



# Article A Green Cyclic Leaching Process for Low-Grade Pyrolusite via a Recyclable Fe(II) Reductant

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**Abstract:** The low-cost Fe(II) reductants used in the leaching of pyrolusite usually cause high concentrations of iron ions in the leaching solution, which are difficult to treat and recover. Herein, a green cyclic leaching process for pyrolusite with recycling and reusing of Fe(II) reductants was developed. Sodium sulfide was introduced to reduce and precipitate iron ions in the leaching solution. Ep-H diagrams show that Fe<sup>3+</sup> can be reduced to Fe<sup>2+</sup> by S<sup>2-</sup> and form a precipitate with the high efficiency of 93.09%. Since the main component of the precipitate was ferrous disulfide with reducibility, it was used as a reducing agent for low-grade manganese oxide ores. A total of 97.96% of the manganese was highly reductively leached by the obtained precipitate of 0.28 g·g<sup>-1</sup> ore. Furthermore, the leaching efficiency was almost unchanged after five iterations of cyclic experiments. The cyclic leaching process enables the efficient leaching of manganese and the recycling of iron, which provides a green and economic method for the efficient utilization of low-grade pyrolusite resources.

Keywords: cyclic leaching; reductive precipitation; low-grade pyrolusite; Fe(II) reductant; sodium sulfide



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## 1. Introduction

In recent years, the global annual demand for manganese has increased significantly with the soaring steel production, which has exacerbated the depletion of manganese-rich ore [1–3]. Therefore, the efficient utilization of low-grade pyrolusite has attracted the attention of many researchers. The current processing methods of pyrolusite are divided into pyrometallurgy and hydrometallurgy [4]. Pyrometallurgy mainly reduces high-valent manganese by reduction roasting, which has the problems of high energy consumption and high pollution [5]. By contrast, hydrometallurgy plays an increasingly important role in the exploitation of low-grade pyrolusite due to its low energy consumption and environmental friendliness.

Reduction leaching is frequently used in the hydrometallurgy of low-grade pyrolusite, which is subsequent with an impurity removal process due to the gangue minerals and the introduction of reductant [2]. First, insoluble manganese is reduced to soluble manganese into the solution by inorganic reducing agents [6,7] or organic reducing agents [8,9]. The most commonly used are Fe(II) reductants such as pyrite, ferrous sulfide, and ferrous sulphate. However, iron in the gangue minerals and reductants leads to a high impurity iron concentration in the leaching solution, making it difficult to precipitate and filter [10]. Traditional methods for iron removal are oxidation/filtration [11,12], ion exchange [13], and adsorption [14,15], which are high-cost and not applicable to high iron concentrations. Meanwhile, the impurity iron in the traditional decontamination process is left in the leaching residue, which increases the heavy metal pollution of the leaching residue. Additionally, the iron in the residue cannot be conveniently separated and recovered, leading to a certain amount of iron resource waste. In addition, the iron precipitates are gelatinous, metastable, and difficult to precipitate and filter when the iron concentration in the solution is high,

which hinders the process of continuous production [16]. Consequently, it is urgent to develop a green process to separate and recover the impurity iron from the leach solution.

It is envisaged that if the impurity Fe(III) in the leaching solution can be converted to Fe(II) and reused in the leaching process, it will be conducive to resource recovery and environmental protection. Sodium sulfide can both reduce Fe(III) to Fe(II) and provide  $S^{2-}$  to form a precipitate with it. Therefore, in this study, a green cyclic leaching process for low-grade pyrolusite was designed by introducing reductive precipitation, as shown in Figure 1. Firstly, ferrous sulfide efficiently leached manganese from pyrolusite and provided iron as a reduction carrier for the subsequent recirculation leaching of pyrolusite. Then, sodium sulfide achieved the separation of iron and manganese in the leaching solution. The high concentration of iron ions was reduced to divalent iron, and then a precipitate with negative divalent sulfur ions was formed. The precipitate with reducibility could therefore be used as a reducing agent for pyrolusite, and the leaching efficiency of manganese remained above 97% after several cycles. The process recycles the impurity iron in the leaching solution as the reductant of low-grade pyrolusite, which has the advantages of high atom-utilization efficiency, convenient operation, and low economic cost.



Figure 1. Flow chart of the reductive leaching process of pyrolusite.

