Effect of pH on Aqueous Se(IV) Reduction by Pyrite

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Supporting Information

ABSTRACT: Interaction of aqueous Se(IV) with pyrite was investigated using persistently stirred batch reactors under O2-free (<1 ppm) conditions at pH ranging from ~4.5 to ~6.6. Thermodynamic calculations, an increase in pH during the experiments, and spectroscopic observation indicate that the reduction of aqueous Se(IV) by pyrite is dominated by the following reaction: FeS2 + 3.5H2SeO3 − 1.5H2O −→ 2SO4 2− + Fe2+ + 3.5Se(0) + 2.5H2O. The released Fe(II) was partitioned between the bulk solution and pyrite surface at pH ≈ 4.5 and 4.8, with the Fe2+ density at pyrite-solution interface about 4 orders of magnitude higher than that in the bulk solution, while iron oxyhydroxide precipitated at pH ≈ 6.6, resulting in the decrease of dissolved iron. In the Se(IV) concentration range of the experiments, aqueous Se(IV) reduction rate follows the pseudofirst order which is in the form of ln mSe(IV) = − k′ t + ln mSe(IV) 0, where k′ is apparent rate constant combining the rate constant k and pyrite surface area to mass of solution ratio (A/M). And the aqueous Se(IV) reduction rate constant for a standard system (k) with 1 m2 pyrite surface area per 1 kg solution was obtained to be 1.65 × 10−3 h−1, 3.28 × 10−4 h−1, and 4.76 × 10−3 h−1 at pH around 4.5, 4.8, and 5.1, respectively. The positive correlation between reaction rate and pH disagrees with the theories that protons are consumed when HSeO3− is reduced to Se0, and negative charge density on pyrite surface increases as pH increases. Thus, a ferrous iron mediated electron transfer mechanism is proposed to operate during the reduction of aqueous Se(IV) by pyrite. pH and iron concentration affect significantly on Se(IV) reaction rate and reaction product.

INTRODUCTION

The safe disposal of high level nuclear waste (HLW) has been a challenge worldwide, and deep geological disposal is so far the most widely accepted approach to permanently isolate the radionuclides from biosphere. Evolution scenarios of the repository suggest that over geological time scale releases of radionuclides are inevitable.1 The radioactive isotope 79Se with a half-life of 2.95 × 105 years2 is presently considered as the key mobile fission product for the disposal of spent fuel (SF) and high-level radioactive waste (HLW).3 In addition, selenium is an essential micronutrient for humans and animals, and problems of both Se toxicity and deficiency occur in different parts all over the world.4,5 Therefore, the mobility and bioavailability of Se has long been a major interest of soil and environment sciences6–8 and an important concern for the safe disposal of HLW.9–16

53Se is a redox-sensitive radionuclide and its solubility is largely controlled by oxidation state, depending on redox conditions. Selenite and selenate prevail as mobile aqueous oxyanions, while the oxidation states 0, -I, and -II prevail as solids with low solubility.9,12 Pyrite is the most widely occurring of sulfide minerals in geological environment17 and is known to buffer reducing conditions in clay formation.18,19 Numerous studies have revealed that pyrite can reduce and immobilize redox-sensitive radionuclides (such as U, Se, Tc).20–28 For pyrite interaction with aqueous Se(IV), previous research was concentrated on the identification of selenium species on pyrite surface.20,23 But Se speciation on the pyrite surface should be a function of environmental parameters. Moreover, the rate and reaction mechanism of the aqueous reduction of Se(IV) by pyrite were unknown prior to this study.

MATERIALS AND METHODS

Chemicals. Pyrite samples used in this study were obtained from Jiguanshan ore mine, Tongling, Anhui, China. The natural sample was crushed, and the size fractions of 90–120 μm were selected through sieving. Magnetic separation was employed to

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remove any pyrhhotite and iron oxide impurities. The pyrite crystals were ultrasonically washed using deionized water and ethanol to remove fine grains adhered to the crystals. The washed samples were soaked in hydrochloric acid to remove oxidized coating. After rinsing with deionized water followed by acetone, the pyrite sample was dried and stored in a O₂-free glovebox. Before adding to the reaction solution, crystals were further grinded using agate mortar in the glovebox. The specific surface area of the grinded pyrite was measured to be 0.11 m²·g⁻¹ by the BET-N₂ method using a single point adsorption nitrogen process. The purity of the pyrite powder is higher than 99% according to XRD analysis (shown in Figure S1).

