

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^{3+} can be reduced to Fe^{2+} by S^{2-} 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 $0.28 \text{ g}\cdot\text{g}^{-1}$ 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

Supporting Material for

2.3. Analytical Techniques

According to the national standard GB/T 1506-2016, manganese in low-grade pyrolusite and residue was determined by titration with ammonium iron (II) sulphate. 0.20 g of ore or residue was weighed and placed in a 250 mL conical flask. 5 mL hydrochloric acid was added and shaken well. Then 20 mL of phosphoric acid was added and shaken thoroughly. The solution in the conical flask was heated to a slight boil and 5 mL of nitric acid was added while still hot. The conical flask was shaken sufficiently to destroy the carbon and organic matter and then heated until a slight phosphoric acid fume was present (the liquid level was calm). The conical flask was shaken sufficiently to destroy the carbon and organic matter and then heated until a slight phosphoric acid fume was present (the liquid level was calm). Then it was removed and 2 mL of perchloric acid was added while shaking. Continue heating until the solution was calm to allow complete oxidation of the divalent manganese. The solution obtained was cooled to about 70°C , 50 mL of water was added while shaking, and then the conical flask was shaken well to dissolve the salts. The conical flask was cooled to room temperature by running water. The solution obtained was titrated to a light red colour with a solution of ammonium iron (II) sulphate. The solution was continued to titrate to a bright yellow endpoint after being added 2 drops of N-phenyl-o-aminobenzoic acid indicator solution. The manganese content was calculated from the volume of ammonium iron (II) sulphate solution consumed.

3.1. Reductive Leaching of Low-Grade Pyrolusite

3.1.3. Characterization of Minerals Before and After Leaching

The effect of temperature on manganese leaching was investigated under the experimental conditions of optimal reducing agent dosage. The effect of temperature on manganese leaching was shown in Figure S1a. The leaching efficiencies of manganese for both reducing agents increased with the increase of temperature. The leaching efficiency of manganese was less affected by temperature using ferrous sulfate as the reducing agent. The manganese leaching efficiency increased from 88.17% at 30°C to 94.45% at 90°C. The reduction leaching of ferrous sulfide was greatly affected by temperature. When the temperature increased from 30°C to 90°C, the manganese leaching efficiency increased from 78.43% to 97.23%. It can be seen that the reduction effect of Fe^{2+} on manganese ore is less affected by temperature, and the reduction effect of S^{2-} is greatly affected by temperature. This is because the reaction of S^{2-} and MnO_2 has a higher reaction energy barrier, so higher temperature is required to increase the number of activated molecules to promote the reaction. Taking into account comprehensively, 80°C and 90°C were selected as the optimum leaching temperatures for ferrous sulfate and ferrous sulfide reduced ores, respectively.

Under the same leaching experimental conditions, the effect of sulfuric acid dosage on manganese leaching was optimized. The effect of sulfuric acid dosage on manganese leaching efficiency was shown in Figure S1b. The dosage of sulfuric acid had little effect on the leaching efficiency of manganese using ferrous sulfate as a reducing agent, and the leaching efficiency of manganese fluctuated between 90% and 94%. When the dosage of sulfuric acid was less than $0.70 \text{ g} \cdot \text{g}^{-1}$ ore, the pulp was colloidal after the reaction, and the viscosity was very large, so that it was impossible to carry out suction filtration sampling. This was because under neutral or slightly acidic conditions, pyrolusite was reduced to a low-grade manganese. Meanwhile, Fe^{2+} was oxidized to Fe^{3+} , and formed $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})\text{SO}_4$ insoluble colloids, resulting in increased slurry viscosity and difficulty in solid–liquid separation. Moreover, insoluble colloids adhered to the surface of mineral particles, which hindered the reduction and leaching of manganese in the minerals. When ferrous sulfide was used as reducing agent, with the increase of sulfuric acid dosage, manganese leaching first increased sharply, and then increased slowly. When the dosage of sulfuric acid was $1 \text{ g} \cdot \text{g}^{-1}$ ore, the leaching efficiency of manganese reached 94.29%. When no sulfuric acid was added, the manganese leaching efficiency was 0. The reason was that under alkaline conditions, the insoluble Mn (IV) in the ore could be reduced to soluble low-valent manganese such as $\text{Mn}(\text{OH})_2$ and Mn_3O_4 , which was consistent with the results in Figure 3. With the addition of sulfuric acid, it reacted with $\text{Mn}(\text{OH})_2$, and Mn^{2+} entered the solution. However, the excessive dosage of sulfuric acid would cause acid waste, and the acidity of the leachate was large, and the subsequent neutralization treatment would consume a large dosage of alkali. Comprehensive consideration, the choice of sulfuric acid dosage was $1.00 \text{ g} \cdot \text{g}^{-1}$ ore.

Under the above optimal conditions, the effect of leaching time on manganese leaching was investigated, as shown in Figure S1c. The manganese leaching efficiency first increased and then stabilized with the increase of leaching time. It had a high reaction efficiency using ferrous sulfate as a reducing agent to leaching pyrolusite, and the reaction could be completed in a short time. The leaching speed of using ferrous sulfide as reducing agent was slow, and the increase of manganese leaching efficiency was not fast. This was attributed to the good solubility of ferrous sulfate, which could quickly release Fe^{2+} , while FeS was insoluble in water, and the release of Fe^{2+} and S^{2-} needed to be carried out gradually with the redox reaction, thus limiting the speed of the whole reduction leaching. To ensure the full progress of the reaction, 30 min and 40 min were selected as the reduction leaching time of ferrous sulfate and ferrous sulfide.

