Article

Release of Heavy Metals from the Pyrite Tailings of Huangjiagou Pyrite Mine: Batch Experiments

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Received: 23 November 2015; Accepted: 18 January 2016; Published: 20 January 2016

Academic Editor: Marc A. Rosen

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Abstract: To provide the basic information about the release of heavy metals from the pyrite tailings of Huangjiagou pyrite mine, the pyrite tailings were investigated through a series of batch experiments under different initial pH of extractant, temperature, liquid-solid (LS) ratio, and soaking time conditions. Moreover, calcium carbonate was added in the pyrite tailings to determine the reduction effect on the release of heavy metals. The results show that Fe, Cr, Cu, Mn, Zn, and Ni were the major heavy metals in the pyrite tailings. Low initial pH and high LS ratio significantly promoted Fe, Cu, Mn, Ni, and Zn release, and high temperature significantly promoted Fe, Cu, Mn, and Ni release. Only small amounts of Cr were detected at low LS ratios. With the increase of soaking time, the released amount of Fe, Cu, Mn, Ni, and Zn increased to the maximum value within 48 h, respectively. After adding calcium carbonate, the released amounts of Fe, Cu, and Zn reduced at least 70.80% within 48 h soaking time. The results indicate that summer and the early soaking stage are the main phases for the release of heavy metals from the pyrite tailings. In the pyrite tailings, Cr is difficult to release. Adding calcium carbonate can effectively reduce the release of Fe, Cu, and Zn.

Keywords: heavy metal; release; pyrite tailings

1. Introduction

Pyrite tailings are sulfide-rich waste materials. In the natural environment, sulfide-rich tailings can be oxidized spontaneously once exposed to air and water [1]. The oxidation of sulfide-rich tailings may form acid mine drainage (AMD) [2]. AMD can cause the sustained dissolutions of heavy metals from tailings. Moreover, tailings generally with low organic matter content and without buffering capacity tend to easily release metals into the environment [3–5]. Therefore, the sulfide-rich tailings can cause the serious heavy metal pollution, and then controlling the pollution has become an important issue in the past decades. A large number of studies were successfully carried out to control the heavy metal pollution from tailings by using physical methods [6–9], chemical methods [10–14], and biological methods [15–19]. Whatever method is used in practical pollution control in a mine area, the release information of heavy metals of tailings must be, firstly, understood. The reason of this is that the
properties of tailings are distinctive in different mines owing to the compositional differences in ore and the diverse processing methods [5,20,21]. The distinctive properties of tailings can lead to the different release information of heavy metals from tailings, such as the types of released heavy metal element, the main release period, etc. Overall, understanding the release information of heavy metals of tailings can effectively guide the practical pollution control.

The column experiment method and the batch experiment method have been widely used to investigate the release of heavy metals from solid materials [2,22–29]. The column experiment method has the advantage of simulating a long-term release process and finding temporal variations of heavy metal release from solid materials compared with the batch experiment method. However, the column method is complex and expensive [30]. In recent years, some researchers have indicated that the low-cost and simple batch experiment method can substitute the column experiment method in studying the release of heavy metals from mining tailings [30]. In this case, the batch experiment method can be used to rapidly find the release information of heavy metals of tailings in a mine area where the release information is missing, if the control of the heavy metals pollution is urgently to be performed.

The Chuannan pyrite mine area is one of the five bases of pyrite in China. Since the 1950s, approximately 10 million tons of pyrite tailings have been generated in the pyrite mining and beneficiation process. The pollution of heavy metals caused by the pyrite tailings have attracted more and more attention of the Chinese government. At present, the Huangjiagou pyrite mine was selected as the demonstration area to control heavy metals pollution in the Chuannan pyrite mine area. However, there is a lack of basic information about the release of heavy metals from the local pyrite tailings.

In this study, the pyrite tailings of the Huangjiagou pyrite mine were investigated through a series of batch experiments. The aims of this study are as follows: (1) to provide the basic information about the release of heavy metals from the pyrite tailings for the following-up pollution control; (2) furthermore, to investigate the reduction effect on the release of heavy metals by adding calcium carbonate.