Sodium selenite was taken from Guangzhou Chemical Co., Ltd., with a purity >97%. All other chemicals used were of analytical grade. The water used was deionized (18.3 mΩ) and was boiled out before introducing to the glovebox.

**Batch Experiments.** Two series of batch experiments were conducted in an oxygen-depleted (<1 ppm O₂) glovebox (Mikrouna Company) flushed with highly purified nitrogen at room temperature (26 °C). Each reactor contained 1000 mL of solution and 7.5 g of pyrite. The suspension was continuously stirred by magnetic stirring apparatus. After 4 days equilibrium with deionized water, 0.58 g of NaCl solid was introduced as ion medium.

In the preliminary experiments which lasted 7 days, the solution pH were set around 4.5 and 6.6 using CH₃COONa (2.63 g)-CH₃COOH. Then, 4.2, 4.8, and 4.5 mL of 0.1 mol·L⁻¹ Na₂SeO₃ solution were added, respectively, to reactors C, B, and A, respectively, and was buffered using CH₃COONa-CH₃COOH. Then, 4.2, 4.8, and 4.5 mL of 0.1 mol·L⁻¹ Na₂SeO₃ solution were added, respectively, to reactors C, B, and A. The solution pH was monitored using a Satorius pH meter and adjusted using 0.1 M HCl and concentrated CH₃COOH.

At a given time interval, 5 mL suspension was sampled and immediately filtered in the glovebox using 0.22 μm pore diameter membrane. Both iron and Se(IV) concentrations in the filtrate were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES).

**X-ray Absorption Spectroscopy.** In order to investigate the selenium speciation on pyrite surface, 0.3 g of pyrite sample was sampled from reactor C (pH around 4.5) after 21 days reaction. XANES spectroscopic measurements were performed at the Se K-edge (12.658 keV) on the BL14W1 Beamline at Shanghai Synchrotron Radiation Facility (Shanghai, China). The sample was measured in fluorescence mode using a 7 element Ge detector. Red and gray Se(0), FeSe, FeSe₂, and Na₂SeO₃ were used as references and measured in transmission mode. The pyrite sample was sealed with Kapton tape in the glovebox (O₂ < 1 ppm). To avoid photoinduced redox reactions, the measurement was conducted in a chamber filled with inert N₂. For monochromator’s energy calibration, reference gold foil (K-edge at 11919 eV) was chosen because of its greater inertness in comparison to Se. Data were collected at a step of 0.5 eV. Background subtraction and edge normalization were performed using Athena version 0.8.06.¹⁰

**Geochemical Modeling Calculations.** Geochemical modeling calculations were performed with PHREEQC code²⁰ or Geochemist’s Workbench package,³⁷ using the latest NEA thermodynamic data for Se⁴⁺ and ANDRA thermodynamic data for iron chemicals,³³ implemented into the Iln.dat or the thermo V8.R6+.dat provided by Lawrence Livermore National Laboratories. The activity coefficient calculation is illustrated in the Supporting Information.

### RESULTS

**Rate Determination.** The experimental data of the reactors are listed in Tables S2 and S3. Thermodynamic calculations indicate that HSeO₃⁻ is the predominant aqueous Se(IV) species in the pH range between 2.56 and 8.12 (Figure S2). Furthermore, greater than 99% of the dissolved Se(IV) is HSeO₃⁻ at pH around 5.0. On the other hand, probable reduction product of Se(IV) by pyrite includes Se(0), FeSe₂, and FeSe.