Under the same experimental conditions as above, the effect of liquid–solid ratio ($6\text{--}16 \text{ mL} \cdot \text{g}^{-1}$) on manganese leaching was investigated as shown in Figure S1d. When ferrous sulfate was used as a reducing agent, the liquid–solid ratio could increase the leaching

efficiency of manganese to a certain extent, but the effect was relatively limited. Changing the liquid-solid ratio had little effect on the leaching efficiency of manganese using ferrous sulfide as a reducing agent. When the liquid-solid ratio was low, the viscosity of the pulp was high and filtration was difficult. However, the manganese concentration in the leachate was low when the liquid-solid ratio was high. The liquid-solid ratio was selected to be $10 \text{ mL}\cdot\text{g}^{-1}$, and the manganese ion concentration of the leaching solution was about $22 \text{ g}\cdot\text{L}^{-1}$.

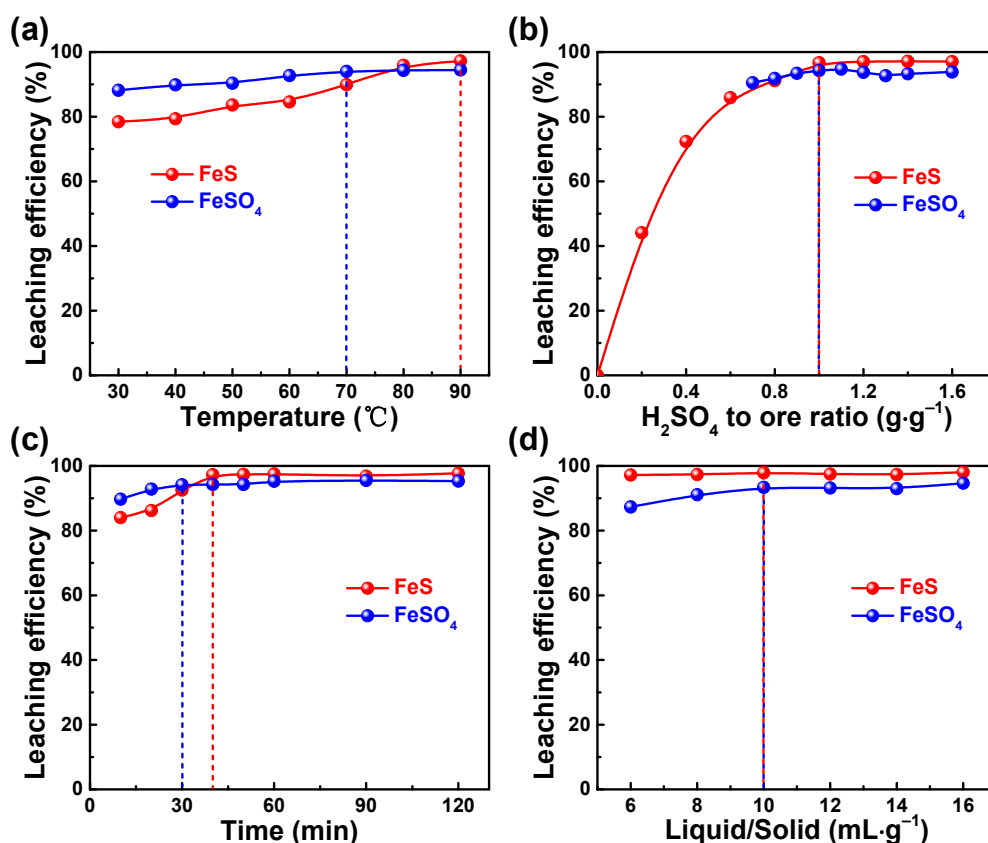


Figure S1. Effect of (a) temperature, (b) H_2SO_4 to ore ratio, (c) time, and (d) liquid-solid on the leaching efficiency.

3.2. Removal of Impurities by Sodium Sulfide

Effect of holding time on iron precipitation efficiency: Under the above optimal conditions, the effect of holding time on the precipitation efficiencies of manganese and iron was investigated, as shown in Figure S2. With the increase of holding time, the precipitation efficiency of iron did not change much, and the precipitation efficiency of manganese decreased slightly. After the reaction, the manganese precipitation efficiency was measured to be 11.76%. After 20 min, sedimentation of the precipitate was observed. The precipitation efficiency of manganese dropped to 5.80% after 30 min. During standing, the precipitate gradually agglomerated and slowly settled out of solution. The precipitation state became stable with the prolongation of the holding time, and the precipitation efficiency no longer changed. After 30 min, the sulfide in the solution basically settled completely and the upper layer solution was relatively clear.

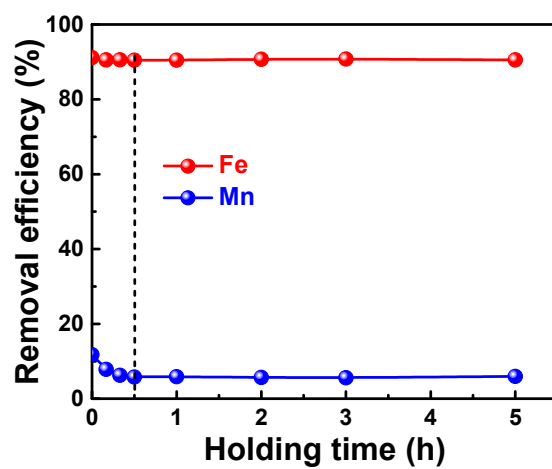


Figure S2. Effect of holding time on the precipitation of impurity metal ions by sodium sulfide.