ARSENIC WASTE MANAGEMENT: KINETICS OF ARSENIC RELEASE FROM ORPIMENT

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ABSTRACT

Preventing arsenic release from mine waste materials, i.e., source control, is the preferable option for controlling arsenic discharge to the environment. Designing effective source control requires comprehensive knowledge on the leaching behavior of arsenic from its bearing minerals. To determine the release kinetics of arsenic, we carried out leaching experiments using crystalline arsenic trisulfide known as orpiment as one model arsenic sulfide mineral. The effect of pH, the dissolved oxygen concentration, and temperature on the release rate of arsenic was investigated using a fully controlled batch reactor system. In general, the arsenic release rate increased with pH, the dissolved oxygen concentration, and temperature. A kinetic equation was derived from the leaching data to describe the release rate as a function of the three leaching parameters. The kinetic equation derived serves as a useful tool for pinpointing the key factors that can be manipulated to prevent arsenic release from mine waste materials.

KEYWORDS

Arsenic release, Source control, Arsenic trisulfide, Leaching kinetics

Introduction

Arsenic release associated with the mining industry is of great environmental concern due to the toxicity of the element. Elevated concentrations of arsenic resulted from mine waste rock piles, effluent discharges, tailings runoff, and smelters have been reported at different mine locations around the world (Hajalilou et al., 2011; Ko et al., 2003; Straskraba and Moran, 1990; Wu et al., 2017). Arsenic release results from weathering of rocks generated by mining activities (Flora, 2005). Arsenic bearing sulfides are common in waste rocks produced from extraction of valuable metals, such as copper and gold (Aazami et al., 2014; Boonsrang et al., 2017; Zhang et al., 2015). The common arsenic-bearing minerals are primary sulfides, such as arsenopyrite (FeAsS), loellingite (FeAs2) that is often associated with arsenopyrite, realgar (AsS), orpiment (As2S3) and enargite (Cu3AsS4) (McKibben et al., 2008). Upon exposure to water and air, arsenic can be released from these minerals to the receiving soils and waters (Palumbo-Roe et al., 2007). A preferable option to minimize the environmental and ecosystem effects of arsenic release is to prevent its dissolution from its sources. To select and implement an appropriate source control measure, it is essential to understand the rate controlling steps that determine the arsenic release from its bearing minerals.

The release of arsenic from orpiment (As2S3) has not been investigated systematically compared with the case of arsenopyrite and enargite (Lattanzi et al., 2008; Walker, 2004; Yu et al., 2007; Yunmei et al., 2004). Orpiment is a common arsenic bearing sulfide mineral found in gold and copper mines. The key parameters affecting the release of arsenic are pH, the concentration of dissolved oxygen, the presence of oxidizing agents, the presence of microbes, and temperature
Eary, 1992; Ehrlich, 1963; Floroiu et al., 2004; Lengke et al., 2009). Orpiment is insoluble at acidic pH, whereas the leaching is enhanced at alkaline pH (Darban et al., 2011). The presence of oxygen and other oxidants, such as Mn (III and IV) and Fe(III), and/or microorganisms causes an increase in the oxidation of As(III) to As(V) (Lengke and Tempel, 2002; Henke, 2009). Even in the absence of oxygen and at more acidic pH, arsenic can be released from As₂S₃ as non-charged H₃AsO₃ (Eary, 1992).

On the other hand, precipitation processes are widely used for arsenic removal from contaminated waters/effluents. In light of its high arsenic content (up to 61% theoretically), arsenic trisulfide (As₂S₃) is a promising precipitate for arsenic removal (Battaglia-Brunet et al., 2012). The major barrier to widely implementing the sulfidization process is the stability of arsenic trisulfide. It was shown in previous experiments (data not shown) that precipitated amorphous As₂S₃ is unstable, specifically under alkaline and oxidizing conditions. However, crystallographic differences between crystalline orpiment and amorphous As₂S₃ can significantly affect the arsenic and sulfur release behaviors.

