

Process for Reduction Leaching Pyrolusite Using Hull

Zhang Tian^{1,2}, Wang Haifeng^{1,2*}, Wang Jiawei^{1,2}, Zhao Pingyuan^{1,2}

¹College of Materials and Metallurgy, Guizhou University, Guiyang 550025, China

²Research and Application Center of Mn-based Materials for Battery, Guizhou Province, China

*Corresponding author's E-mail: scofield.tian@foxmail.com

Abstract. In order to solve the problem of excessive accumulation of hull and leaching low-grade soft manganese ore, the reductive leaching of pyrolusite with hull by single factor experiment and orthogonal experiment were studied. The effects of leaching temperature, reductant quantity, sulfuric acid dosage and leaching time on the leaching rate of manganese were investigated. The results showed that the rate of manganese can reach over 95% when leaching temperature is 90°C, reducing agent dosage is 30g, amount of sulfuric acid is 40mL and leaching time is 5h.

1. Introduction

Manganese is a very important transition metal, which mainly existing in the form of manganese compounds in the nature, the vast majority of manganese ore is concentrated distributed in South Africa, former soviet, China, Gabon, Brazil, India and other countries^[1]. Manganese and manganese compounds are widely used in various industries such as iron and steel industry, chemical industry, building materials industry, electronic industry, light industry, etc. ^[2].

The soft manganese ore mainly contains MnO₂, where the manganese exists in the form of quadrivalence Mn. It was difficult to production leaching quadrivalence Mn directly by acid, therefore reducing quadrivalence Mn into manganous before leaching process is necessary. Leaching process can be divided into the following two categories^[3] according to process of pyrite reduction leaching: roasting-reduction leaching and direct reduction leaching method. Roasting-reduction method has been unable to meet current industrial requirement because of complex processes, high energy consumption and serious environmental pollution, while direct reduction leaching method has become the main research focus due to simple process and high recovery rate ^[4,5].

Considered organic reductants are expensive generally, most of the industrial use of inorganic as a reducing agent ^[6,7,8]. Owing to high cost and severe pollution, choosing a kind of environment-friendly, high leaching rate, cheaper reducing agents are of great significance.

2. Experimental

2.1. Experimental materials

The ore samples used in the experiment was derived from Guiyang Import Australia Manganese Company, and the hull was taken from the surrounding farm, the main mineral element analysis of ore samples and chemical composition of hull were shown in Table 1 and Table 2 separately.



Table 1. The main element contents of Pyrolusite (wt %)

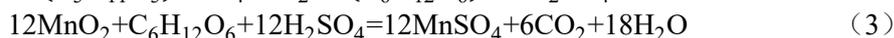
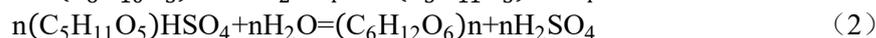
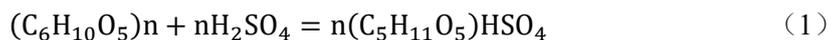
Mn	Fe	Al	Ba	Mg	Others
48.5	2.8	0.6	0.3	0.2	trace

Table 2. The chemical composition of hull (wt %)

chemical composition	Crude fiber	Protein	Fat	Ash	Others
content	35~40	15~22	12~23	7~12	3~8

2.2. Experimental principle

Mn in the pyrolusite is mainly in the form of manganese dioxide and is oxidized in the acidic medium. Therefore, it is difficult to be directly reduced by sulfuric acid, and it is necessary to be dissolved in sulfuric acid by the presence of reducing agent or by reduction roasting to MnO. The gluten is rich in crude fiber and other reducing ingredients, in concentrated sulfuric acid conditions will resolve into glucose, oligosaccharides and monosaccharides, and redox reaction takes place with oxidizing MnO₂ in acidic solution, reducing quadrivalence Mn into manganous. The response of the whole leaching process is:



The general response equation is:



2.3. Experimental process

50 g of manganese ore powder having a particle size of less than 109 μ m, and a liquid-solid mass ratio of 5 ml/g and a stirring strength of 200 r/min. Test procedure: 250 ml of sulfuric acid-water solution was placed in a 1000 ml beaker and stirred and heated Adding the gluten ore reducing agent with particle size less than 120 μ m. When the temperature reaches the reaction setting value, the soft manganese ore is slowly added. After setting the reaction time, the leaching solution is filtered and the residue is filtered and the manganese content is calculated.

