlet in the same order of magnitude for the three columns. This shows that also a smaller amount of As-bearing sulfide minerals can release a significant arsenic amount in the pore water and sustain an arsenic plume with high concentration. Interestingly, the shape of the breakthrough curves in the columns is different. The outlet arsenic concentrations of column 1 and 2 reach a plateau, whereas in column 3 the As concentration shows a peak after 1.18 pore volumes and subsequently declines until reaching a concentration of 5.32 mg/L at the end of the experiment. This behavior is well captured by the model including the mechanisms of Fe and As secondary phase minerals precipitation and the surface passivation of the reactive sulfide mineral grains (Fig. 2). The precipitation of the secondary mineral phases also entails the removal of Fe and S from the pore water, causing an excess of As concentration compared to the stoichiometric ratios of these elements in the ore. The kinetics of the oxidative dissolution of arsenopyrite and löllingite was simulated by using the rate expression described in Eq. [7], while the precipitation of the secondary amorphous phases was defined in Eq. [8-9]. The model is able to capture both the magnitude and the shape of the arsenic breakthrough curves as well as the other dissolved species released upon the oxidative dissolution of the sulfide minerals. The simulated spatial profiles of arsenic (Fig. 5d-f) allow visualizing the As distribution in the column setups. In columns 1 and 2, as soon as the oxic solution propagates through the reactive mineral inclusions, the As concentration rapidly increases and remains stable once O₂ attains steady-state conditions (after 5 hours) in the setup. In contrast, in column 3 the arsenic released from the mineral downgradient to the inclusion shows and initial increase followed by a progressive decrease after 10 hours. The different oxidation rates of the two sulfide minerals result in a faster dissolution of löllingite compared to arsenopyrite. For this reason, the outcomes of the simulations show that more than 96% of the total arsenic released in the systems after 20 pore volumes of experiment comes from löllingite and less than 4% from arsenopyrite. The arsenic that precipitates and/or is reincorporated in an amorphous secondary phase after 20 pore volumes of experiment is 1.17 mg in column 1, 1.13 mg in column 2, and 0.95 mg in column 3. The coating on the minerals surface formed by the freshly
precipitated secondary phases creates a layer that hinders the oxidation reaction. This effect has a notable impact on the As breakthrough in column 3 where it results in an arsenic concentration decreasing with time (Fig. 5c). However, such effect is negligible in columns 1 and 2 due to the higher mass of As-bearing sulfide minerals included in these setups (Fig. 5a-b). In addition, the high bulk concentration of the inclusions in these two columns is responsible for a more extensive oxygen consumption, reducing the possibility of secondary minerals formation, and therefore, the ability of passivate the reactive surface of the minerals. For this reason, in column 1 and 2, compared to column 3, a smaller percentage of the total released As is sequestrated in the ferric arsenate phase (33% of arsenic reincorporated in FeAsO₄ in column 1 and 2 and 42% in column 3, Table S7). Only a small portion of As is instead sorbed onto the freshly precipitated Fe-(hydr)oxides phase (between 0.18% and 0.36% of the total arsenic released in the three columns).

3.2 2-D flow-through experiments

The oxygen dynamics during the oxidation of the two As-bearing sulfide inclusions embedded in the 2-D flow-through chamber was monitored by the spatially distributed high-resolution O₂ sensor strips, and the impact of the minerals oxidative dissolution on the pore water chemistry was measured at the outlet ports of the flow-through setups. The experimental data were simulated with the multicomponent transport model described in section 2.2, using the same set of kinetics parameters determined for the 1-D columns (Table 2). Fig. 6a shows the photograph of the 2-D experimental setup in which are clearly visible the reactive inclusions embedded in the setup and the O₂ sensor strips. In Fig. 6b the oxygen spatial profiles measured along the strips after 98 hours of experiment are displayed together with the outcomes of the reactive transport simulations. The first two O₂ sensors placed at 16 and 32 cm from the inlet capture the oxygen consumption in the first inclusion, whereas the effects of the oxidative dissolution and oxygen depletion in the second inclusion are visualized in the spatial profiles collected from the sensor strips located at 48 and 64 cm. The simulation results capture the oxygen spatial profiles at the location of the four strips and are also capable to reproduce the shape of the O₂-depleted plumes that are affected by hydrodynamic
dispersion and mixing with the surrounding oxic water. This behavior is particularly visible for the measuring points located downgradient of the first inclusion where the oxygen-depleted plume progressively widens and reaches an approximately Gaussian shape due to lateral mixing at the plume’s fringes. A discrepancy between the experimental and simulated oxygen concentrations is mainly seen in the second inclusion at x = 48 cm, where the simulation shows a higher consumption of O₂ compared to the experimental measurements. This is probably due to the blending of the two porous media (i.e., the quartz sand and the As-bearing ore minerals) in the experimental setup, which diluted the reactive minerals bulk concentration at the left edge of the inclusion and resulted in a less pronounced oxygen consumption compared to the prediction of the numerical model.