2. Materials and Methods

2.1. Study Area Description and Samples Collection

The Huangjiagou pyrite mine is located at 104°59′48″E, 28°13′47″N in Xingwen County, Sichuan Province, China. The total pyrite storage of the Huangjiagou mine is about 5.2 million tons. The sulfur grade of ore is about 19%. The orebody occurs in the bottom of the Longtan Formation of the Upper Permian. The mineral deposit is a sedimentary mineral deposit. The main ore minerals are pyrite, kaolinite, and calcite. The crystallization of pyrite is mainly occurring as euhedral and subhedral textures. The crystal size distributes between 0.5 to 5 mm. The mining has been performed since 2003. The flotation process is the used beneficiation technology. In the past twelve years, approximately 250,000 tons of pyrite tailings have been generated. The pyrite tailings were directly dumped into a field and exposed to open air. In this study, the pyrite tailings samples were collected from the tailing reservoir. The area of the tailing reservoir is about 1 km². 20 sampling points were selected in the tailing reservoir following a snake-shape pattern [31,32], and they were mainly distributed in the recent tailings dumping area. At each sampling point, approximately 2.5 kg of pyrite tailings were collected from the surface 10 cm of the tailings reservoir. The samples of all 20 sampling points were mixed, and the mixed tailings were air-dried in the laboratory. At present, the surrounding environment pollution of the Huangjiagou pyrite mine is prominent because of the mining activity. Figure 1 shows the current status of water and soil pollutions around the mining area. The study area belongs to a humid subtropical climate area with abundant rainfall, long frost-free period, and equal duration of rainy and hot seasons. The annual average temperature and precipitation are 17.4 °C and 1234.7 mm, respectively. Furthermore, the study area is a moderate acid rain area. The pH of rain in this area is less than 5.0 in recent decades.
2.2. Batch Experiments

The batch experiments were conducted under different initial pH of extractant, temperature, liquid-solid (LS) ratio, and soaking time conditions by using a single-factor experiment design. The test conditions for each single-factor experiment are given in Table 1. The mixture of sulfuric and nitric acids (5:1, w/w) was used as the stock solution to prepare the liquid extractant [33]. The different initial pH extractant was diluted from the stock solution with gradient dilution method. Sodium hydroxide (0.01 M, 0.1 M) and hydrochloric acid (0.01 M, 0.1 M) were used for minor pH adjustment, and a digital pH meter (Shanghai Rex Instrument Factory PHB-4, Shanghai, China) was used for pH measurement.

In each experiment, a certain amount of pyrite tailings was added in each container (100 mL round-bottom plastic centrifuge tube). Then, 50 mL liquid extractant was added in each tube. After that, the tubes were sealed with plastic plugs and shaken for a period of time at 150 rpm·min⁻¹ in a thermostatic shaker. Thereafter, the shaken tubes were transferred in a high-speed centrifuge and centrifuged for 10 min at 8000 rpm to separate the suspended solids. Finally, a 20 mL supernatant liquid was transferred into a 50 mL plastic bottle. A 200 µL nitric acid was added into the supernatant liquid.

The supernatant liquid was stored in a refrigerator at 4 °C until its test analysis. For investigating the reduction effect of calcium carbonate on the release of heavy metals, the reduction-release experiment was conducted under the same conditions as the soaking time experiment. Nevertheless, in the reduction-release experiment, 1.00 g calcium carbonate powder was added in each tube (i.e., 1.00 g calcium carbonate in 10.00 g pyrite tailings) and mixed with the pyrite tailings before adding liquid extractant.

Table 1. The designs and conditions of experiments.