3. Results and discussion

3.1 Effect of leaching temperature on leaching rate of manganese

Leaching temperature on the manganese leaching rate under the conditions of reductant quantity 30g, sulfuric acid dosage 40mL and leaching time 5h of the results shown in Figure 1. Leaching rate of manganese increases with the temperature increasing from 60°C to 90°C with the increase of temperature, which indicates that the leaching rate of manganese is about 27%, which indicates the effect of temperature on leaching rate when the temperature exceeds 90°C, the leaching rate is only about 1%, and the leaching curve tends to be gentle. From the thermodynamic point of view, the leaching reaction belongs to the exothermic reaction. With the increase of the temperature, the equilibrium constant of the reaction is bigger, the Gibbs free energy is more negative, the greater the trend of the spontaneous reaction; According to the kinetic principle, With the increase of temperature, the viscosity of the solution decreases, accelerates the migration rate of ions, solvent molecules and solid particles, increases the probability of collision between molecules, and facilitates the diffusion of leaching agent to unresponsive nuclear, thus increasing the leaching rate of manganese. Taking into account leaching temperature of 90°C was more appropriate.

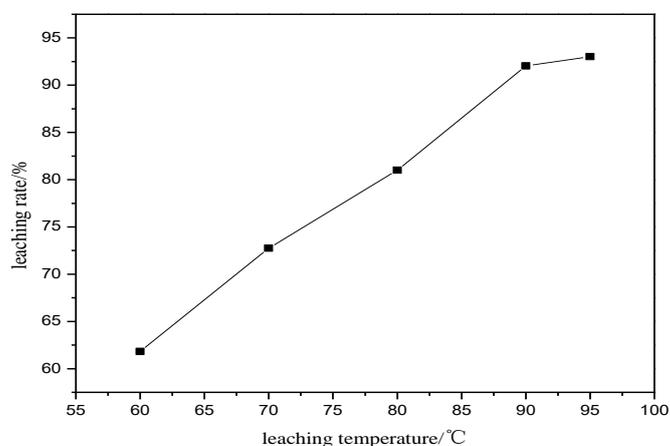


Figure 1. Effect of leaching temperature on leaching rate

3.2 Effect of reductant quantity on leaching rate

Reductant quantity on the manganese leaching rate under the conditions of leaching temperature 90°C, the amount of sulfuric acid 40mL and leaching time 5h of the results shown in Figure 2. The leaching rate of manganese increased with the increase of the amount of reducing agent. When the amount of reducing agent increased from 15g to 30g, the leaching rate of manganese increased by about 24%, and the increase rate was higher. If the amount of reducing agent is increased, the leaching curve tends to be gentle. From the thermodynamic point of view, with the increase of reducing agent, the concentration of reactants increased, to promote the reaction to the positive direction, the probability of reduction of quadrivalence Mn increased, increasing the leaching rate of manganese. When the leaching rate of manganese is about 90%, there is only a small part of the non-leaching of MnO₂ in the solution, and the probability of the remaining reducing agent entering the unresponsive nuclear is small and the reaction basically reaches the end. Taking into account the amount of reducing agent was more suitable for 30g.

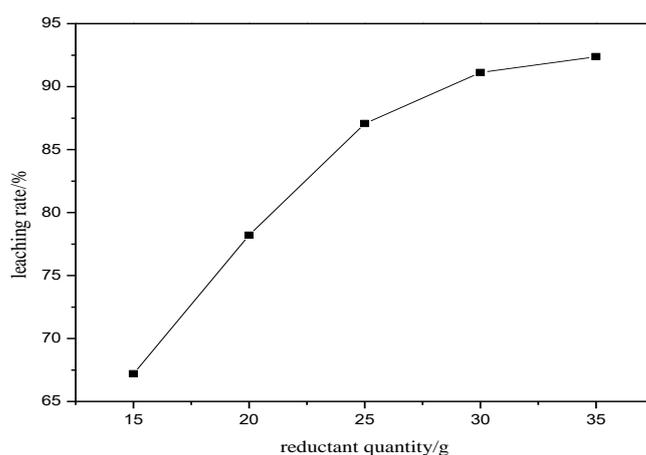


Figure 2. Effect of reductant quantity on leaching rate

3.3 Effect of sulfuric acid dosage on leaching rate

Leaching rate under the conditions of leaching temperature 90°C, reducing agent dosage 30g and leaching time 5h of the results shown in Figure 3. The leaching rate of manganese increased from