#### 2. Materials and Methods

### 2.1. Reagents and Materials

The low-grade pyrolusite was obtained from Chongqing, China. The sample composition was analyzed by X-ray fluorescence (XRF, ZSX Priums, Rigaku, Japan), as shown in Table 1. The manganese content in the sample was 24.77%. Other impurities were mainly silicon, iron, and aluminum, accounting for 16.76%, 15.39%, and 3.27%, respectively. As shown in Figure 2a, the X-ray diffraction (XRD, TTR III, Rigaku, Japan) pattern of the ore sample revealed the phase of the metal. Mn mainly existed in the form of  $MnO_2$  [17]. Si and Fe mainly existed in the form of  $SiO_2$  and  $FeAl_2O_4$ . This indicates that the mineral is a low-grade manganese oxide ore with high silicon and high iron levels. The particle size distribution of the ore after grinding is shown in Figure 2b. The median diameter ( $D_{50}$ ) of the sample was 36.90 µm, half of the dust particles were smaller than 39.79 µm, and about 90% were smaller than 127.30 µm. The crushed pyrolusite was in the shape of lumps with a rough surface and had a compact structure without voids, as shown in Figure 2c. The chemical analytical pure reagents used in this study such as ferrous sulphate, ferrous sulfide, and sodium sulfide were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

Table 1. The chemical composition (wt.%) of the low-grade pyrolusite.

Element	Mn	Fe	Al	K	Ca	Ni	Zn	0	S	Si	Others
Content	24.77	15.39	3.27	0.61	0.37	0.14	0.10	37	0.02	16.76	1.57



**Figure 2.** (a) XRD pattern and figure of the low-grade pyrolusite, (b) particle size distribution (D: particle diameter), and (c) SEM image of the low-grade pyrolusite.

#### 2.2. Experimental Procedure

#### 2.2.1. Cyclic Leaching of Manganese Oxide Ore

The leaching experiments of low-grade manganese oxide ore were carried out in 100 mL round-bottom flasks equipped with a magnetic stirrer and immersed in a constant temperature water bath. Mineral samples and reducing agents (ferrous sulphate, ferrous sulfide, or precipitate) were added to the flask in a certain proportion, and then a sulfuric acid solution prepared by sulfuric acid and deionized water was added to react. At different dosages of reducing agent, different temperatures, different dosages of sulfuric acid, different liquid–solid ratios, ore leaching batch experiments were carried out. The effects of experimental conditions on the leaching of valuable components from pyrolusite were mainly investigated. After the reaction was completed, the liquid–solid separation was completed by suction filtration. The ion concentration in the solution was measured, and the leaching efficiency was calculated.

### 2.2.2. Precipitation of Impurity Metal Ions

The apparatuses for the leachate precipitation experiments were the same as for the leaching experiments. First, sodium hydroxide solution and sodium sulfide were added to the same volume of leaching solution, stirred, and held for 1 h to investigate the iron removal effect of different precipitants. Then the sodium sulfide precipitation batch experiments were carried out in a water bath equipped with magnetic stirring and the effects of temperature, reaction time, pH, and holding time were investigated. The solution and precipitate were separated at the end of the reaction. The manganese and iron ion concentrations in the solution were measured, and the precipitation efficiencies of manganese and iron were calculated.

#### 2.3. Analytical Techniques

The mineralogy of the low-grade pyrolusite, leaching residue, and precipitate was studied by XRD. Inductively coupled plasma (ICP-OES, Blue SOP, Spectro, Kleve, Germany) was used to determine metal concentrations in solutions. According to Chinese national standards GB/T 1506–2016 [18], manganese in the ore was determined using the ammonium iron (II) sulfate titrimetric method. After the sample was dissolved in hydrochloric acid, nitric acid, and phosphoric acid, the added perchloric acid oxidizes the manganese to trivalent in the phosphoric acid medium. The manganese solution was titrated with a standard titration solution of ammonium iron (II) sulfate with N-phenyl o-aminobenzoic acid as an indicator. The MIRA 3 LMU (TESCAN, Brno, Czech Republic) microscope was used to acquire scanning electron microscope (SEM) images. Energy dispersive spectroscopy (EDS, EDX-GENESIS 60S, EDAX, Pleasanton, CA, USA) was used to measure the composition of the microdomains (see Supplementary Materials for details).

