Preparation of High Purity Manganese Sulphate from Low-Grade Rhodochrosite

Zefang ChenLi, Laijun Ma, Lei Mao and Fang Lian*

School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, China

Abstract: In our work, the preparation technique of high pure manganese sulfate directly from low-grade rhodochrosite ore (MnCO_3) was studied and improved intensively, including the effective leaching process and the short purifying process. Based on the same ion effect, the repeated leaching of rhodochrosite with sulfuric acid is proposed to improve the solubility of Mn^{2+} and inhibit the dissolution of the impurities Ca^{2+} and Mg^{2+} . Moreover, the repeated leaching process could make full use of rhodochrosite and lower the dosage of sulfuric acid raw material. With the aid of theoretical calculation, Ba(OH)_2 was chose to adjust the pH value of manganese sulfate solution, and BaF_2 to remove Ca^{2+} and Mg^{2+} completely in the process of purifying. The results demonstrate that the extraction ratio and the recovery ratio of manganese reached 94.3% and 92.7%, respectively, which shows the prospect of industrial application. In manganese sulfate production, the heavy metal impurities have been decreased to less than 1ppm. Moreover, the content of calcium, magnesium and sodium has been decreased to less than 20ppm, which meets the standards of high pure reagent for energy and electronic materials. Our study enlightens an approach to the sustainable application of low-grade rhodochrosite.

Keywords: low-grade rhodochrosite; effective leaching; short purifying process; recovery ratio; high purity

1. Introduction

Low-grade manganese carbonate ores ($\leq 14\%$) becomes gradually the main resources for exploitation and applications in China according to national mineral resources survey (Tan et al 2004 and Singh et al 2017). Therefore, the electrolytic deposition technique of rhodochrosite faces great challenges including low electrolysis efficiency, high-resource input and high-pollution discharge (Fu et al 2010, Michelis et al 2009, Zhang et al 2013). Recently, more and more amount of manganese series with high or super high purity such as MnSO_4 , MnO_2 , Mn_3O_4 and MnO is demanded with the development of energy and electronic materials. Due to low-grade ores containing multiple elements such as iron, silicon, calcium and magnesium, conventional preparation of manganese sulphate with high purity from electrolytic product is characterized by long production-cycle and high-energy consumption (Subrat et al 2011, Mpho et al 2013). By contrast, hydrometallurgical method combined with thermal decomposition, hydrothermal synthesis and sol-gel processes has been widely studied because of its high efficiency, low consumption and low cost (Chen et al 2008). But the key problem in direct preparation of manganese series form low-grade rhodochrosite is to remove completely the multiple impurities such as iron, silicon, calcium and magnesium (Liu et al 2014). So it is urgent to develop a sustainable alternative approach with character of short process, high efficiency and environmental friendly.

In our work, the preparation technique of manganese sulphate with high purity directly from low-grade

rhodochrosite ore (Mn grade of concentration is 13.86%) was studied and improved intensively. In detail, the leaching process was optimized firstly using orthogonal experiment, where the effects of solid-liquid ratio, temperature and duration on the leaching rate of manganese were discussed under certain conditions of mineral-to-acid ratio (1:0.7) and stirring speed (300 r/min). More importantly, the repeated leaching of rhodochrosite with sulfuric acid is proposed herein to improve the solubility of Mn^{2+} and inhibit the dissolution of the impurities Ca^{2+} and Mg^{2+} , simultaneously. Additionally, the short purifying process is also explored with the aid of theoretical calculation. The recovery ratio of manganese and removal ratio of the impurity were evaluated via chemical titration and ICP analysis, respectively. Furthermore, comparison between conventional preparation technique from electrolytic manganese and a sustainable approach directly from low-grade rhodochrosite have also been done herein.

2. Experimental

The rhodochrosite samples were provided by BaoJing Tianhe Manganese Industry Company, Hunan province, China. And the samples were ground to powder with ≤ 2 mm in diameter.

Firstly, the leaching process was optimized using orthogonal experiment. 10g rhodochrosite powder, 3.6ml sulfuric acid solution (98%) and deionized water were added into a 150 ml conical flask with solid-liquid ratio of 1:5–1:7 in weight and mixed for 1–3 h at 75–95°C under vigorous stirring (300 r/min). Then the residues in the flask were filtered, washed and dried. Finally, the optimal

* Corresponding Author: F. Lian, lianfang@mater.ustb.edu.cn, phone: +86 10-82377985

parameters were determined by employing the leaching rate of manganese as the primary standard.