73.29% to 91.33% when the amount of sulfuric acid was 25 ~ 45mL. When the sulfuric acid dosage exceeded to 45mL, the leaching curve appeared inflection point and in the gentle. From the thermodynamic point of view, the increase in the amount of sulfuric acid to promote the hydrolysis of crude fiber in the husk, increase the content of reducing sugar, but also to meet the redox reaction process required acid content, is conducive to the reaction to the positive direction. From the dynamic point of view, increasing sulfuric acid concentration was beneficial to increase the diffusion coefficient of the reducing agent in the solution, so as to improve the chemical reaction rate. However, with the increasing amount of sulfuric acid, more than the amount of acid required for the reaction, the acid concentration of the solution is too high, which not only caused the waste of resources, but also brought out the impurity element to react with the acid into the leaching solution. Taking into account the determination of sulfuric acid dosage of 40mL was more appropriate.

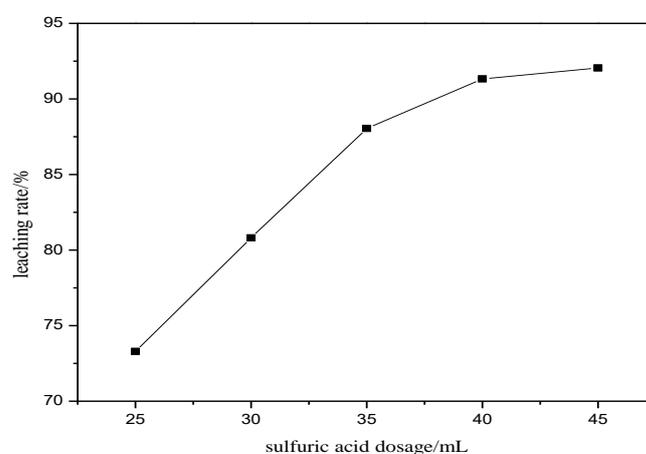


Figure 3. Effect of sulfuric acid dosage on leaching rate

3.4 Effect of leaching time on leaching rate

Leaching rate under the conditions of leaching temperature 90°C, reducing agent dosage 30g and amount of sulfuric acid 40mL of the results shown in Figure 4. When the leaching time was more than 5h, the leaching rate of manganese increased gradually. The leaching rate of manganese increased from 75.44% to 90.28% when the leaching time ranged from 2h to 5h. In the view of diffusion kinetics, the reaction rate is proportional to the reaction time. The longer leaching time is, the faster leaching rate of manganese is. In addition, the longer the reaction time, the greater probability that the leaching agent diffuses into the unresponsive nuclear is greater and the reaction is more complete, and the metal impurities in the ore participated in the reaction leaching solution, consumed acid content and reduced ion activity and activation energy. When the leaching time increased to 5h, the concentration of each component involved in the reaction was low, the probability of collision between molecules was relatively small, the reaction was basically gentle, close to the end point, continued to increase the reaction time, not only the leaching rate of manganese less impact, but also increased energy consumption. Taking into account, determined the leaching time 5h was more appropriate.

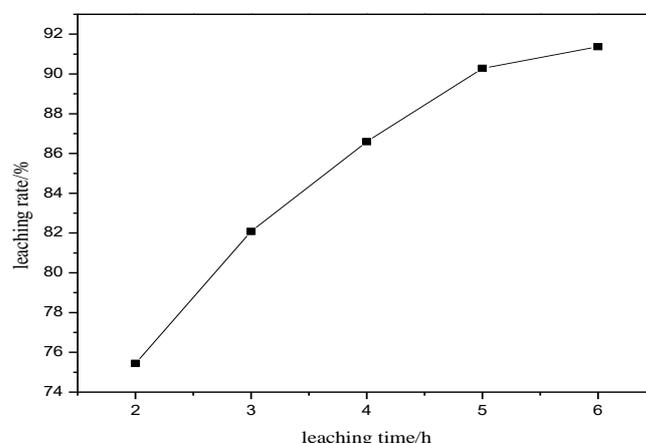


Figure 4. Effect of leaching time on leaching rate

3.5 Orthogonal experiment

The effects of leaching temperature, reductant quantity, amount of sulfuric acid and leaching time on the leaching rate of manganese were investigated. The experimental results were shown in Table 3 by L_9 (3^4) orthogonal design.