Figure 6. Photograph of the 2-D experimental setup (a) and measured (symbols) and simulated (lines) O₂ concentration profiles at the four sensors strips locations (x = 16, 32, 48, and 64 cm) after 98 hours of experiment.
The arsenic, iron and sulfur sampled at the outlet of the flow-through chamber after 98 hours of experiment are plotted in Fig. 7 together with the outcomes of the reactive transport model. The oxidation of the mineral inclusions results in two distinct arsenic peaks at the outlet of the setup (Fig. 7a). The arsenic concentration reaches 7.9 mg/L at the outlet of the first inclusion and 10.3 mg/L at the outlet of the second one. At the location of the first inclusion no iron concentration is measured, whereas a value of 0.5 mg/L is reached downgradient of the second inclusion. Sulfur displays the same shape of the outlet spatial profile of As, with two distinct peaks corresponding to the two reactive minerals’ inclusions.

**Figure 7.** Measured (symbols) and simulated (lines) vertical profiles of arsenic (a), iron (b), and sulfate (c) at the outlet of the 2-D flow-through chamber after $t = 98$ h.

The stoichiometric ratio of the reaction products at the outlet of the flow-through chamber highlights both the faster dissolution of löllingite (FeAs$_2$) with respect to arsenopyrite (FeAsS), leading to a greater excess of As compared to S and the precipitation of secondary mineral phases. The precipitation of such secondary minerals causes the removal of Fe from the pore water. The reactive transport simulations incorporating the dissolution and precipitation processes displayed in Fig. 2 and described in Eq. [1-9] allowed us to reproduce the trend and the values of the reaction products observed at the outlet of the 2-D flow-through chamber. The model could reproduce well the pattern and magnitude of arsenic measurements at the outlet ports and could also capture the trends of smaller concentration of other species such a Fe and S produced by the oxidative dissolution of löllingite and
arsenopyrite. Such good agreement was obtained in a purely forward reactive transport simulation based on the outcomes of the column setups and with no additional fitting parameters.

Figure 8. Simulated spatial distributions of $O_2$ concentration (a-c), total aqueous As (d-f), and aqueous As released from arsenopyrite (g-j) and löllingite (k-m) in the 2-D flow-through setup at three different times.

The oxygen and arsenic dynamics of the 2-D experiment is visually displayed in Fig. 8. The oxygen front propagation during the oxidative dissolution of the sulfide minerals (Fig. 8a-c), as well as the total aqueous arsenic plume (Fig. 8d-f), and the As released from arsenopyrite (Fig. g-j) and from löllingite (Fig. 8 k-m) are shown at three different time steps. The figure clearly illustrates that the contact with the inflowing oxygen causes the dissolution of the reactive minerals embedded in the inclusion, which consume oxygen and create continuous plumes of arsenic in the system. After 5 hours the oxic inlet solution has reached the first inclusion and the arsenic starts to be released in the pore water. The oxygen front advances in the system and after 20 hours also the second inclusion undergoes oxidative dissolution and contributes to the arsenic release. At this time, arsenic already reached the outlet of the domain, while the oxygen front is delayed by partitioning with the entrapped
gas phase and arrived about halfway through the second inclusion. At late times, the system approaches a pseudo steady-state condition with two oxygen depleted plumes and two arsenic plumes propagating from the inclusions. The shape of both the O$_2$ depleted plume and the arsenic plume is impacted by the flow field in the unconfined setup. Moreover, the oxygen concentration increases at the fringes of the depleted plumes due to the effect of the lateral hydrodynamic dispersion, and for the same reason the As concentration decreases at the fringe of the plumes. As already observed in the 1-D column setups, the difference in the oxidation rates between the two sulfide minerals implies that most of the aqueous arsenic released in the system dissolves from löllingite, creating a contaminated plume that can reach more than 10 mg/L of arsenic (Fig 8 j), whereas a less concentrated plume (~1 mg/L of As) is formed from the oxidative dissolution of the arsenopyrite present in the inclusions.

