Experimental study on oxidation mechanism of pyrite under acidic conditions

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Abstract. In this study, pyrite samples from the Yankan Coal Mine near the Shandi River in Yangquan City were studied in an oxidation dissolution experiment. Pyrite was studied at different solid-liquid ratios (1:100, 1:50, and 1:20), and the oxygen concentration used was equal to the value in the ambient environment, about 20.95% of the air volume. The pH, oxidation-reduction potential (Eh), and soluble salt concentration (EC), total iron concentration, and SO₄²⁻ concentration in the solution at different reaction times were measured with respect to time. The oxidation reaction rate of pyrite was calculated using the SO₄²⁻ concentration and the factors influencing the oxidation rate at different conditions were discussed. The experimental results showed that, after pyrite was oxidized and dissolved at solid-liquid ratios of 1:20, pyrite decreased from acid generation of the SO₄²⁻ formation, then the pH of the solution increased, at solid-liquid ratios of 1:100, 1:50, and 1:20, the overall Eh and EC values decreased. No matter what solid-liquid ratio is adopted for the reaction, the Fe²⁺ concentration is higher than Fe³⁺ concentration, and the Fe²⁺ and total iron concentration all increase with the increase of solid-liquid ratio, while Fe³⁺ gradually increases, reaching a trend of relatively stable and slowly decreasing. The average apparent release rate of Fe was proportional to the different solid-liquid ratios. The oxidation reaction rate of pyrite under acidic conditions was directly related to the concentration of reactants, and a faster oxidation rate was observed at higher concentrations due to the larger reaction contact area.

1. Introduction

China has abundant coal resources, and underground spaces formed by mining, such as goafs, become storage spaces for groundwater. Due to various physical and chemical processes and microorganisms, the water in goafs is gradually acidified [1-4]. The water level can rise after the groundwater becomes acidic, which may generate outcrops in some places and pollute surrounding river systems and the local environment, and also poses a pollution risk by leaking into nearby groundwater [5-8].

During the mining process, pyrite and other mineral substances that contain metal sulfides may oxidize and dissolve, which releases heavy metal ions and H⁺ in accumulated water. This could further produce highly saline acidic mine wastewater [9-11]. The acidification of kiln water can be accelerated by a variety of factors, including high sulfur content, sufficient oxygen content, complete groundwater recharge, drainage, and time [12-14].
Much research has been conducted to determine the cause of formation of acidic mine water, as well as the mechanism of oxidative dissolution of iron pyrite. Several research groups [15-17] have studied the geochemical control of acidic mine water (AMD) and the hydrogeochemical characteristics of water pollution. Liu [18] used Dexing Copper Mine as an example to analyze the generation process of acidic products produced by pyrite oxidation, and what factors influenced it. Dold[19] summarizes the work of 20 years of research on AMD, this work focuses on the very beginning of the process in the transport channels of the tailings onto the tailings impoundments and the processes occurring in active operations. Yuemei et al.[20] studied the hydrochemical characteristics and the causes for the formation of acidic water in the Yongan Mining Area. Zhong et al. [21] discussed how thiobacillusferrooxidants influenced the formation of acidic mine water. Dold et al. [22] also has described biogeochemical processes that lead to the generation of acid rock drainage (ARD) and rock weathering on the Antarctic landmass and described why they are important sources of iron into the Antarctic Ocean. However, there have been no studies that analyzed the oxidation reaction rate of pyrite using oxidation dissolution experiments at different solid-liquid ratio combinations of iron pyrite, which, also discuss the implication factors of oxidation rate under different conditions. In this study, the formation conditions of acidic mine wastewater were analyzed by performing oxidation dissolution experiments of iron pyrite which was collected from an industrial mine site. The water-rock interaction law of acidic mine wastewater in ore layers is discussed. This work provides the theoretical basis for exploring the causes of acidic mine wastewater and its prevention and control.

2. Materials and methods

2.1. Samples

Pyrite samples were taken from the goaf of a coal mine near the mountain river in Yangquan City. Firstly, pyrite samples were crushed into granules, soaked in deionized water for 8 hours, and then dried and crushed by agate to ensure even granules. Through a 200-mesh sieve, 75-micron granular samples were screened out and washed with deionized water, then dried, and reserved for further use. Samples were sent to Shanxi Institute of Rock and Mineral Testing and Application for mineral composition and chemical composition analyses, which are shown in Table 1.

| Na  | Mg  | Al  | Si  | K   | Fe  | Cu  | Zn  | Pb  | Total sulfur | Pyrite | Sulfate |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|--------------|--------|---------|
| 310 | 1620| 4630| 17600| 1050| 388600| 1860| 3300| 1231| 467600       | 443800 | 4780    |