<table>
<thead>
<tr>
<th>Experiment Name</th>
<th>Liquid Extractant (L)</th>
<th>Initial pH of Extractant</th>
<th>Temperature (°C)</th>
<th>LS Ratio (L·kg⁻¹)</th>
<th>Soaking Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial pH</td>
<td>0.05</td>
<td>2.00, 3.00, 4.00, 5.00, 6.00, 7.00</td>
<td>25</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>Temperature</td>
<td>0.05</td>
<td>2.00</td>
<td>15, 25, 35, 45</td>
<td>20</td>
<td>8</td>
</tr>
<tr>
<td>LS ratio</td>
<td>0.05</td>
<td>2.00</td>
<td>25</td>
<td>1, 2, 5, 10, 20, 30, 50</td>
<td>8</td>
</tr>
<tr>
<td>Soaking time</td>
<td>0.05</td>
<td>2.00</td>
<td>25</td>
<td>5</td>
<td>1, 2, 4, 8, 12, 24, 48, 72, 96, 120</td>
</tr>
</tbody>
</table>

2.3. Analytic Method

The metal contents of the pyrite tailings were detected through four-acid (HNO₃, HClO₄, HF, and HCl) digestion with an inductively-coupled plasma optical emission spectrometer (ICP-OES, Thermo Scientific CAP 6000 Series ICP, Waltham, MA, USA). The mineralogy analysis of the pyrite tailings was performed by using an X-ray diffractometer (Panake Company X’Pert PRO, Almelo, The Netherlands). Fe concentration in the supernatant liquid was analyzed by using an atomic absorption spectrometer (Beijing Puxi General Instruments Co. Ltd. TAS-990, Beijing, China), while the concentrations of Cu, Mn, Ni, and Zn in the supernatant liquid were analyzed by using ICP-OES.
2.4. Quality Control

In the study, all containers were soaked in 10% HNO₃ for 48 h, rinsed with deionized water, and dried before use. All experiments were conducted in triplicate.

2.5. Data Analysis and Processing

SPSS statistics 19 for Windows software was used to data analysis. In the reduction-release experiment, the reduced percentages of the released amounts were used to determine the influence of calcium carbonate on the release of heavy metals. The reduced percentages were calculated as:

\[ R = \frac{R_{A1} - R_{A2}}{R_{A1}} \times 100\% \]  

where, \( R \) represents the reduced percentage of the released amount of each heavy metal, \( R_{A1} \) and \( R_{A2} \) represents the released amount of each heavy metal in the soaking time experiment and the reduction-release experiment during the same soaking time, respectively.

3. Results and Discussion

3.1. Characteristics of Pyrite Tailings

Table 2 shows the metal contents in the pyrite tailings of the Huangjiagou pyrite mine. The results indicate that the pyrite tailings contained a variety of metals and heavy metals such as Fe, Cr, Cu, Mn, Zn, and Ni were rich. In this study, the release of the six heavy metals (Fe, Cr, Cu, Mn, Zn, and Ni) was examined considering their contents and impact on the environment. Figure 2 presents the X-ray diffraction pattern of the pyrite tailings. Based on Table 2 and Figure 2, the mainly mineral compositions of the pyrite tailings of the Huangjiagou pyrite main were kaolinite, pyrite, and calcite.

![Image of X-ray diffraction pattern](image)

**Figure 2.** X-ray diffraction pattern of the pyrite tailings.

**Table 2.** Total contents of metals in the pyrite tailings.

<table>
<thead>
<tr>
<th>Element</th>
<th>Content (mg kg⁻¹)</th>
<th>Element</th>
<th>Content (mg kg⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>68,500.00</td>
<td>Zn</td>
<td>98.00</td>
</tr>
<tr>
<td>Al</td>
<td>145,588.24</td>
<td>Hg</td>
<td>0.29</td>
</tr>
<tr>
<td>Cu</td>
<td>118.00</td>
<td>Mn</td>
<td>115.00</td>
</tr>
<tr>
<td>Ni</td>
<td>63.50</td>
<td>Cr</td>
<td>319.00</td>
</tr>
<tr>
<td>Cd</td>
<td>1.12</td>
<td>Ca</td>
<td>17,928.57</td>
</tr>
</tbody>
</table>
3.2. Released Amounts of Heavy Metals under Different Initial pH of Extractant Conditions