To assess the behavior of the reactive system on a longer timeframe compared to the performed experiment, we also run a one-year simulation. Fig. 9 displays both the solutes concentration and the solid content at two times: at the end of the experiments (after 98 hours) and after one year of injecting oxic water into the 2D flow-through setup.

**Figure 9.** Simulated spatial distributions of O$_2$ (a-b) concentration, total aqueous As (c-d), aqueous As released from arsenopyrite (e-f), and aqueous As released from löllingite (g-h), arsenopyrite (i-j),...
and löllingite content (k-l), ferric arsenate phase (m-n), and iron (hydr)oxide precipitated (o-p) in the 2-D flow-through chamber at \( t = 98 \) hours and after one year of simulation.

Completely depleted oxygen plumes (Fig. 9a-b) indicate that the sulfide minerals oxidation reaction is still ongoing after one year of experiment, producing an arsenic plume that propagates from the reactive inclusions (Fig. 9c, d). It is worth noting that the different dissolution rates of the minerals lead to a sequential release of aqueous arsenic, first from löllingite and then from arsenopyrite. After 80 hours the dissolution of löllingite sustains a highly concentrated As-contaminated plume (Fig. 9c), while a considerably lower concentration originates from arsenopyrite (Fig. 9d). Over a longer time, the reactive system evolves and shows a progressive shift in the contribution of the two reactive minerals. After one year of flushing the oxic solution, the arsenic concentration released by löllingite decreases, while that released by arsenopyrite increases (Fig. 9e-h), although löllingite dissolution still remains the main mechanism of arsenic release. Despite this dynamic evolution of the system, the total concentration of aqueous As at one year is only slightly smaller compared to the one after 98 hours (Fig. S3a).

It is also of interest to visualize the behaviour of the solid mineral species in the setup. The effect of the continuous inflow of oxic water leads to the consumption of the minerals in the reactive inclusions (Fig. 9i-l). The content of both arsenopyrite and löllingite decreases in time. After 98 hours there is only a small minerals consumption, located especially on the left side of the inclusions, whereas after one year of simulation the mineral consumption is apparent also in the lateral direction. However, both minerals are present in large stoichiometric excess and only a small percentage of them dissolves (~2.6% for löllingite and ~0.6% of arsenopyrite) after one year (Fig. S3). The rate of As-release is then still dominated by löllingite that will release arsenic until the ore will be exhausted. The important implication of this is that the combination of the two As-bearing sulfide minerals is able to generate continuously released arsenic plumes that persist in time.

The secondary minerals formed in the system increase in time and their amount is larger after one year of simulation. The precipitation of the ferric arsenate phase at the lateral fringes of the
contaminated plume occurs upon the contact between O₂, Fe, and As dissolved from the sulfide mineral inclusions (Fig. 9m-n). The precipitation of Fe-(hydr)oxides after one year is substantial and follows the shape of the As-contaminated plumes (Fig. 9o-p).

The spatial distribution of the arsenopyrite and löllingite oxidation reaction rates is displayed in Fig. 10 (panels a and b) together with their temporal evolution at selected locations in the 2-D domain (panels c and d).