2.2. Experimental methods and schedules

2.2.1. Experimental method. Previous studies on the oxidation mechanism of iron pyrite have noted that the particle size, composition, initial solution iron ion (Fe^{2+},Fe^{3+}) concentration, reaction time, temperature, and other factors can affect the formation of acidic mine wastewater [23-26]. Combined with these previous results, the present experiment was designed as an oxidation dissolution experiment which considered the reaction time and various factors generated by acidic wastewater, using pyrite at different solid-liquid ratios (1:100, 1:50, and 1:20). The pH value of the reaction solvent was 2, the reaction temperature T was 20 ℃, and the oxygen concentration used was the value in the ambient atmosphere. Microbial participation was not considered in this experiment, and the reaction time was 7 days.

The pH, Eh, EC value, total iron concentration, and SO_4^{2-} concentration in the solution at different reaction times were measured, and their changes over time were analyzed. The oxidation reaction rate of pyrite was calculated by monitoring the SO_4^{2-} concentration and the factors influencing the oxidation rate under different conditions were discussed [27-31].
2.2.2. **Experimental schedules.** Deionized water was used as the reaction solvent, and its pH value was adjusted to 2 using hydrochloric acid. Deionized water (100 ml) was poured into a 250-ml conical flask for each experiment. Then, the prepared pyrite samples were added proportionally to prepare reagents with solid-liquid ratios of 1:100, 1:50, and 1:20. Finally, these reagents were placed into a digital thermostat oscillator for oscillation during reactions in an experimental setup as shown in Figure 1.

![Digital thermostat oscillator](image)

**Figure 1.** Schematic diagram of experiment setup.

The reaction temperature was set at 20 °C, and the experiments in each group lasted 7 days, and samples were extracted at certain time intervals. Solution samples were centrifuged using a high-speed centrifuge and then filtered for analysis. A Thunder Magnetism pH-3C Acidimeter, Complementary pH composite electrode, and a redox potential composite electrode were used to measure the pH and Eh values of the filtrate, respectively. A HACH LA-EC20 conductivity meter was used to measure the EC values. The total iron concentration was determined by o-phenanthroline spectrophotometry and SO$_4^{2-}$ concentration via the barium chromate method.

3. **Results and discussion**

The following chemical reactions are proposed to have occurred during oxidative dissolution of iron pyrite.

1. FeS$_2$ was oxidized to H$_2$SO$_4$ and FeSO$_4$ under the action of free oxygen.

   \[ 2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \]

2. FeS$_2$ and FeSO$_4$ are converted into Fe$_2$(SO$_4$)$_3$ under the action of O$_2$:

   \[ 4FeS_2 + 15O_2 + 2H_2O = 2Fe_2(SO_4)_3 + 2H_2SO_4 \]
   \[ 4FeSO_4 + 2H_2SO_4 + O_2 = 2Fe_2(SO_4)_3 + 2H_2O \]

3. FeSO$_4$ further oxidizes to Fe$_2$(SO$_4$)$_3$:

   \[ 12FeSO_4 + 3O_2 + 6H_2O = 4Fe_2(SO_4)_3 + 4Fe(OH)_3 \]

4. Fe$_2$(SO$_4$)$_3$ in water promotes the dissolution of sulfide minerals:

   \[ Fe_2(SO_4)_3 + MS + H_2O + 3/2O_2 \rightarrow MSO_4 + 2FeSO_4 + H_2SO_4 \]

5. In mildly acidic water, Fe$_2$(SO$_4$)$_3$ will hydrolyze to produce H$_2$SO$_4$:

   \[ Fe_2(SO_4)_3 + 6H_2O = 2Fe(OH)_3 + 3H_2SO_4 \]

The experimental results to measure the oxidative dissolution of pyrite were analyzed, and the pH, Eh, EC value, total iron concentration, and SO$_4^{2-}$ concentration changes with respect to reaction time were determined.