Oxidative dissolution of pyrite by dissolved oxygen and ferric iron (Fe³⁺) has intensively been studied,³⁴⁻³⁵ and the reactions are

\[
2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} = 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \quad (1)
\]

and

\[
\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} = 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (2)
\]

These reactions show that the oxidation process does not oxidize iron in the mineral (it remains Fe³⁺ as it is released into the solution). Therefore, the possible electrochemical reactions between pyrite and aqueous Se(IV) in the reactors are

\[
\begin{align*}
\text{FeS}_2 + 3.5\text{HSeO}_3^- + 1.5\text{H}^+ &= 2\text{SO}_4^{2-} + \text{Fe}^{2+} + 3.5\text{Se(0)} + 2.5\text{H}_2\text{O} \\
\Delta G^{\circ}_{298.15} &= -579.82\text{kJ/mol} \quad (3)
\end{align*}
\]

\[
\begin{align*}
\text{FeS}_2 + \frac{14}{5}\text{HSeO}_3^- + \frac{2}{5}\text{Fe}^{2+} &= 2\text{SO}_4^{2-} + \frac{7}{5}\text{FeSe}_2 + \frac{2}{5}\text{H}_2\text{O} + 2\text{H}^+ \\
\Delta G^{\circ}_{298.15} &= -383.98\text{kJ/mol} \quad (4)
\end{align*}
\]

\[
\begin{align*}
\text{FeS}_2 + \frac{7}{3}\text{HSeO}_3^- + 4\text{Fe}^{2+} + \text{H}_2\text{O} &= 2\text{SO}_4^{2-} + \frac{7}{3}\text{FeSe} + \frac{13}{3}\text{H}^+ \\
\Delta G^{\circ}_{298.15} &= -180.62\text{kJ/mol} \quad (5)
\end{align*}
\]

Because no additional Fe²⁺ was introduced to the reactors, the aqueous Fe²⁺ at the start of the experiment results from the oxidative dissolution of the pyrite surface and/or the oxidation of pyrite by the residual oxygen during the pre-experiment equilibrium. Assuming that the quantity in moles of SO₄²⁻ is two times that of Fe⁵⁺ released from pyrite, the calculated equilibrium Se(IV) content in the initial solution (t = 0) of the experimental system should be in the range between 10⁻³⁵ mol and 10⁻³⁸ mol, significantly lower than the initial Se(IV) content in the reactors. Thus, reduction of Se(IV) by pyrite is expected to occur during the experiment.

For pyrite oxidation by DO and Fe³⁺, it has been demonstrated that electron transfer from the sulfide to the oxidant, at the cathodic site, is the rate-determining step.³⁶,³⁷ This is also true for the oxidation of many other sulfide minerals such as galena, sphalerite, chalcopyrite, and arsenopyrite.³⁸ Thus, it can be deduced that the rate of reactions 3, 4, and 5 are controlled by electron transfer from pyrite to aqueous Se(IV) species. Further, because these reactions are very far from equilibrium, there is no significant back reaction. These observations allow us to presume a simple rate law for the consumption of aqueous Se(IV)
Combination Fit. reconstruction spectra by gray Se(0) and Na2SeO3 using Linear interacted with Se(IV) at pH 4.5 for 21 days. Red line represents the At a constant pH, the rate can be simpliﬁed adsorption mechanism. In this study, experimental interaction of pyrite with aqueous Se(IV) moved away from a phase or by a reductive adsorption altogether. Bruggeman et al. (2005) reported that after a short equilibration time (~7 days), distribution of 54% gray-Se(0) and 46% Se(IV) in the sample, under which R-factor equal to 0.92%. XANES results demonstrate that gray-Se(0) is the reduction product when natural pyrite is reacted with aqueous Se(IV) at pH around 4.5.

DISCUSSION

Effect of pH on Reaction Rate. The aqueous Se(IV) consumption rate constant for a standard system ($k$) with 1 m$^2$ pyrite surface area per 1 kg solution can be calculated by the following equation

$$k = k'/(A/M)$$

(10)

For the experiments conducted in this study, A/M is 0.825 and the $k$ values at pH = 4.5, 4.8, and 5.1 are calculated to be $1.65 \times 10^{-4} \text{h}^{-1}$, $3.28 \times 10^{-4} \text{h}^{-1}$, and $4.76 \times 10^{-4} \text{h}^{-1}$, respectively. Thus, the positive correlation between pH and log $k$ obtained by least-squares linear regression is as follows with $R^2 = 0.97$

$$\log k = 0.77pH - 7.22$$

(11)

Because HSeO$_3^-$ constitutes more than 99% of the aqueous Se(IV) and its reduction product should be elemental Se in the reactors (Figure 3), the proton consuming nature of reaction 3 suggests a negative correlation between the reaction rate and pH. Furthermore, Formasiero et al. (1992) indicated that above pH of 2, pyrite has a negative surface charge, the density of which increases as pH increases. Thus, increasing pH will inhibit the adsorption of HSeO$_3^-$ . From this point of view, increasing pH will reduce the rate of pyrite-Se(IV) reaction, which also conflicts with the observation of our experiment.