Table 3. Results of orthogonal experiment

Number	A Leaching temperature/ °C	B Reductant quantity/g	C Sulfuric acid dosage/mL	D Leaching time/h	Leaching rate of manganese /%
1	80	20	30	3	68.58
2	80	25	35	4	73.93
3	80	30	40	5	91.09
4	90	20	35	5	89.23
5	90	25	40	3	88.77
6	90	30	30	4	89.31
7	95	20	40	4	89.19
8	95	25	35	5	87.43
9	95	30	30	3	86.61
<i>K1</i>	77.87	82.33	81.50	81.32	
<i>K2</i>	89.10	83.38	83.53	84.14	
<i>K3</i>	87.74	89.01	89.68	89.25	
<i>R</i>	11.23	6.68	8.18	7.93	

From the above table, we can see that the effect of the factors on the leaching rate of manganese can be obtained, that is, the leaching temperature > the amount of sulfuric acid > leaching time > the amount of reducing agent. The optimum extraction conditions were as follows: A2B3C3D3, extraction temperature 90°C, sulfuric acid dosage 40mL, reducing agent dosage 30g, leaching time 5h. The leaching rate of manganese was 95.37%.

4. Conclusion

It is feasible to reduce the leaching of pyrolusite under the condition of concentrated sulfuric acid. It is concluded that the leaching of manganese is more than 95% under the optimum process conditions. The process of low energy consumption, high leaching rate, green, with good research value.

1) The leaching temperature of the soft manganese ore is mainly affected by the factors such as the amount of sulfuric acid, the amount of reducing agent, the amount of sulfuric acid and the leaching time, and the leaching temperature has the greatest effect on it.

2) The optimum extraction conditions were as follows: leaching temperature 90°C, sulfuric acid dosage 40mL, reducing agent dosage 30g, leaching time 5h.

Acknowledgment

Fund project: Guizhou Province scientific cooperation project project (Qianke together LH word [2015] 7656).

References

- [1]Tan Zhuzhong *Manganese Metallurgy* [M]. Central South University Press, 2004. (In Chinese)
- [2]Li Yanling *Iron rich rhodochrosite preparation of high purity manganese carbonate experiment* [D]. Guizhou University, 2014. (In Chinese)
- [3]Chang Wei Study on dynamics of low-grade soft manganese ore reduction leaching process [D]. Central South University, 2014. (In Chinese)
- [4]Fu Lipan, Zhang Yimin, Liu Tao, Huang Jing, Yang Xiao, Zhao Jie *Effect of Additive DN on Roasting Effect of Vanadium from Stone Coal* [J]. Metallurgical Engineering, 2013, (01): 65-68. [J]. Metallurgical Engineering, 2013, (01): 65-68. (In Chinese)
- [5]Wu Haiying, Dai Zilin, Gu Lijun, Li Guiying *Study on the effect of Fluoride Baptist on Sulfuric Acid Leaching and Extraction of Vanadium from Vanadium Ore* [J]. Metallurgical Engineering, 2010, (02): 83-84 + 88. (In Chinese)
- [6]Zhu Guoxiang *New technology of direct leaching of pyrolusite* [J]. Nonferrous Metals (smelting part), 1991, 03: 22-24. (In Chinese)
- [7]Naik P K, Sukla L B, Das S C. *Aqueous SO₂, leaching studies on Nishikhal manganese ore through factorial experiment* [J]. Hydrometallurgy, 2000, 54(s2-3):217-228.
- [8]Shi Wen, Yan Wenbin, Xiong Shaofeng *Study on the Technology of Reducing Low Grade Soft Manganese Ore by Iron Flake* [J]. Metallurgical Engineering, 2012, (01): 84-86. (In Chinese)