Then based on the optimal process parameters, the repeated leaching approach for rhodochrosite is performed herein. In detail, 10g rhodochrosite powder, Xml sulfuric acid solution (98%) and deionized water were added into the initial leaching solution with solid-liquid ratio of 1:7 in weight and stirred for 2 h at 85°C (stirring speed 300 r/min). Then the residues were filtered to get the first repeated leaching solution. And the aforementioned procedures were repeated 0-4 times, so the total leaching times disperse in the range of 1-5. Moreover, the amount of sulfuric acid solution for each addition was calculated as the following formula:

$$X=0.0779a-ab/38.25 \quad (1)$$

where X is the volume of sulfuric acid solution (ml), a is the total volume of the leaching solution (ml) and b is the concentration of H^+ in the leaching solution (mol/l).

In the purification process, the coarse manganese sulphate solution was adjusted to pH=4.0 using $Ba(OH)_2$ solution. After standing for 24h, the precipitate was filtered. Subsequently, BaF_2 powder was introduced in the solution and stirred at 25°C for 3h. Then the precipitate was separated and the filtrate was adjusted to pH=8.0 using $Ba(OH)_2$ solution. Finally, the precipitate was filtered repeatedly and pure $MnSO_4$ solution was expected to be obtained.

The mineral and chemical composition of the rhodochrosite samples was chemically analyzed via XRD and chemical titration, respectively. The recovery ratio of manganese was evaluated via chemical titration with ammonium ferrous sulfate. The concentration of impurities such as calcium and magnesium ions was determined by ICP analysis.

3. Results and Discussion

3.1 The composition of rhodochrosite samples

The chemical composition of rhodochrosite samples is listed in Table 1. And the concentration of manganese is only 13.86%, which is typical low-grade manganese carbonate ores. In addition, the rhodochrosite samples are mainly composed of $MnCO_3$, SiO_2 , $CaMg(CO_3)_2$, $FeSO_3$ and Al_2O_3 as shown in Figure 1.

3.2 The initial optimization of leaching process

The experiments for orthogonal analysis on leaching were performed, and the detail parameters are shown in Table 2. The maximum of the extraction ratio of Mn reaches 98.41%. Moreover, R is calculated to represent the influence of each factor on the leaching efficiency. The results demonstrate that the liquid:solid ratio has the greatest effect on the leaching efficiency, followed by temperature and duration.

Table 1. The major chemical composition of the rhodochrosite samples (% by weight).

Mn	Ca	K	Mg	Ni	Zn	Na	Fe	Si
13.86	3.80	1.80	1.32	<0.005	0.023	0.86	3.10	16.63

Table 2. The leaching process parameter for the orthogonal experiments.

Number	Liquid-to-solid ratio	Temperature /°C	Duration /h	Leaching efficiency /%
S1	5:1	75	1	80.25
S2	5:1	85	2	90.48
S3	5:1	95	3	88.89
S4	6:1	75	2	88.89
S5	6:1	85	3	90.48
S6	6:1	95	1	87.30
S7	7:1	75	3	95.24
S8	7:1	85	1	95.24
S9	7:1	95	2	98.41
Mean value 1	86.540	88.127	87.597	-
Mean value 2	88.890	92.067	92.593	-
Mean value 3	96.297	91.533	91.007	-
Range	9.757	3.940	4.996	

Table 3. Variance analysis of orthogonal experiment.

Variance originates	Sum of squares	Freedom degree	Fratio	F crit
liquid-solid ratio	155.574	2	2.078	5.140
temperature	27.413	2	0.366	5.140
Duration	41.607	2	0.556	5.140

Figure 1. XRD results of the manganese ore.

Furthermore, the variance analysis is shown in Table 3. Fratio value is far less than the critical one, indicating that the experimental error is within the allowable range. It is important to note that Fratio value of liquid:solid ratio was obviously higher than that of the other two factors, demonstrating the greatest effect of liquid:solid ratio among the considered three main factors and consistency with the range analysis. The optimal parameters including leaching temperature at 85°C, liquid-to-solid ratio of 7:1 and leaching duration of 2h are determined and adopted in the further studies.