Cu, Fe, Mn, Ni, and Zn were detected in the initial pH experiment. Figure 3 presents the release profiles of Fe (Figure 3a), Cu, Mn, Ni, and Zn (Figure 3b). The maximum released amount of Fe, Cu, Mn, Ni, and Zn was 371.40, 10.20, 6.82, 4.06, and 13.74 mg kg⁻¹, respectively. The maximum released amounts of the five heavy metals all appeared at pH 2. The released amount of Fe, Cu, Mn, Ni, and Zn at pH 2 was 4.35, 5.00, 1.79, 1.40, and 1.76 times higher than that at pH 7, respectively.

![Figure 3](image-url) Released amounts of heavy metals from the pyrite tailings within initial pH 2 to 7. (a) Fe (b) Cu, Mn, Ni, and Zn. (at 25 °C, LS ratio 20, and 8 h soaking time).

In Figure 3, the released amounts of Fe, Cu, Mn, Ni, and Zn had significant differences (one-way ANOVA, p < 0.05) from pH 2 and 7. The results imply that initial pH of extractant was an important factor for the release of Fe, Cu, Mn, Ni, and Zn. Moreover, it can be found that the release profiles of heavy metals were as a function of initial pH and the released amounts of the heavy metals increased with decreasing initial pH value. The results were consistent with other similar studies [25,30]. In an acidic environment, the release of heavy metals occurred mainly due to acid attack [30]. In the study area, the pH of rain is less than 5.0. The acid rain promotes the release of heavy metals and causes more released amounts of heavy metals from the pyrite tailings of the Huangjiagou pyrite mine. Thus, the serious pollution of heavy metals appeared in this study area. At present, the pH of rain has the decreasing trend in this study area [33]. Therefore, the heavy metal pollution caused by the pyrite tailings will be more serious if the pollution control is not carried out in the Huangjiagou mine area.

3.3. Released Amounts of Heavy Metals under Different Temperature Conditions

Figure 4 shows the released amounts of heavy metals from the pyrite tailings within temperature range of 15–45 °C. Fe, Cu, Mn, Ni, and Zn were detected in the batch experiment. In Figure 4, the released amounts of each metal had an increasing trend from 15–45 °C. For Fe (Figure 4a), Cu, Mn, Ni, and Zn (Figure 4b), the released amounts changed from 369.60, 8.76, 6.33, 3.76, and 13.10 mg kg⁻¹ (at 15 °C) to 523.40, 12.72, 8.95, 4.88, and 16.86 mg kg⁻¹ (at 45 °C), respectively. Compared with the released amounts at 15°C, the released amounts of Fe, Cu, Mn, Ni, and Zn at 45°C increased 1.42, 1.45, 1.41, 1.30, and 1.28 times, respectively.

In Figure 4, the released amounts of Fe, Cu, Mn, and Ni had significant differences (p < 0.05) from 15 to 45 °C. The results indicate that the effect of temperature was significant for the release of Fe, Cu, Mn, and Ni from the pyrite tailings of the Huangjiagou pyrite mine. The release characteristic caused by temperature is related to the solubility product constant Ksp, which is positively correlated with temperature [29]. In the temperature range of this study, the solubility product constants of the mineral composition of Fe, Cu, Mn, and Ni may be more sensitive than that of Zn in the pyrite tailings accompanying with the variety of temperatures. Thus, the released amounts of Fe, Cu, Mn, and Ni significantly increased with the increase of temperature. Generally, high temperature can significantly promote the release of Fe, Cu, Mn, and Ni from the pyrite tailings.
The maximum and minimum released amount of Cr was 0.06 (LS ratio 2 L kg⁻¹) and 0.03 mg kg⁻¹ (LS ratio 1 L kg⁻¹), respectively.