**Figure 10. Simulated spatial distribution and temporal evolution of the minerals’ oxidative dissolution rates after one year of simulation: arsenopyrite reaction rate (a, c), löllingite reaction rate (b, d). The stars in (a) and (b) correspond to the position at which the reaction rates were plotted in panels (c) and (d). In the legend I refers to the top inclusion and II to the bottom inclusion.**

The values of the reaction rates have a similar spatial distribution pattern for both sulfide minerals. In the upgradient part and in the lateral fringes of the inclusions the rate of the reaction is fast, and it decreases through the inclusions until reaching zero in the core of the reactive mineral inclusions. The spatial distribution of the reaction rates values depends on the oxygen concentration: the fastest dissolution rates are located where the oxic solution contacts the reactive mineral in the inclusions through advective transport in the upgradient locations and through lateral dispersion at the inclusion fringes (Fig. 10a, b). The reaction occurring in these locations consumes all the oxygen supplied, thus protecting the core of the mineral inclusions from oxidation. The temporal evolution of the reaction
rates at different locations within the inclusions is displayed in Fig. 10c, d. In both the initial part of
the inclusions (blue lines in the figure) and the lateral fringes (orange line in the figures) the reaction
rate increases during the first 50 days until it reaches an approximately stable value. Around 150 days
the values of the oxidation reaction rates start decreasing, affected by the passivation of the surface
due to the precipitation of the secondary minerals. The comparison between the values of the
simulated rates for the two As-bearing sulfide minerals shows that löllingite oxidative dissolution is
almost twice as fast as arsenopyrite thus justifying its greatest contribution to arsenic release in the
flow-through setup.

4 Conclusions

The outcomes of this study show that the oxidative dissolution of spatially-distributed sulfide
minerals in porous media releases arsenic plumes that are transported downgradient by the flowing
groundwater. The different rates of dissolution of the As-bearing sulfide minerals present in the
natural ore material used in the flow-through setups result in a considerably higher contribution
(>96% within the time frame of the experiments) of the fast dissolving löllingite to the total arsenic
released in the pore water. A scenario simulation run for the 2-D setup for a longer timeframe shows
that the importance of arsenopyrite increases at late times. The results of our experiments show that
As-bearing sulfide mineral inclusions of limited size can sustain high concentration arsenic plumes
for a long time. This appears to be particularly important if the mineral source is composed of different
minerals, whose distinct rates of kinetic dissolution can cause a longterm release of arsenic and thus
a long term groundwater contamination.

Another main outcome of the flow-through experiments and the numerical modeling performed in
our study is the demonstration of the complex interplay and feedback between the primary As-bearing
sulfide minerals, the dissolved products of the oxidative dissolution, and the secondary mineral
phases. The latter can sequester arsenic through precipitation and sorption reactions and can also
induce passivation of the primary reactive minerals. The surface passivation effect was clearly
observed in the column system in presence of smaller concentration (10% v/v) of sulfide minerals in the reactive inclusion. The different experiments also show the importance of dimensionality effects on reactive transport problems involving mineral dissolution and precipitation. Such conclusion is apparent from the spatial distribution of primary and secondary minerals, as well as the reaction rates, which in a multidimensional system are strongly impacted by the lateral mixing of reactants and products (Rolle and Le Borgne, 2019).

To the best of our knowledge, this study is the first contribution that assesses the reactivity of As-bearing sulfide minerals in multidimensional flow-through systems. The approach could be extended to other reactive systems involving reactive minerals important in subsurface applications such as carbonate minerals (e.g., Li et al., 2014; Salehikhoo and Li, 2015; Tartakovsky et al., 2008). Concerning the environmentally relevant As-bearing sulfide minerals, further research is needed to address the impact of both chemical and physical heterogeneities. The latter will induce complex flow patterns (e.g., Chiogna et al., 2014; Ye et al., 2015b) and will impact mass transfer processes and geochemical reactions in groundwater flow systems. This will be relevant to upscale the effects of spatially-distributed reactive mineral inclusions in field-scale scenarios. We also envision future studies focusing on characterizing the mechanistic link between arsenic release and the spatio-temporal distribution of the contamination sources by experimentally investigating the combined interaction and evolution of spatial gradients of the primary and secondary minerals together with those of the dissolved species. Future investigation should also explore the behavior of oxidative dissolution of As-bearing sulfide minerals under different hydrochemical conditions, such as at the interface between different environmental compartments and in engineering applications such as managed aquifer recharge and in situ remediation of contaminated groundwater.

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The mineral characterization, the description of the batch experiments, the calibration of the modeling parameters, as well as additional outcomes of the simulations for this study are provided in the Supplementary Material.
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