The present study investigated the effect of pH, the dissolved oxygen concentration, and temperature on the rate of arsenic release from orpiment mineral (As₂S₃). The leaching tests were conducted to quantify the effects of pH, the concentration of dissolved oxygen (DO), and temperature on arsenic release from orpiment mineral (As₂S₃). Table 1 shows the ranges of the variables for the leaching tests.

### Experimental design

Experimental design: The leaching tests were conducted to quantify the effects of pH, the concentration of dissolved oxygen (DO), and temperature on arsenic release from orpiment mineral (As₂S₃). Table 1 shows the ranges of the variables for the leaching tests.

<table>
<thead>
<tr>
<th>Variable</th>
<th>pH</th>
<th>DO, ppm</th>
<th>T, ℃</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.0</td>
<td>8.3</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>7.0</td>
<td>8.3</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>8.3</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>8.3</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>8.3</td>
<td>23</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>8.0</td>
<td>0.0</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>1.5</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>5.0</td>
<td>23</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>8.3</td>
<td>23</td>
</tr>
<tr>
<td>Temperature</td>
<td>8.0</td>
<td>8.3</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>8.3</td>
<td>40</td>
</tr>
</tbody>
</table>
Characterization and pre-treatment of the solid samples: All chemicals used in this study were of analytical grade. All solutions were prepared with deionized water. Orpiment mineral As$_2$S$_3$ was supplied by Ward’s Science in Nevada. The sample was ground using a mortar and pestle and screened to obtain a particle size of 75+53 µm. The purity of the sample was examined by X-ray diffraction using a representative sample prepared as a finely ground powder (Rigaku MultiFlex XRD). The composition of the solid were also verified by scanning electron microscopy coupled with energy dispersive X-ray (FEI Quanta 650 SEM/EDX) spectroscopy. To remove fine and pre-oxidized particles from the solid surfaces, the sample was washed with 10% sulfuric acid followed by washing in ethanol in an ultrasonic bath. The washing process was repeated until the solution was clear. The sample was then dried and stored in a vacuum desiccator until use for the leaching experiments.

Leaching test procedure: The leaching tests were carried out in a 500 mL jacketed glass reactor, into which 250 mL of leaching solution was introduced. The solution temperature was kept constant by using a water bath to circulate water at a constant temperature through the jacket wall. A mass of 50 mg of solid samples was added into the reactor. A Teflon-coated magnetic stirring bar was used to keep the solid particles suspended. pH and the dissolved oxygen concentration in the leaching solution were measured and controlled at constant values in the course of leaching. The pH control was achieved using a pH controller (HACH SC200 Universal Controller) with a metering pump (Iwaki, Hi-Resolution Pump) attached. Specifically, the controller compares the pH value measured by the pH (Accumet pH/ATC Electrode from Fisher Scientific) probe with the setpoint and sends signals to the metering pump to supply NaOH for pH adjustment. Pure oxygen and nitrogen were introduced continuously to the system to achieve a constant dissolved oxygen concentration. The concentration of dissolved oxygen was measured by a dissolved oxygen probe (Oakton Dissolved Oxygen). Figure 1 shows the schematic of the experimental apparatus setup. In the course of leaching, 1 mL of aqueous samples was taken at specific time intervals and filtered by a 0.45 µm filter. The filtrate was analyzed for arsenic concentration by an ICP-OES (Agilent 5100).
Figure 1. Schematic of the leaching experimental setup

Kinetic modeling: The progressive-conversion and shrinking core models (SCMs) are the most common kinetic models used for modelling leaching kinetics (Levenspiel, 1999; Wen, 1968). However, these models are not always suitable to describe the leaching kinetic data. A general model applied by Bouffard and Dixon (2007) was used in the present study to relate the fraction of arsenic released from orpiment as a function of leaching time.

Eq. (1) shows the integral form of the model, in which $x$ is the fraction of the total arsenic released from orpiment, $t$ is the leaching time (in days), $\varphi$ is a topological exponent, and $\tau$ is the timescale of the reaction (in days), which is given by Eq. (2).