Figure 4. Released amounts of heavy metals from the pyrite tailings within temperature range of 15–45 °C. (a) Fe; (b) Cu, Mn, Ni and Zn. (at initial pH 2, LS ratio 20 and 8 h soaking time).

3.4. Released Amounts of Heavy Metals under Different LS Ratio Conditions

Figure 5 shows the released amounts of the six detected heavy metals under the different LS ratio conditions (1–50 L·kg⁻¹). For Fe (Figure 5a), the minimum and maximum released amount (104.97 and 681.00 mg·kg⁻¹) appeared correspondingly at LS ratio 1 and 50 L·kg⁻¹. The maximum released amount was 6.49 times higher than the minimum released amount. In the range of LS ratios 1–50 L·kg⁻¹, the released amount of Fe had an increasing trend. Figure 5b shows that Cu, Mn, Ni, and Zn had the same release trends as Fe. The maximum released amount of Cu, Mn, Ni, and Zn was 13.70, 10.32, 4.90, and 16.95 mg·kg⁻¹, respectively. The ratio of the maximum and minimum released amount corresponding to Cu, Mn, Ni, and Zn was 6.40, 5.09, 3.76, and 4.26, respectively. For Cr (Figure 5c), the released amounts of Cr were absent under the condition of high LS ratios because the concentrations of Cr in the supernatant liquid were lower than the detection limit. However, the released amounts of Cr also had an increasing trend with increasing LS ratio according to the existing data in Figure 5c. The maximum and minimum released amount of Cr was 0.06 (LS ratio 2 L·kg⁻¹) and 0.03 mg·kg⁻¹ (LS ratio 1 L·kg⁻¹), respectively.

Figure 5. Released amounts of heavy metals from the pyrite tailings within LS ratio 1 to 50. (a) Fe; (b) Cu, Mn, Ni, and Zn; (c) Cr. (at initial pH 2, 25 °C, and 8 h soaking time).
In Figure 5, a significant difference ($p < 0.05$) had been found among the released amounts of each heavy metal under the different LS ratio conditions. The results show that the LS ratio can significantly influence Fe, Cu, Mn, Ni, and Zn release from the pyrite tailings. The effect of LS ratio on the release of heavy metals from the mining tailings can be summarized as the dissolution effect because of the promotion of the mass transfer process of the solid–liquid interface by increasing the solution volume or as the diffusive transport effect because of a concentration gradient [30,34,35]. Figure 5 illustrates that the released amounts of Fe, Cu, Mn, Ni, Zn, and Cr had an increasing trend with the increase of LS ratio. The results indicate that dissolution is the predominant effect for the release of heavy metals from the pyrite tailings. Thus, the rainy days are the prominent period of heavy metal release from the pyrite tailings in the study area. Integrating the result with those of pH and temperature experiments, it can be concluded that summer is the main phase for the release of heavy metals from pyrite tailings in the Huangjiagou mine area.

3.5. Released Amounts of Heavy Metals under Different Soaking Time Conditions

Figure 6 shows the trends of the released amounts of the detected metals within the experimental duration (120 h). In Figure 6a, the maximum and minimum released amount of Fe was 287.37 (12 h) and 5.65 mg kg$^{-1}$ (120 h), respectively. Initially, the released amount of Fe increased slowly from 251.10 to 287.37 mg kg$^{-1}$ with the increase of soaking time. Thereafter, the released amount of Fe decreased rapidly from the maximum value to 10.78 mg kg$^{-1}$. Finally, the released amounts gradually maintained stability at the level of a few milligrams in the last stage of the experiment. The similar trends as Fe were found for Cu, Zn, and Ni (Figure 6b). The maximum and minimum released amounts of Cu, Zn, and Ni were 6.31 (4 h), 10.75 (12 h), and 3.31 (24 h), 0.92 (120 h), 4.29 (120 h), and 1.82 mg kg$^{-1}$ (120 h), respectively. In Figure 6c, the released amounts of Mn also followed the same trend as the other four metals. Accompanying with the increase of soaking time, the released amount of Mn increased from 4.41 mg kg$^{-1}$ to the maximum value (i.e., 6.72 mg kg$^{-1}$). However, the released amounts of Mn maintained stability near the maximum value until it decreased after 96 h.