### 3. Results and Discussion

# 3.1. Reductive Leaching of Low-Grade Pyrolusite

3.1.1. Reduction of Manganese Dioxide by FeSO<sub>4</sub> and FeS

Ferrous sulfate and ferrous sulfide, as common Fe(II) reductants, were used in the reductive leaching of pyrolusite. The reduction process was analyzed by using Eh-pH data (90 °C) calculated by the HSC Chemistry 6.0 program (Outotec Research Oy, Helsinki, Finland). The reduction behavior of FeSO<sub>4</sub> to MnO<sub>2</sub> in aqueous medium is shown in Figure 3a. Insoluble Mn(IV) in ore can be reduced by FeSO<sub>4</sub> in aqueous medium to soluble low-valent manganese under alkaline conditions [19,20]; it is directly reduced to Mn<sup>2+</sup> into solution, and the Fe(II) reductant is oxidized to Fe<sup>3+</sup> into the solution under acidic conditions. The process of reduction of MnO<sub>2</sub> by FeS is shown in Figure 3a,b. Fe(II) and S(II) can provide more charges for the redox process when FeS is used as the reducing agent. Insoluble Mn(IV) is reduced to Mn(OH)<sub>2</sub> by Fe<sup>2+</sup> and S<sup>2-</sup> under alkaline conditions, and insoluble Mn(IV) can be directly reduced to Mn<sup>2+</sup> by Fe<sup>2+</sup> and S<sup>2-</sup> into solution under acidic conditions. Meanwhile, the reducing agent is oxidized to Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup> [21,22].



Figure 3. Eh-pH diagram of (a) Mn-Fe-H<sub>2</sub>O system at 90 °C and (b) Mn-S-H<sub>2</sub>O system at 90 °C.

#### 3.1.2. Effect of the Dosage of Reducing Agent

In the batch leaching experiment, a 5.00 g ore sample was reductively leached by a different dosage of ferrous sulfate under the conditions of a temperature of 90 °C, a dosage of  $H_2SO_4$  of 1.00 g·g<sup>-1</sup> ore, a leaching time of 60 min, and a liquid–solid ratio of 10 mL·g<sup>-1</sup>, as shown in Figure 4a. With the increase of the dosage of the reducing agent, the leaching efficiency of manganese increased rapidly. Without adding a reducing agent, the manganese leaching efficiency was 0, that is, all of the manganese in the manganese oxide ore existed in the form of insoluble Mn (IV). When the dosage of ferrous sulfate was less than 2.00 g·g<sup>-1</sup> ore, the leaching efficiency of manganese increases linearly with the increase of ferrous sulfate, as shown in Equation (1) [19,23,24]. When the dosage of ferrous sulfate was 2.40 g·g<sup>-1</sup> ore, the leaching efficiency of manganese tended to be flat.

In the experiment of ferrous sulfide as a reductant (Figure 4b), the increase of ferrous sulfide dosage significantly improved the leaching efficiency of manganese. The leaching efficiency of manganese was 96.77% when the dosage of ferrous sulfide was 0.20 g·g<sup>-1</sup> ore, which was only one twelfth of that of ferrous sulphate. The Fe<sup>2+</sup> and S<sup>2-</sup> in ferrous sulfide simultaneously provided electrons as reductants, greatly improving the reduction equivalent, which was consistent with the results of the theoretical analysis in Figure 3. Fe<sup>2+</sup> and S<sup>2-</sup> are oxidized to Fe<sup>3+</sup> and SO<sub>4</sub><sup>2-</sup>, respectively, after the reduction of manganese dioxide (Equations (2)–(4)).

$$MnO_{2}(s) + 2Fe^{2+}(aq) + 4H^{+}(aq) = Mn^{2+}(aq) + 2Fe^{3+}(aq) + 2H_{2}O(l)$$
(1)

$$FeS(s) + H^{+}(aq) = Fe^{2+}(aq) + HS^{-}(aq)$$
 (2)

$$4MnO_2(s) + HS^{-}(aq) + 7H^{+}(aq) = 4Mn^{2+}(aq) + SO_4^{2-}(aq) + 4H_2O(l)$$
(3)

$$9MnO_2(s) + 2FeS(s) + 20H^+(aq) = 9Mn^{2+}(aq) + 2SO_4^{2-}(aq) + 2Fe^{3+}(aq) + 10H_2O(l)$$
(4)



Figure 4. Effect of (a) ferrous sulfate to ore ratio and (b) ferrous sulfide to ore ratio on the leaching efficiency.