3.1. **Changing trends of pH, Eh, EC value**

Pyrite samples were oxidized and dissolved at different solid-liquid ratios, and the variation trends with time of the solution pH, Eh, and EC values are shown in Figure 2, Figure 3, and Figure 4, respectively.
The charts of pH, Eh, and EC values in pyrite oxidation solutions, at solid-liquid ratios of 1:20, pyrite decrease from acid generation of the SO$_4^{2-}$ formation, then the pH of the solution increased, at solid-liquid ratios of 1:100, 1:50, and 1:20, the overall Eh and EC values decreased. At higher solid-liquid ratios, the pH was larger when it became stable, and the plateau values of Eh and EC were smaller. At the same time, the reaction time to reach a stable state was positively correlated with the solid-liquid ratio. When the solid-liquid ratio was 1:100, pH, Eh and EC values began to stabilize after 48h. When the solid-liquid ratio was 1:50, pH, Eh and EC values began to stabilize after 72h. Under the condition of solid-liquid ratio 1:20, pH value tends to be stable after 150h, and Eh and EC value starts to be stable after 120h. The solid-liquid ratio of 1:20, in the first four hours of the reaction, the pH value first increased and then decreased. This is because in the initial stage of the reaction, after the pyrite granules were placed into acidic solution at a pH of 2, soluble minerals such as carbonates and metal oxides were dissolved, and the oxidative dissolution of FeS$_2$ increased the acidity. As the reaction proceeded, the dissolution rate of FeS$_2$ decreased more rapidly than the acid being consumed in the reaction, and the pH value gradually increased and then became steady. Six hours before the start of the reaction, the Eh value also increased first before decreasing. FeS$_2$ dissolved in the acidic environment and produced Fe$^{2+}$, and the Eh value gradually increased.

In subsequent reactions, the concentration of H$^+$ decreased because it was being consumed. The Eh value decreased gradually until it stabilized since the H$^+$ concentration in the solution is used to determine the Eh value. The conductivity, the EC value, gradually decreased and finally stabilized in the reaction because it was relatively high before the oxidation and dissolution reaction. Although a part of H$^+$ was consumed during the reaction, a smaller amount was consumed than was generated by dissolution.

**Figure 3.** Change in the Eh value over time at different solid-liquid ratios.

**Figure 4.** Change in the EC value over time at different solid-liquid ratios.

**Figure 5.** The change trend diagram of iron concentration of pyrite at the ratio of solid-liquid to 1:100.

**Figure 6.** The change trend diagram of iron concentration of pyrite at the ratio of solid-liquid to 1:50.
3.2. Changing trends of Fe ion

The variation trend of Fe$^{2+}$, Fe$^{3+}$ and total iron concentration in different solid-liquid ratios of pyrite samples was compared, and the difference of total iron concentration in different solid-liquid ratios was also compared. The specific variation trend over time was shown in Figure 5-8.

As can be seen from the above trend chart, regardless of the solid-liquid ratio, the concentration of Fe$^{2+}$ was higher than that of Fe$^{3+}$. In addition, Fe$^{2+}$ and total iron concentrations increase with the increase of solid-liquid ratio, while Fe$^{3+}$ increases gradually, reaching a trend of relatively stability and slowly decreasing. When the solid-liquid ratio was 1:100, the Fe$^{2+}$ concentration showed a gradually increasing trend, while the Fe$^{3+}$ concentration first increased and then decreased in the reaction time of about 2h. This is mainly because the resulting Fe$^{3+}$ hydrolyzes and then precipitates with some of the dissolved substances, thereby reducing the total iron concentration and stabilizing it. When the solid-liquid ratio was 1:50, the Fe$^{2+}$ concentration showed a trend of gradual increase, and the Fe$^{3+}$ concentration also gradually increased. After 72h, the Fe$^{3+}$ concentration gradually decreased and tended to stable, and the total iron continued to increase and reached a stable level, which was not affected by the decrease of Fe$^{3+}$. When the solid-liquid ratio is 1:20, the Fe$^{2+}$ concentration tends to increase gradually, while the Fe$^{3+}$ concentration first increases and then decreases at the reaction time of 1h or so, and then increases and gradually reaches stability. The concentration changes are mainly caused from the precipitation caused by hydrolysis.

The data shows that the total iron concentration reached 183 mg/L, 325 mg/L, and 905 mg/L, respectively at solid-liquid ratios of 1:100,1:50 and 1:20, respectively, after the reaction stabilized, which showed that the reactants was proportional to the product.

Due to the hydrolysis and adsorption of Fe ions, the solid-liquid ratio of pyrite stabilized for 1:100, 1:50, and 1:20 at 72, 96, and 120 hours, respectively. The average apparent dissolution rate and average apparent release rate of Fe ions can be calculated using Formulas (1) and (2)[25], whose calculated results are shown in Table 2.

### Table 2. Calculation results of the average apparent dissolution rate and average apparent release rate at different solid-liquid ratios.

| Solid-liquid ratios | Average apparent dissolution rate (%) | Average apparent release rate (mg/h) |
|---------------------|---------------------------------------|-------------------------------------|
| 1:100               | 4.86                                  | 0.26                                |
| 1:60                | 4.69                                  | 0.351                               |
| 1:20                | 4.58                                  | 0.764                               |

Average apparent dissolution rate(%)=

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**Figure 7.** The change trend diagram of iron concentration of pyrite at the ratio of solid-liquid to 1:20.