The released amounts of Fe, Cu, Mn, Ni, and Zn increased at a certain maximum value and then decreased in Figure 6. The results were consistent with the previous similar studies [26,29,36]. The maximum released amounts of Fe, Cu, Mn, Ni, and Zn represented the fractions of dissolved metals in the tailings [29]. In Figure 6, the released amount of Fe, Cu, Ni, Zn, and Mn at 1 h reached 87.23%, 97.46%, 81.57%, 86.98%, and 65.63% of the maximum released amount of the five metals, respectively. The results indicate that the metals in the pyrite tailings could easily release in the early soaking stage once the pyrite tailings are exposed to acid water.

Figure 7 shows the final pH value of extractant after soaking within the experimental duration (120 h). The final pH value had the increasing trend in the experiment period. The increase of the final pH value indicates that the hydrogen ions were consumed gradually. Combined with Figure 6, it can be found that the released amount of each heavy metal increased initially with the increase of the final pH value. The result reflects the gradual release process of heavy metals caused by acid attack. Accompanying with the increase of the soaking time, the final pH value reached 2.72 at 12 h. In the pH range of 2.8–4.5, a Fe-hydrolysate, Schwertmannite, can form in iron-rich solution [37]. This may be the main reason that the released amount of Fe decreased rapidly after it reached the maximum released amount at 12 h. Meanwhile, Schwertmannite can co-precipitate Cu, Zn, and Ni in acid solution [38]. In Figure 6, Cu, Zn, and Ni had the similar release trends to Fe. Thus, it can be deduced that part of the released Cu, Zn, and Ni may be removed after the formation of the Fe-hydrolysate. This is maybe a reason for the decrease of the released amounts of Cu, Zn, and Ni in Figure 6. In addition, kaolinite was one of the mineral compositions in the pyrite tailings (Figure 2). Previous research has proven that the kaolinite particle can absorb Fe, Cu, Zn, Ni, and Mn in aqueous solution [39–41]. This may be another reason for the decrease of Fe, Cu, Zn, and Ni released amounts and the reason for the decrease of Mn released amount in Figure 6.
Figure 6. Released amounts of heavy metals from the pyrite tailings in different soaking time periods. 
(a) Fe; (b) Cu, Ni, and Zn; (c) Mn. (at initial pH 2, 25 °C, and LS ratio 5).

Figure 7. The final pH value of extractant after soaking with the pyrite tailings. (at initial pH 2, 25 °C, and LS ratio 5).

3.6. Released Amounts of Heavy Metals after Adding Calcium Carbonate

Figure 8 shows the released amounts of all detected heavy metals from the pyrite tailings in different soaking time periods. For Fe (Figure 8a), the released amount initially decreased rapidly from 57.50 (1 h) to 1.25 mg·kg⁻¹ (8 h) and then remained stable in the range of 1–4 mg·kg⁻¹ in the
later stages of the experiment. In Figure 8b,c, Ni, Zn, and Mn showed the similar trends to that of Fe. The released amounts of Ni, Zn, and Mn only decreased gradually at the beginning of the experiment from 1.78 mg·kg⁻¹ (1 h) to 0.18 mg·kg⁻¹ (48 h), 2.73 mg·kg⁻¹ (1 h) to 0.18 mg·kg⁻¹ (24 h), and 2.56 mg·kg⁻¹ (1 h) to 0.56 mg·kg⁻¹ (48 h), respectively, and then remained constant at approximately 0.10, 0.15, and 0.50 mg·kg⁻¹, respectively, at the later stages of the experiment. Cu (Figure 8b) had a different trend compared with the above mentioned metals. At the beginning of the experiment, the released amounts of Cu were below the detection limit. With the increase of soaking time, a small released amount (i.e., 0.05 mg·kg⁻¹ (8 h)) appeared, and the released amounts remained stable in the range of 0.05–0.08 mg·kg⁻¹ until the end of the experiment.