$1 - x = \begin{cases} \exp\left(\frac{-t}{\tau}\right) & @ \varphi = 1 \\ \left(1 - (1 - \varphi)\right)^{\frac{t}{\tau}}^{\frac{1}{1-\varphi}} & @ \varphi \neq 1 \end{cases}$

(1)

$\frac{1}{\tau} = k t = \frac{1 - (1 - x)^{(1-\varphi)}}{1 - \varphi}$

(2)

In Eq. (2), $k$ is the apparent rate constant, which is a function of the proton concentration ([H$^+$] in mol/L), the dissolved oxygen concentration ([O$_2$] in ppm), and temperature (T in kelvin). This function is shown in Eq. (3), where $a$ and $b$ are the reaction orders with respect to the proton concentration and the dissolved oxygen concentration, $k_{ref}$ is the reaction rate constant at the reference temperature $T_{ref}$, and $E_a$ is the activation energy of the leaching reaction calculated using...
the Arrhenius equation. Finally, the kinetic equation is expressed as Eq. (4), which relates the cumulative fraction of arsenic released to the proton concentration, the dissolved oxygen concentration, and temperature. The method of non-linear least squares regression was used to calculate the unknown parameters using the Solver feature of Microsoft Excel in this study.

\[
k = \frac{1}{\tau} = k_{ref} \exp \left( \frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right) [H^+]^a [DO]^b
\]

\[
x = 1 - \left\{ 1 - (1 - \phi) k_{ref} \exp \left[ \frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right) \right] (H^+)^a (DO)^b t_{days} \right\}^{\frac{1}{1-\phi}}
\]

Results

Characterization of orpiment sample: Figure 2 shows the X-ray diffraction pattern of the solid sample. The Rietveld refinement shows that the mineral consists of 95% orpiment (As$_2$S$_3$) and 5% realgar (As$_4$S$_4$).

Effect of pH, DO level and temperature on arsenic release: The effect of pH on arsenic release from orpiment was investigated by carrying out a series of leaching tests at different pH values from 6 to 10. Figure 3 shows the percentage of the total arsenic dissolved from orpiment over time at different pH values. Increasing pH had a positive effect on the arsenic release. The increases were not pronounced at pH 6 and 7, but more apparent at higher pH values. The dependency of arsenic release on solution pH observed in this study agrees with other studies on orpiment and realgar dissolutions (Lengke and Tempel, 2002; Lengke et al., 2009; Suess and Planer-Friedrich, 2012). As$_2$S$_3$ is shown to have a layered S-As-S structure, where arsenic atoms are located in the interlayer space between sulfur atoms (Mamedov and Mikhailov, 1997). As a result of hydration and the presence of hydroxide ions in the environment, hydroxyl groups can be developed on the surface of the sulfide. Adsorption of hydroxide ions onto the arsenic surface sites can change the charge of the solid surface (Hsieh and Huang, 1991), rendering it more negatively charged. This would weakens the arsenic-sulfur interstitial bonds through bond polarization, thereby facilitating the
release of arsenic from solid surfaces (Furrer et al., 1986). Therefore, increasing the alkalinity of the leaching solution increased the arsenic release from orpiment.

The dependence of arsenic release on the concentration of dissolved oxygen (DO) was investigated via a series of experiments at different dissolved oxygen levels. Pure oxygen and nitrogen gases were used to vary the dissolved oxygen concentration from 0.0 to 8.3 mg/L in the system at 23 °C and pH 8.0. Figure 4 shows the total arsenic released versus the leaching time at different levels of dissolved oxygen. Higher levels of arsenic release were observed at elevated concentrations of dissolved oxygen. However, the system in which oxygen was removed also showed the release of arsenic from orpiment. It was reported that arsenic can be dissolved from As$_2$S$_3$ under N$_2$ sparging or in anoxic conditions, such as in ground waters (Floroiu et al., 2004; Kim et al., 2000). Floroiu et al. (2004) suggested H$_3$AsO$_3$ and H$_2$As$_3$S$_6^-$ as the possible species produced in anoxic systems.

![Figure 3](image3.png)

Figure 3. Effect of leaching environment pH on arsenic release from orpiment, DO 8.3 ppm, and 23 °C.