3.1.3. Characterization of Minerals before and after Leaching

Under the same experimental conditions mentioned above, the effects of temperature, sulfuric acid dosage, leaching time, and liquid–solid ratio on the leaching efficiency of pyrolusite were further investigated, as shown in Figure S1. It was found that the reduction efficiencies of the two reductants were not much affected by conditions such as temperature. However, compared with ferrous sulphate, ferrous sulfide exhibited a great advantage in the dosage, which was only one twelfth of the dosage of ferrous sulphate.

To further compare the advantages and disadvantages of the two reductants, the physical phases of pyrolusite and leaching residues through the two reductants were analyzed. As shown in Figure 5a, the peak of manganese oxide in the leaching residue after reduction and leaching by ferrous sulfate had disappeared, and the peak of silica could be clearly seen, indicating that the leaching residue was mainly composed of residual silica [25]. In addition, the presence of iron salts in the leaching residue was also observed. The reduction equivalent of ferrous sulfate was small, and the efficient leaching of manganese could be achieved only when the dosage reached 2.40  $g \cdot g^{-1}$  ore, which meant that the concentration of iron ions in the solution was very high. The high concentration of ferrous ions in the solution resulted in iron being trapped in the leach residues. The peak of the leaching residue after the reduction and leaching of ferrous sulfide was mainly silica, and there were almost no other impurity peaks, as shown in Figure 5b. This shows that the leaching of pyrolusite was relatively complete, indicating that most of the iron in the ore sample was also leached into the solution. The high silicon and low impurity characteristics of the leaching residue provided the possibility of being used as a raw material for ceramics or glass [26].

To further determine the composition, EDS spectra were then performed on representative areas of the pyrolusite and the two leaching residues, as shown in Figure 6. It was observed that after reductive leaching, the manganese in the minerals was significantly reduced, indicating that the manganese was fully leached. The iron content in the manganese ore, which was reduced by ferrous sulfate, decreased slightly, which may be because the reducing agent ferrous sulfate brought too many iron ions, and inhibited the leaching of iron in the manganese ore. The overall change trend of the remaining elements was small. The iron content of the manganese ore reduced by ferrous sulfide showed a more pronounced reduction, demonstrating that a significant portion of the iron in the ore sample was also leached into the solution [27,28].



**Figure 5.** XRD analyses of (**a**) leaching residue using ferrous sulfate as reducing agent and (**b**) leaching residue using ferrous sulfide as reducing agent.



**Figure 6.** The EDS spectra of the representative area of (**a**) low-grade pyrolusite and leaching residues with (**b**) ferrous sulfate or (**c**) ferrous sulfide as reducing agent.

### 3.2. Removal of Impurities by Sodium Sulfide

### 3.2.1. Chemical Analysis of Solution

To address the problem that it was hard to remove high-concentration iron ions from the leaching solution, the iron removal rules of sodium hydroxide and sodium sulfide were studied. Sodium hydroxide aqueous solution and sodium sulfide were added to the leaching solution and left to hold for 1 h. It was discovered that when the pH of the leaching solution was adjusted to 4 with an aqueous sodium hydroxide solution, the leaching solution was reddish-brown gelatinous, making it viscous and unfilterable, as shown in Figure 7a. In stark contrast to this, a black precipitate formed after the addition of sodium sulfide, and after holding, the precipitate was settled to form a clear two-phase. The principle of removing iron ions by sulfide precipitation was that the solubility of FeS was much lower than that of manganese sulfide (the pKsp values of ferrous sulfide and manganese sulfide are 17.20 and 12.60 at 25 °C, respectively), as shown in Figure 7b and Equation (5) [29]. Regulating the dosage of sodium sulfide added could selectively precipitate ferrous ions and other impurity metal ions without excessive loss of manganese ions [30–33]. As shown in Equations (6)–(9), there were two processes in the reaction of sodium sulfide precipitation, namely an iron ions-redox reaction and a precipitation reaction. When sodium sulfide was added to the ferric sulfate solution, a redox reaction occurred only when Fe<sup>3+</sup> was excessive. Fe<sup>3+</sup> was reduced to Fe<sup>2+</sup> by S<sup>2-</sup> in aqueous medium. Fe<sup>2+</sup> then precipitated promptly with S<sup>2-</sup> in solution [34], as shown in Figure 7c. The consumption of Fe<sup>2+</sup> in solution further promoted the redox reaction. All Fe<sup>3+</sup> was reduced to Fe<sup>2+</sup> when the added sodium sulfide reaches a certain dosage. We proceeded to add sodium sulfide, S<sup>2-</sup>, and Fe<sup>2+</sup>, which reacted to form FeS precipitate (Equation (7)). FeS<sub>2</sub> is formed based on the reaction between Fe<sup>2+</sup>, FeS, S, and H<sub>2</sub>S, as shown in Equations (8)–(10) [35–38].