On the other hand, Fe$^{2+}$ can easily be adsorbed by a negatively charged surface and the Fe$^{2+}$ density on pyrite surface in the reactors is several orders of magnitude higher.
than that in bulk solution (see below). Previous research indicated that aqueous Fe(II) sorbed on solid in heterogeneous solution could quickly reduce Se(IV) to Se(0).14,40 We propose that the first electron transfer for pyrite-Se(IV) reaction is from Fe$^{2+}$ that is adsorbed on pyrite surface to HSeO$_3^-$, which produces a Fe$^{3+}$. Subsequently, the Fe$^{3+}$ receives an electron, at a cathodic site, from Fe$^{2+}$ in the mineral surface. Then, an electron moves from an anodic site to the cathodic site, resulting in sulfur oxidation. The indirect electron transfer between selenite and pyrite may account for the observed relation between pH and aqueous Se(IV) reduction rate and for the much slower reaction rate as compared with pyrite oxidation rate by Fe$^{3+}$. Actually, the significance of dissolved ferrous iron on pyrite oxidation by DO$^{41}$ and Cr(VI)$^{42}$ has been emphasized in previous studies.

**Reaction Products.** Although the XANES measurement indicates that Se(0) is the Se(IV) reduction product at pH = 4.5, other Se-bearing solid phase may form as Fe$^{3+}$ content and pH change, and a thermodynamic consideration can help to better understand the process. In the experimental system, probable Se(IV) reduction products include Se(0), FeSe$_2$, and FeSe as are indicated by reactions 3, 4, and 5, respectively. At certain pH, the stability of these solid phases is determined by Eh and Fe$^{3+}$ activity (Figure 3). In the nonequilibrium heterogeneous system, however, the Eh at the reacting mineral (pyrite) surface cannot be represented by that of the bulk solution and has to be constrained by electrochemical reactions that would occur in the system. The following reaction of pyrite oxidation provides the lower Eh limit

\[ \text{FeS}_2 + 8\text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ + 14\text{e}^- \]  
\[ \Delta G^0 = 474.76\text{kJ/mol} \]  
\( \text{Eh} = 0.3514 - 0.0676\text{pH} + 0.0084\text{log}[\text{SO}_4^{2-}] \]

Assuming that SO$_4^{2-}$ content is two times of the iron released to the solution due to pyrite oxidation, the Eh for oxidative dissolution of pyrite can be calculated as a function of Fe$^{2+}$ activity (Figure 3). Meanwhile, the upper Eh limit would be provided by the reduction of HSeO$_3^-$ or the precipitation of Fe(OH)$_3(s)$, whichever has a lower Eh or take effect. Thermodynamically, goethite is more stable than Fe(OH)$_3$, but at ambient condition and the time scale of experiment, precipitation of metastable amorphous Fe(OH)$_3(s)$ is kinetically favorable. Therefore, we have

\[ \text{Fe}^{2+} + 3\text{H}_2\text{O} = \text{Fe(OH)}_3 + 3\text{H}^+ + \text{e}^- \]  
\[ \Delta G^0 = 96.48\text{kJ/mol} \]  
\( \text{Eh} = 0.9998 - 0.1774\text{pH} - 0.0591\text{log}[\text{Fe}^{2+}] \)  

The Eh vs log$[\text{Fe}^{2+}]$ relation for reactions 12 and 14 are also depicted in Figure 3.