![Figure 4](image4.png)

Figure 4. Arsenic release from orpiment versus time at different concentrations of dissolved oxygen, pH 8.0 and 23 °C.

Arsenic solubility from orpiment was affected by temperature at a constant pH and dissolved oxygen level. Figure 5 shows the release of arsenic at different temperatures from 23 °C to 50 °C. Increasing the leaching temperature resulted in higher concentrations of arsenic being released from orpiment for the same period of leaching.
Derivation of the kinetic equation: Using the experimental results of the leaching tests, a kinetic equation was derived by the method of non-linear least squares. The set of optimal model parameters was obtained and also shown in Table 2, which gave the best fit to the experimental data.

<table>
<thead>
<tr>
<th>Model parameter</th>
<th>Topological factor, φ</th>
<th>Reaction order with respect to H⁺</th>
<th>Reaction order with respect to DO</th>
<th>Activation energy, Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimal value</td>
<td>3.73</td>
<td>−0.35</td>
<td>0.67</td>
<td>35.0</td>
</tr>
</tbody>
</table>

The kinetic model with the set of optimal model parameters is shown as Eq. (5). In this equation, the topological factor, φ, was 3.73. A value larger than 1 means that the leaching reaction would not reach completion. The reaction orders with respect to H⁺ and DO were −0.35 and 0.67, and the activation energy was 35 kJ/mol. These parameters were further explained to uncover the possible rate-limiting step that controls arsenic release. To show the reaction order with respect to each parameter, Eq. (5) was rearranged to Eq. (6). The coefficient of the right-hand side of Eq. (6) stands for the apparent rate constant, which is a function of proton concentration, dissolved oxygen concentration and temperature.

\[
x = 1 - \left\{1 + 4.68 \times 10^{-5} \exp\left[\frac{34999}{8.314} \left(\frac{1}{296} - \frac{1}{T(K)}\right)\right]\right\}^{-\frac{1}{(1-3.73)}} \left[H^+\right]^{-0.35} \left[\text{DO}\right]^{0.67} \left[\text{t}(\text{days})\right]^{1/(1-3.73)}
\]

\[
\frac{1 - (1 - x)^{(1-3.73)}}{(1 - 3.73)} = 1.71 \times 10^{-5} \exp\left[\frac{E_a}{8.314} \left(\frac{1}{296} - \frac{1}{T}\right)\right]\left[H^+\right]^{a} \left[\text{DO}\right]^{b} \left[\text{t}\right]
\]

Reaction order with respect to H⁺ concentration: Orpiment leaching experimental data obtained at different pH values were plotted together with the model fitted values derived from Eq. (6) at DO 8.3 ppm and 23 °C. Figure 8A shows that the model could describe the leaching results at all pH
values except at pH 10. The experimental results at pH 10 was excluded in the calculation of the reaction order with respect to H⁺ concentration. The slope of each line represents the apparent rate constant k at a specific proton concentration. The reaction order with respect to the concentration of H⁺ was derived by plotting the logarithm of the apparent rate constant versus the logarithm of the proton concentration, as shown by Eq. (7).

\[
\log k = -0.35 \log(H^+) + \log(1.71 \times 10^{-5}(DO)^{0.67})
\]  

(7)

Figure 8-B shows that plotting Eq. (7) gave a linear line with a slope of –0.35, which represents the reaction order with respect to proton concentration. The negative value means that increasing the proton concentration would result in a decrease in the apparent rate constant and thus a decrease in arsenic release from orpiment. The value of 0.35 supports that the surface reaction between OH⁻ and arsenic-sulfur bonds is one of the rate-limiting steps. Further surface analysis (data not shown) of the leaching solid residues showed that an arsenic-deficient sulfur-enriched layer was produced at lower pH values. However, due to the low chemical stability of elemental sulfur at pH 10 and above, the sequential oxidation of sulfur on the solid surfaces may mainly produce thiosulfate instead of elemental sulfur (Kleinjan et al., 2005). This result implies that the leaching process is no longer controlled by diffusion of dissolved oxygen through the sulfur-enriched layer, which agrees with the linear leaching kinetics observed at this pH.