**Figure 8.** The trend chart of total iron concentration with time at different solid-liquid ratio.
\[
\text{Average apparent dissolution rate (mg/h)} = \frac{\text{Average apparent dissolution rate (mg/h)} \times \text{Solid-liquid ratio}}{\text{Fe content (mg/g)} \times \text{Sample mass (g)}} \times 100\% \tag{1}
\]

\[
\text{Average total release amount (mg) / time (h)} \tag{2}
\]

It can be seen from Table 2 that the average apparent dissolution rate was inversely proportional to the solid-liquid ratio. This mainly occurred because pyrite hydrolysis also resulted in adsorption and precipitation, which affected the dissolution of total iron ions, and the average apparent release rate was proportional to the solid-liquid ratio[26]. A larger contact area was available at higher reactant concentrations, which increased the reaction rate.

3.3. Changing trends of \( \text{SO}_4^{2-} \):

The change in the \( \text{SO}_4^{2-} \) concentration at different solid-liquid ratios in pyrite samples was measured, and the details are shown in Figure 9.

As shown in Figure 6, the concentration of generated \( \text{SO}_4^{2-} \) increased as the solid-liquid ratio increased. After a reaction time of 7 days, the \( \text{SO}_4^{2-} \) concentration eventually rose to 52 mg/L, 81 mg/L, and 163 mg/L under the three ratios. The change trend with time is gradually rising, initially rising rapidly, and then rising gradually and slowly. At the beginning of the reaction, the sulfates present in pyrite dissolved, and the sulfate ion concentration in solution suddenly increased. At the later reaction stage, pyrite began to oxidize and dissolve, and the sulfate ion concentration slowly increased. Sulfate ions and other ions also simultaneously produced hydrolytic precipitation during the reaction. After a reaction time of 48 hours, the \( \text{SO}_4^{2-} \) concentration increased steadily at the three solid-liquid ratios. The production rate was calculated using the steady growth data of the \( \text{SO}_4^{2-} \) concentration after 48 hours. The change in the \( \text{SO}_4^{2-} \) concentration with respect to reaction time is shown in Figure 10.

**Figure 9.** Change in the \( \text{SO}_4^{2-} \) concentration with time at different solid-liquid ratios.

**Figure 10.** The relationship between \( \text{SO}_4^{2-} \) concentration and time after 48 hours.

In this experiment, the concentration of \( \text{SO}_4^{2-} \) was used to calculate the reaction rate \( (R) \) using Formula 3:

\[
R = \frac{d[\text{FeS}_2]}{dt} - 0.5 \frac{d[\text{SO}_4^{2-}]}{dt} \tag{3}
\]

The production rate of \( \text{SO}_4^{2-} \) at solid-liquid ratios of 1:100, 1:50, and 1:20 were obtained from the trend line in Figure 6. The oxidation reaction rates of pyrite at different solid-liquid ratios can be calculated by Formula 3. The results are shown in Table 3.

**Table 3.** Reaction rates \( (R) \) of pyrite at different solid-liquid ratios.

| Solid-liquid ratio | \( \text{SO}_4^{2-} \) production rates (mg/(L·h)) | \( \text{FeS}_2 \) reaction rate (mg/h) |
|-------------------|-----------------------------------------------|-------------------------------------|
| 1:100             | 0.264                                         | 0.0165                              |
| 1:50              | 0.404                                         | 0.0253                              |
| 1:20              | 0.778                                         | 0.0486                              |
4. Conclusions

After pyrite was oxidized and dissolved at solid-liquid ratios of 1:20, pyrite decrease from acid generation of the SO$_4^{2-}$ formation, then the pH of the solution increased, at solid-liquid ratios of 1:100, 1:50, and 1:20, the overall Eh and EC values decreased. No matter what solid-liquid ratio is adopted for reaction, Fe$^{2+}$ concentration is higher than Fe$^{3+}$ concentration, and Fe$^{2+}$ and total iron concentration all increase with the increase of solid-liquid ratio, while Fe$^{3+}$ gradually increases, reaching a trend of relatively stability while slowly decreasing.

The average apparent release rates of pyrite at solid-liquid ratios of 1:100, 1:50, and 1:20 were 0.26 mg/h, 0.351 mg/h, and 0.764 mg/h, respectively. The production rates of SO$_4^{2-}$ were 0.264 mg/h, 0.404 mg/h, and 0.778 mg/h, and the reaction rates of FeS$_2$ were 0.0165 mg/h, 0.0253 mg/h, and 0.0486 mg/h, respectively.

The experimental results showed that the average apparent release rate of Fe was proportional to the different solid-liquid ratios. The pyrite oxidation rate under acidic conditions was directly related to the concentration of reactants because at higher concentrations, there was more contact area which increased the oxidation reaction rate.

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