![Figure 8](image-url)

**Figure 8.** Released amounts of heavy metals from the pyrite tailings in different soaking time periods after adding calcium carbonate. (a) Fe; (b) Cu, Ni, and Zn; (c) Mn. (at initial pH 2, 25 °C, and LS ratio 5).

The added calcium carbonate in tailings can consume hydrogen ions and increase the alkalinity of the soaking liquor [42–44]. In the experiment, the amount of added calcium carbonate was excessive through neutralization reaction calculation. On the one hand, the excessive calcium carbonate was enough to exhaust the hydrogen ions of the extractant. Then, the release process of heavy metals
caused by acid attack was prevented. The acid-soluble heavy metals could not release from the pyrite tailings. On the other hand, the excessive calcium carbonate changed the acid environment of the extractant to the weak alkaline environment at the beginning of the experiment. For the water-soluble Fe, Cu, Mn, Ni, and Zn, they can precipitate gradually under weak alkaline condition [45]. This led to the trend that the release amount of heavy metals decreased with the increase of soaking time in Figure 8. Based on the above two reasons, the released amounts of heavy metals in Figure 8 were less than those in Figure 7. In addition, the released amounts of heavy metals still remained stable at low levels at the end of the experiment. The result indicates that the weak alkaline environment of the extractant did not change. Thus, it can be deduced that the Fe precipitate may be ferrihydrite or hydroxide and the Cu, Mn, Ni, and Zn precipitates may be hydroxide according to the previous researches [44,45].

Due to the release of heavy metals from the pyrite tailings mainly occurs in the early soaking stage (Figure 6), the reduced percentages of the released amounts of heavy metals in the early stage can effectively reflect the influence of calcium carbonate on the release of heavy metals. Combining the results with those of Section 3.5, Table 3 shows the reduced percentages of the released amounts of all five detected metals within 48 h soaking time after adding calcium carbonate. In Table 3, the maximum reduced percentage of Fe, Cu, Mn, Ni, and Zn was 99.51%, 100%, 91.67%, 93.43%, and 98.23%, respectively, whereas the minimum reduced percentage was 77.06%, 98.51%, 41.95%, 34.07%, and 70.80%, respectively. The results indicate that the released amounts of Fe, Cu, and Zn can be effectively reduced by adding calcium carbonate in the pyrite tailings, and the moderate reduce can be acquired for Mn and Ni.

Table 3. Reduced percentages of the released amounts of Fe, Cu, Mn, Ni, and Zn after adding calcium carbonate in the pyrite tailings (1.00 g calcium carbonate in 10.00 g pyrite tailings).

<table>
<thead>
<tr>
<th>Soaking Time (h)</th>
<th>Reduced Percentage (%)</th>
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<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>1</td>
<td>77.06</td>
</tr>
<tr>
<td>2</td>
<td>95.68</td>
</tr>
<tr>
<td>4</td>
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</tr>
<tr>
<td>12</td>
<td>99.27</td>
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<tr>
<td>24</td>
<td>99.13</td>
</tr>
<tr>
<td>48</td>
<td>98.83</td>
</tr>
</tbody>
</table>

3.7. Implication of the Study

Compared with column experiment method, the batch experiment method has the advantages of simple experiment process and low cost. However, the released amounts of heavy metals can be overestimated by using the batch experiment method because the mass transfer limitations is ignored and geological and hydrological factors are absent in the batch experiment [30]. Generally, the batch experiment method is suitable to investigate the qualitative release information of heavy metals from mining tailings, such as released element types, influence of external conditions, release phase, and so on. Therefore, it is feasible to use the batch experiment method in this study.