$$M^{2+}(aq) + S^{2-}(aq) = MS(s)$$
(5)

$$2Fe^{3+}(aq) + S^{2-}(aq) = 2Fe^{2+}(aq) + S(s)$$
(6)

$$Fe^{2+}(aq) + S^{2-}(aq) = FeS(s)$$
 (7)

$$FeS(s) + S(s) = FeS_2(s)$$
(8)

$$S^{2-}(aq) + 2H^+ \rightleftharpoons H_2S(aq) \tag{9}$$

$$FeS(s) + H_2S(aq) = FeS_2(s) + H_2(g)$$
 (10)



**Figure 7.** (a) Effect of  $S^{2-}$  concentration in solution on the precipitation of metal ions (pS =  $-lg[c(S^{2-})]$ , pM =  $-lg[c(M^{n+})]$ ). (b) Comparison of precipitation effect of sodium hydroxide and sodium sulfide. (c) Fe-S-H<sub>2</sub>O system at 80 °C.

#### 3.2.2. Effect of Sodium Sulfide Dosage on Iron Precipitation Efficiency

Under the conditions of a temperature of 80  $^{\circ}$ C, reaction time of 60 min, initial pH of 1.56, and holding time of 5 h, the effect of sodium sulfide dosage on the precipitation of manganese and iron in the simulated solution was investigated. The dosage of sodium sulfide refers to the molar ratio of sodium sulfide to iron ions in the solution. The precipitation efficiencies of both manganese and iron increased with the increase of the dosage of sodium sulfide, as shown in Figure 8a. The precipitation efficiencies of manganese and iron were very low when the dosage of sodium sulfide was less than 0.60 mol $\cdot$ mol $^{-1}$  iron. The initially added sodium sulfide was used to reduce  $Fe^{3+}$  to  $Fe^{2+}$ , without producing iron sulfide precipitate, so the initial iron and manganese precipitation efficiency was 0. The sodium sulfide reaction produced sulfide precipitate after all Fe<sup>3+</sup> had been reduced. When the dosage was less than  $1.50 \text{ mol} \cdot \text{mol}^{-1}$  iron, the iron precipitation efficiency increased sharply and linearly with the increase of sodium sulfide dosage. Additionally, the precipitation efficiency of manganese was very small, indicating that the added sodium sulfide mostly precipitated the iron. Iron was completely precipitated when the dosage of sodium sulfide was greater than 1.80. However, excessive sodium sulfide would lead to a sharp increase in the precipitation efficiency of manganese, resulting in the loss of manganese in the leaching solution and the waste of sodium sulfide. To ensure high iron removal efficiency and low manganese loss efficiency, the dosage of sodium sulfide was selected as  $1.50 \text{ mol} \cdot \text{mol}^{-1}$  iron, and the iron precipitation efficiency was 91.57% and the manganese precipitation efficiency was 5.12%.



**Figure 8.** Effect of (**a**) sodium sulfide to iron ratio and (**b**) temperature on the precipitation of impurity ions by sodium sulfide.

## 3.2.3. Effect of Temperature on Iron Precipitation Efficiency

It can be seen from Figure 8b that with the increase of temperature, the precipitation efficiency of iron increased gradually, and the precipitation efficiency of manganese decreased slowly. When the temperature was 40 °C, the iron precipitation efficiency was 79.97%, and the manganese precipitation efficiency was 12.86%. The iron precipitation efficiency increased to 94.09%, and the manganese precipitation efficiency decreased to 3.14% at 90 °C. A high temperature promoted the direct reaction of Fe<sup>3+</sup> and S<sup>2-</sup> to form ferrous sulfide and ferrous disulfide, which led to the reduction of S<sup>2-</sup> in solution. Additionally, the amount of S<sup>2-</sup> that precipitated with Mn<sup>2+</sup> was smaller, resulting in a decrease in the precipitation efficiency of Mn. The precipitation efficiencies of manganese and iron tended to be stable when the temperature reached 80 °C. Considering the reduction of energy consumption, the reaction temperature was selected to be 80 °C.