Figure 8. A) Application of the kinetic model to derive the apparent rate constant at different pH; B) Linear regression between the logarithm of the apparent rate constant and the logarithm of the H⁺ concentration, with the slope representing the reaction order with respect to proton concentration. (DO 8.3 ppm and 23 °C).

Reaction order with respect to DO level: Figure 9-A plotted the results from the leaching experiments conducted at different DO levels at pH 8.0 and 23 °C against the model fitted values derived by Eq. (6). The apparent rate constant at each DO level was calculated as the slope of the linear line. To obtain the reaction order with respect to the DO concentration, the logarithm of the apparent rate constant was plotted against the logarithm of the DO concentration, as shown by Eq. (8).

\[
\log k = 0.67 \log(DO) + \log(1.71 \times 10^{-5}(H^+)^{-0.35})
\]  

(8)

A slope of 0.67 was given by the linear regression of the plotted data in Figure 9-B, which represents the reaction order with respect to the dissolved oxygen concentration. The positive sign of the slope supported the positive dependency of the arsenic release on the dissolved oxygen concentration.
concentration. A value of 0.67 supports that the arsenic leaching rate was controlled by the diffusion of oxygen through a product layer formed on the orpiment surface.

Figure 9. A) Application of the kinetic model to derive the apparent rate constant at different DO concentration; B) Linear regression between the logarithm of the apparent rate constant and the logarithm of the DO concentration, with the slope representing the reaction order with respect to DO concentration. (pH 8 and 23 °C).

Activation energy: Figure 10-A plotted the experimental results for the orpiment dissolution obtained at different temperatures together with the model fitted values derived from Eq. (6). The apparent rate constant for each temperature was calculated as the slope of the corresponding line. The natural logarithm of the apparent rate constant was plotted versus 1/T (Kelvin) as shown by Eq. (9) in Figure 10-B.

\[
\ln k = \frac{E_a}{8.314} \left( \frac{1}{296} - \frac{1}{T} \right) + \ln(1.71 \times 10^{-5} (H^+)^{-0.35} (DO)^{0.67})
\]  

(9)

The linear regression in Figure 10-B gave a slope of -Ea/R, which is − 4.21. An activation energy (Ea) of 35 kJ/mol was calculated. The value of the activation energy has important information regarding the reaction mechanism. Low activations energies (< 20 kJ/mol) are usually assigned to diffusion-controlled reactions, whereas a high activation energy (> 40 kJ/mol) is an indication of a reaction-controlled mechanism (Feng et al., 2015; Lasaga, 1992). A value in the range of 20 to 40 kg/mol is for a reaction under a mixed rate control of reaction and diffusion processes. The magnitude of the activation energy obtained here falls in the range for a mixed-control reaction mechanism.

Figure 10. A) Application of the kinetic model to derive the apparent rate constant at different temperatures; B) Arrhenius plot showing the logarithm of the apparent rate constant plotted against the reciprocal of temperature, with the slope representing -Ea/R. (pH 8 and DO 8.3 ppm).
Based on the values of the reaction orders with respect to H\(^+\) and DO concentrations and the activation energy obtained, we proposed a mixed-control reaction mechanism to explain arsenic release from crystalline orpiment. Specifically, the rate limiting steps were considered to be the surface chemical reaction between OH\(^-\) and orpiment and the diffusion of oxygen through a product layer formed on the solid surfaces.

**Conclusion**

The release rate of arsenic from crystalline orpiment increased with pH, the dissolved oxygen concentration, and temperature. A rate law was derived using the general model to describe the arsenic release rate as a function of these three variables. The reaction order with respect to the proton concentration was -0.35, suggesting that the arsenic release rate decreases with increasing proton concentration in the pH range studied. The reaction order with respect to the dissolved oxygen concentration was 0.67, indicating a positive dependency of arsenic release on the dissolved oxygen concentration. The activation energy was calculated to be 35 kJ/mol. The magnitude of the reaction orders and the activation energy support a mixed-control reaction mechanism, in which the surface chemical reaction and the diffusion of dissolved oxygen through a product layer control the arsenic release rate.

**References**