Fe, Cu, Mn, Ni, and Zn are the main released heavy metals from the pyrite tailings of the Huangjiagou pyrite mine. For pollution control of heavy metal, the control of Fe, Cu, Mn, Ni, and Zn should be focused on. Meanwhile, temperature and LS can significantly affect the Fe, Cu, Mn, and Ni release. Thus, the release amounts of Fe, Cu, Mn, and Ni are variable in different seasons. If ecological restoration technology is adopted, the selected plants should have the strong tolerance to Fe, Cu, Mn, and Ni. Moreover, this study verified the reduction effect of the release of heavy metals by adding calcium carbonate. For pollution control, adding calcium carbonate in the tailings can be taken as a control measure of the pollution source. In addition, the heavy metals could easily release in the
early soaking stage, and the low initial pH of extractant can significantly promote heavy metal release. In this case, the use of a low pH solution may quickly implement the recycling of heavy metals from the pyrite tailings.

Mining tailings are one of the main sources of heavy metal pollution. It has already become the focus of environmental management in the developed countries. In the American legal system, the laws involving the tailings management and control include Resource Conservation and Recovery Act, Comprehensive Environmental Response, Compensation and Liability Act, and Surface Mining Control and Reclamation Act, etc. In the European Union, the European Commission also established the detailed laws and specifications for tailings management and control, such as Directive 2003/105/EC on the control of major-accident hazards involving dangerous substances, Directive 2006/21/EC on the Management of Waste from Extractive Industries, Directive 2006/12/EC on waste, Reference document on best available techniques for management of tailings and waste-rock in mining activities, and so on. At present, although some basic laws have been set up in China, there is a lack of detailed guidance as those of the developed countries. Following this study, the pollution monitoring and assessment and the reuse of the tailings will be launched in the study area. Integrating the results of the above research, the detailed information for the pollution control will be provided. Moreover, this research may provide some reference for establishing the guidance of the pollution control of heavy metals in the Chuannan pyrite mine area.

4. Conclusions

The pyrite tailings of the Huangjiagou pyrite mine mainly contained six types of heavy metals, namely Fe, Cr, Cu, Mn, Zn, and Ni. The main mineral compositions and contents of the pyrite tailing were kaolinite, pyrite, and calcite. For Fe, Cu, Mn, and Ni, low initial pH, high temperature, and high LS ratio significantly promoted their release. For Zn, the release was significantly promoted by low initial pH and high LS ratio. Accompanying with the increase of soaking time, the released amount of Fe, Cu, Mn, Ni, and Zn increased to a certain maximum value within 48 h, and then decreased to a relatively stable value, respectively. The results show that summer and the early soaking stage are the main phases for the release of heavy metals from the pyrite tailings. After adding 1.00 g calcium carbonate in 10.00 g pyrite tailings, the released amounts of Fe, Cu, Mn, Ni, and Zn reduced. Within 48 h soaking time, the minimum reduced percentage of the release amount of Fe, Cu, Mn, Ni, and Zn was 77.06%, 98.51%, 41.95%, 34.07%, and 70.80%, respectively. The result indicates that adding calcium carbonate can effectively reduce the released amounts of Fe, Cu, and Zn, while moderately reducing the released amounts of Ni and Mn. In all batch experiments, only small amounts of Cr were detected at low LS ratios in the LS ratio experiment. Therefore, Cr is difficult to release from the pyrite tailings. Overall, this study provided the basic information of release of heavy metals from the pyrite tailings and an effectively reduction-release measure for pollution control in the Huangjiagou pyrite mine.

Acknowledgments: This work was supported by the China Geological Survey Project (No.12120114032101).

Author Contributions: Liangqian Fan and Likou Zou designed the experiments; Liangqian Fan, Xi Zhou, Hongbing Luo, Li Dai, Jie Deng, and Zhengfu Ju performed the experiment; Liangqian Fan and Xi Zhou analyzed the data; Liangqian Fan, Hongbing Luo, Likou Zou wrote the manuscript; Zhiming Zhu, Lin Ji, Bei Li, and Lin Cheng contributed reagent and materials.

Conflicts of Interest: The authors declare no conflict of interest.

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