#### 3.2.4. Effect of Reaction Time on Iron Precipitation Efficiency

Under the above optimal conditions, the effect of reaction time on the precipitation efficiencies of manganese and iron was investigated, as shown in Figure 9a. With the increase of reaction time, the iron and manganese precipitation efficiencies gradually increased and decreased, respectively. After 10 min of reaction, the precipitation efficiencies of manganese and iron were 8.65% and 85.09%, respectively. After 60 min, the precipitation efficiency of manganese decreased to 5.04%, and the precipitation efficiency of iron increased to 92.67%. The manganese precipitation efficiency decreased slightly during this process. After the addition of sodium sulfide, there was a large dosage of S<sup>2–</sup> in the solution, and more MnS precipitates were rapidly formed in a short time. With the increase of reaction time, part of S<sup>2–</sup> was consumed by Fe<sup>3+</sup> oxidation, and then Fe<sup>2+</sup> and S<sup>2–</sup> reacted to form a ferrous sulfide precipitate with a smaller solubility product and consumed a large dosage of S<sup>2–</sup>. This caused the dissociation equilibrium of MnS precipitate to shift to the right, Mn<sup>2+</sup> was released again, and the Mn precipitation efficiency decreased. The reaction basically reached equilibrium after 60 min, and the concentration of each component did not change.



Figure 9. Effect of (a) reaction time and (b) pH on the precipitation of impurity ions by sodium sulfide.

3.2.5. Effect of pH on Iron Precipitation Efficiency

The effect of solution pH on the precipitation efficiencies of manganese and iron is shown in Figure 9b. The iron precipitation efficiency first increased rapidly and then slowly with the increase of solution pH, while the manganese precipitation first increased slightly and then stabilized. When the pH was very low, a small dosage of black precipitate and a large dosage of yellow precipitate appeared in the solution after the reaction was completed. At this time, the concentration of H<sup>+</sup> in the solution was high, and the combination of H<sup>+</sup> and S<sup>2-</sup> caused the dissociation equilibrium of H<sub>2</sub>S to shift to the left, resulting in the concentration of hydrogen sulfide exceeding the saturation concentration. The hydrogen sulfide gas escaped, resulting in the loss of S<sup>2-</sup> and a small dosage of FeS precipitates, so the iron precipitation efficiency was not efficient. Meanwhile, a large dosage of yellow precipitates in the solution was obviously observed, which was the simple substance of S. As the pH increased, the amount of S<sup>2-</sup> in the solution increased and more black precipitates were formed. After holding for a while, a black precipitate settled to the bottom.

#### 3.3. Reductive Leaching of Low-Grade Pyrolusite Using Precipitate

#### 3.3.1. Characterization of Precipitate

After the reaction was completed, the effect of holding time on the precipitation efficiency of iron and manganese was further investigated, as shown in Figure S2. The precipitation of iron ions ceased to increase and the upper solution was relatively clear after 30 min of holding time. Impurity removal experiments were carried out on the leaching solution of pyrolusite under the above optimum conditions. The chemical composition of the precipitate obtained is listed in Table 2. It was found that the main components of the precipitate were iron and sulfur, accounting for 33.48% and 29.49%, respectively. The manganese content was less at 0.87%, which shows that a small amount of manganese was also involved in the precipitation reaction, consistent with the results in Figure 7, and a small dosage of manganese also participated in the precipitation. The contents

of Al, Ni, and Zn were 4.85%, 0.33%, and 0.22%, indicating that the impurity metal ions in the solution were also removed by precipitation. The oxygen contented to be 28.50%, which may be caused by the oxidation of part of the ferrous sulfide in the air during the drying and grinding of the precipitate. It was observed that the main components of the precipitate were iron and sulfur, consistent with the results in Tables 1 and 2. As shown in Figure 10, iron mainly existed in the form of ferrous disulfide, and sulfur existed in the form of elemental sulfur [39]. The presence of ferrous disulfide provided the possibility for precipitate as a reducing agent for pyrolusite.

Element	Mn	Fe	Al	K	Ca	Ni	Zn	0	S	Si	Others
Content	0.87	33.48	4.85	0.02	0.01	0.33	0.22	28.5	29.49	0.72	1.51

Table 2. The chemical composition (wt.%) of the precipitate.