3.3 The repeated leaching process

In the repeated leaching process, the accumulative content of impurity in the leaching solution and the extraction ratio of Mn were characterized by ICP. The standard deviation for the four parallel experiment results is below 0.73%, and the average concentration values are given in Table 4.

Table 4. The average value of ICP analysis of ionic concentration in the repeated leaching solution.

Total leaching times	1	2	3	4	5
Mn ²⁺ (g/L)	19.42	38.49	56.02	71.44	84.05
Ca ²⁺ (mg/L)	540.2	533.7	522.2	504.0	486.0
Mg ²⁺ (mg/L)	1027.3	1165.0	1277.6	1425.0	1687.2

Figure 2 demonstrates that the concentration of manganese is enhanced significantly and the accumulative content of Ca²⁺ is reduced obviously with the increase of the repeated leaching times. Though the absolute concentration of Mg²⁺ increases, its extraction ratio is reduced in the repeated leaching process. Based on the same ion effect, the repeated leaching approach not only improves the solubility of Mn²⁺ but also inhibits the dissolution of the impurities Ca²⁺ and Mg²⁺.

3.4 The purifying process

The main impurities in the coarse manganese sulphate solution obtained from the leaching process consist of Al³⁺, Fe²⁺, Fe³⁺, Mg²⁺, Ca²⁺ and a small quantity of heavy metals. Among them, a large proportion of Ca²⁺ ions could be precipitated with SO₄²⁻ and removed with insoluble silica. Moreover, iron and aluminum ions are both participate in hydrolysis at pH=3.0–8.0 and separated from the filtrate. Both Ca²⁺ and Mg²⁺ were removed by adding BaF₂ as the precipitant at pH=4.0. Finally, the heavy metals can be removed via adjusting pH=8.0 with Ba(OH)₂.

Figure 2. Effect of the leaching times on the ionic concentration.

Table 5. ICP analysis of the manganese sulfate solution.

Ca /ppm	Mg /ppm	Ni /ppm	Fe /ppm	Al /ppm	Na /ppm
2.599	15.82	0.187	0.083	0.006	15.82

According to ICP analysis of the manganese sulfate solution in Table 5, the heavy metal impurities such as Fe and Ni have been decreased to less than 1ppm, and the content of calcium, magnesium, sodium has been decreased to less than 20ppm, which meet standards of high pure reagent for energy and electronic materials. Mn content in the manganese sulfate solution is determined by titration with ammonium ferrous sulfate. The recovery ratio of manganese reaches 92.7%.

In compare with conventional technique from electrolytic manganese, the power consumption has been reduced to ≤ 2000 kWh/t(product) in our short-process approach. Moreover, comprehensive recovery rate of manganese increases significantly. As know, the quality of wastewater which occurred in the process of electrolytic deposition is complex, containing toxic substances and high content of ammonia/nitrogen. By contrast, the wastewater generated from our short-process approach shows low content of ammonia/nitrogen about 500 mg/t (product) and no toxic emissions. Our study contributes to the sustainable application of low-grade manganese ore.

4. Conclusions

A hydrometallurgical process including the effective leaching process and the short purifying process from low-grade rhodochrosite ore (13.86%) has been developed in the paper. The results demonstrate that the extraction ratio and the recovery ratio of manganese reach 94.3% and 92.7%, respectively.

According to the orthogonal experimental results, the optimal parameters of the leaching process are determined: mineral-to-acid ratio of 1:0.7, leaching temperature at 85°C, liquid-to-solid ratio at 7:1, and duration of 2h. The extraction ratio of Mn reaches more than 98%. Moreover, the concentration of manganese is accumulated in the repeated leaching solution, and simultaneously the extraction ratio of impurities of Ca^{2+} and Mg^{2+} is reduced significantly. The repeated leaching method provides an approach to the effective use of the low-grade rhodochrosite and the reduction of the wastewater discharge. In addition, BaF_2 is chose as precipitant to remove Ca^{2+} and Mg^{2+} completely. The process of purifying is combined with adjustment of the pH value of manganese sulfate solution

using $\text{Ba}(\text{OH})_2$, which contributes to a high removal rate of impurities and a short application process.

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