However, Fe$^{2+}$ content at pyrite surface would be much higher than that is in the bulk solution due to ion adsorption. Parkman et al. (1999) studied the reaction of Cu$^{2+}$ and Cd$^{2+}$ with pyrite and mackinawite in aqueous solution and indicated that about 98% of the dissolved ions were adsorbed on the solid surface at pH around 7.13. According to the experimental data, we estimate the specific surface area of the solid is 60 ± 30 m$^2$g$^{-1}$. Assuming that the adsorbed ions are distributed within 10 Å close to the solid surface, the calculated ions density at the solid surface is about 4 orders of magnitude higher than that in the bulk solution.

According to our experimental results (Figure 4 and Table S3), the aqueous iron content increases as the reaction proceeds at pH 4.5 and 4.8. Because Se$^-$ is expected to be the reduction product under these pH conditions (Figure 3), reaction 3 indicates that 1 mol iron release corresponds to 3.5 mols reductive precipitation of Se$^2$. Figure 5 presents the correlation of the aqueous Se(IV) and iron contents during the same reaction period. Linear regressions of the plots give slopes of −3.79 at pH ≈ 4.5 and −5.17 at pH ≈ 4.8. The absolute values of the slope are larger than 3.5 that is expected by reaction 3. Therefore, the “missing” iron of the bulk solution should be adsorbed on pyrite surface. Assuming that the adsorbed iron is distributed within 10 Å close to pyrite surface, the calculated Fe$^{2+}$ density at pyrite surface is $\sim 2.0 \times 10^5$ and $\sim 4.8 \times 10^5$ times higher than that in the bulk solution at pH ≈ 4.5 and 4.8, respectively. Thus, we infer that Fe$^{2+}$ density at pyrite surface would be in an order of five of magnitude higher than that in bulk.
solution at pH \(\approx 6.6\). Descostes et al. (2010) recently reported 22% of the added \(^{55}\)Fe (2 \(\times\) \(10^{-6}\) mol L\(^{-1}\)) was sorbed at pH 5.26. As the suspension concentration is 8 g L\(^{-1}\) and the specific area of the solid is 0.06 \(\pm\) 0.004 m\(^2\) g\(^{-1}\), the surface Fe density can be calculated as 5.9 \(\times\) \(10^4\) times higher than that in the bulk solution. This value is, as expected, a little higher than that at pH \(\approx 4.8\) derived from our experimental data. Therefore, the estimated Fe\(^{2+}\) activity and constrained Eh range at pyrite surface at different pH are shown in Figure 3.

From Figure 3, we can see that no iron oxyhydroxide should precipitate, and the Se(IV) reduction product is Se\(^0\) at pH = 4.5, and this is also true at pH = 4.8. Hence the relevant assumption made in the calculations above is true. At pH = 6.6, however, a initial quick decrease followed by slow decrease of dissolved iron clearly indicate that iron oxyhydroxide should be responsible for the observed removal of dissolved iron during the experiment (Table S2), and the Eh at pyrite surface would be buffered by the
following reaction

$$\text{HSeO}_3^- + 4\text{Fe}^{2+} + 9\text{H}_2\text{O} = \text{Se}(0) + 4\text{Fe(OH)}_3 + 7\text{H}^+$$

$$\Delta G^0 = 84.612 \text{kJ/mol}$$ (16)

The oversaturation of precipitation of iron oxyhydroxide demonstrates that Se(0) is the reduction product of aqueous Se(IV) at pH 6.6. Thermodynamic calculations suggest that FeSe$_2$ would be the reduction product of Se(IV) as suggested by reaction 3 in these reactions. On the other hand, the relatively stable pH during the experiment at pH $\approx 6.6$ can be explained by the simultaneous occurrence of reactions 3 and 16, which made pH within the buffer capacity of the solution. Noticeably, some aqueous iron was removed from solution on 15th day of the experiment conducted at pH around 5.1. This removal coincides with a pH increase of 0.13 (Figure 4 and Table S3), indicating that precipitation of iron oxyhydroxide may occur due to such a minor pH increase in the system.

## ASSOCIATED CONTENT

### Supporting Information
Details on the XRD pattern for pyrite sample, list of the thermodynamic data used in the present study, theoretical calculation on selenium species distribution, solution analysis of the batch experiments, the principle for the activity coefficient calculation, and the thermodynamic calculation for Se(IV) reduction by pyrite. This material is available free of charge via the Internet at http://pubs.acs.org.

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## REFERENCES