**Figure 10.** (**a**) XRD analysis, (**b**) EDS spectrum, (**c**) SEM image, and (**d**) particle size distribution of precipitate (D: particle diameter).

The particle size distribution of the precipitate is shown in Figure 10d, and it can be observed that the particle size of the precipitates ranged from 0.38 to 75.06  $\mu$ m. Half of the precipitated particles were smaller than 6.85 microns in size, and about 90% were smaller than 34.43 microns. The appearance of double peaks in the particle size distribution of the precipitates may be related to the composition of FeS<sub>2</sub> and S. Figure 10b,c show EDS spectrum of representative region and SEM image of the precipitate. The precipitate after drying was formed by the agglomeration of fine particles. It was observed that the precipitate was also inlaid with some large block particles, which may be caused by the method of solid–liquid separation and drying. The precipitate was mainly composed of Fe, S, and other heavy metal elements, as seen in Figure 10b, indicating that the impurities in the solution have been well removed, which is consistent with the experimental results. Meanwhile, the presence of Mn in the precipitate could be observed, which demonstrates that a small dosage of Mn was also co-precipitated when a better iron precipitation efficiency was achieved. The process of reductively leaching pyrolusite by precipitate could enrich the heavy metal impurities in the sediment, and Mn was also leached back into the solution.

#### 3.3.2. Reductive Leaching of Manganese Using Precipitate

The main component of the precipitate was ferrous disulfide, which had reducing properties, and thus the possibility of reductive leaching of low-grade pyrolusite by precipitation was investigated. As shown in Figure 11a, the precipitate was feasible for reductive leaching of manganese oxide ore. With the increase of the dosage of precipitate, the leaching efficiency of manganese increased, and the overall trend was similar to that of FeS reduction leaching. The leaching efficiency of manganese was 97.96% when the dosage of precipitate was 0.28 g·g<sup>-1</sup> ore, and the leaching efficiency did not change much when the dosage continued to increase. The precipitate used in the experiment was dried and ground, and part of the material was oxidized by air, resulting in a decrease in reducing equivalent, which is consistent with the high oxygen content in the precipitate. The heavy metals in the precipitate were enriched and recycled in the process of reduction and leaching. After the content reaches a certain value, the separation and recycling of heavy metals can be achieved.



**Figure 11.** Effect of (**a**) dosage of precipitation and (**b**) number of cycles on the leaching efficiency of pyrolusite.

To investigate the stability of the cycle process, cyclic leaching experiments were carried out in this study, as shown in Figure 11b. The reductive leaching experiments of pyrolusite were carried out using precipitate as the reductant under the optimum conditions described above, and the leaching efficiency of manganese was 97.89%. The iron in the leaching solution was then reduced and precipitated using sodium sulfide. The cyclic leaching of the next batch of pyrolusite was continued using the precipitate obtained. In the iron removal experiments, too large an addition of sodium sulfide would lead to the co-precipitation of manganese, so the precipitation efficiency of iron ions was kept at about 93%. To compensate for the loss of ferrous ions, ferrous sulfide of  $0.02 \text{ g} \cdot \text{g}^{-1}$  ore was addeed as a supplement to the reduction leaching of pyrolusite using precipitate. After five cycles, the leaching of manganese from the pyrolusite was still able to reach 97.06%, which demonstrated the reliability and stability of the cycle process.

#### 4. Conclusions

In this study, sodium sulfide was introduced to treat a high concentration of Fe(III) in the leaching solution after reductive leaching of manganese oxide ore by the common Fe(II) reductant, resulting in a green cyclic leaching process of low-grade pyrolusite. The employment of sodium sulfide leads to a reduction of Fe(III) to Fe(II) and provides  $S^{2-}$  to form a precipitate simultaneously. A total of 93.09% of the impurity iron in the leachate was recovered by precipitation. Additionally, the precipitate consisted mainly of reducible ferrous disulfide, which can be used in a new cycle of the reductive leaching process. Moreover, the leaching efficiency of the pyrolusite was still 97% even after five cycles, indicating the achievement of the cyclic leaching and the recycling of iron resources, which provides new ideas for the utilization of other oxide ores in hydrometallurgy.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/min13091191/s1, Figure S1: Effect of (a) temperature, (b) H<sub>2</sub>SO<sub>4</sub> to ore ratio, (c) time, and (d) liquid–solid on the leaching efficiency; Figure S2: Effect of holding time on the precipitation of impurity metal ions by sodium sulfide.

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