Engineering Chemistry
ISSN: 2813-6535, Vol. 1, pp 45-56
doi:10.4028/p-6oe21m

Submitted: 2022-12-28
Revised: 2023-01-14
Accepted: 2023-01-16
Online: 2023-03-30

Extraction Technology for Manganese Sulfate Solution Purification

Chenzhe Li[1,2,a], Hongyan Xie[1,2,3,b*], Huixin Jin[1,2,c]

[1]Guizhou University, College of Material and Metallurgy, Guiyang, China

[2]Guizhou Province Key Laboratory of Metallurgical Engineering and Process Energy Saving, Guiyang, China

[3]State Key Laboratory of Pressure Hydrometallurgical Technology of Associated Nonferrous Metal Resources, Kunming, China

[a]Chenzhe2022@163.com, *Corresponding author e-mail: [b]hyxie@gzu.edu.cn, [c]HuixinJin2022@163.com

Keywords: Manganese Sulfate, Removal Technology, Manganese Ion.

Abstract. Manganese sulfate is an important base manganese salt; nearly 80% of the world's manganese products are produced using manganese sulfate or manganese sulfate solution. Furthermore, manganese sulfate has many applications in industry and agriculture; thus, manganese sulfate solution impurity removal technology is important. This study aims to remove impurities from manganese sulfate solution -using complex low-grade manganese ore and manganese-rich fumes after pressure acid leaching to obtain a manganese sulfate solution, which is then purified through iron removal by oxidation neutralization; finally, the purified liquid is treated using extraction-back-extraction. We investigated the effects of various extraction parameters on the extraction rate of manganese, as well as the effects of various back-extraction parameters on the manganese back-extraction rate and manganese ion concentration in the back-extraction solution, and studied the extraction-back-extraction process. We found that the extraction and back-extraction rates of manganese could reach 95% and 96.9%, respectively, under optimal conditions.

Introduction

Manganese sulfate is a water-soluble salt [1]and an indispensable intermediate product in the production of other manganese oxides, electrolytic manganese products [2], lithium manganate cathode material [3], and manganese salts. Consequently, it plays an important role in manganese series products [4]. At present, China's manganese sulfate is primarily obtained by leaching manganese ore with sulfuric acid and then removing impurities, the purpose of impurity removal is to remove iron, calcium, magnesium and other heavy metals and other impurities [5]. However, there are few studies on the deep removal of iron, calcium, magnesium and heavy metals from manganese sulfate solutions [6-8], most of the studies focusing on the purification of some elements, such as the removal of nickel and cobalt using sulfides, the removal of calcium and magnesium using fluorides [9-10], and the extraction and separation of manganese from calcium, magnesium, potassium, sodium, etc. [11].

Depending on the type and content of impurity elements in a manganese sulfate solution, different impurity removal methods can be used, including flocculation precipitation, chemical precipitation, extraction or ion exchange methods, electrolysis, metal manganese replacement, and combinations of a variety of purification methods.

Among them, the chemical precipitation method [12]is relatively mature and the most widely used impurity removal method currently. However, when the precipitation reaction occurs, there may be mutual influence—that is, new compounds that exist stably in the solution may be formed between different ions, resulting in little to no precipitation or incomplete precipitation being achieved.

The solvent extraction method has the advantages of simple equipment, simple operation, the ease of realizing continuous, automatic control, and high recovery rates [13]. However, the extraction method usually extracts other impurity ions too, so that the removal of impurities is incomplete, making this method only suitable for the preliminary separation and purification of manganese sulfate. If the impurity ions in the solution are to be completely removed, other purification methods need to supplement the process.

The manganese replacement method [14] does not introduce other impurities into the solution, but manganese can only replace less active than its metal ions—that is, non-metallic impurities, such as silicon and phosphorus cannot be removed at all, making the removal of impurities insufficiently thorough.

The combined purification process combines chemical precipitation [15], electrolysis, and other techniques, which can generally obtain better results, but such combined methods are more complicated, inconvenient to operate, and more expensive.

The primary reasons for using the extraction-back-extraction technique to treat manganese sulfate solutions in this paper are as follows:

(1) Deep impurity removal from manganese sulfate solution. Although manganese sulfate solutions can be treated using several purification and impurity removal techniques—such as oxidation and concentration—a small quantity of metal impurities will remain in the purified solution, which will need to be removed. Because P204 is an acidic phosphorus extractant, it is also one of four types of extractant commonly used in China [16]. Its water solubility is small, its properties are stable, its extraction ability is strong, and its phase separation effects are good. Consequently, P204 was selected as the extractant for this study;

(2) Instead of using the traditional evaporation and concentration technique, a lower concentration of manganese sulfate solution was produced to reach the manganese ion concentration required by electrolytic manganese. Due to the large area, high energy consumption, and disturbing environmental pollution of the traditional evaporation and concentration technique, the extraction and back-extraction technology was adopted in this study to replace the previous evaporation and concentration process. As such, a concentration process for low-concentration manganese sulfate solution with low cost, low energy consumption, and environmentally friendly outcomes could be realized [17].

Instruments and Reagents

Instruments: Electronic balance, acidity meter, separatory funnel, Korn oscillator, beaker, measuring cylinder, dropper, pipette.

Reagents: P204, commercial kerosene, sulfuric acid, sodium hydroxide.

In this experiment, the extraction dope is the purification liquid for leaching manganese sulfate solutions under pressure. Since this solution is obtained after purification and impurity removal, the influence of impurities on the extraction rate of manganese in the extraction process can be ignored. The chemical composition of extraction dope is shown in Table 1. The process flow chart is shown in Fig. 1.

Table 1 The chemical composition of extraction dope.

Component	Mn	Fe	Al	Ca	Mg	Co	Ni	Cu	H_2SO_4
Content(g/L)	21.20	0.000387	0.00016	0.06	0.21	0.00023	0.00046	0.00007	0.46

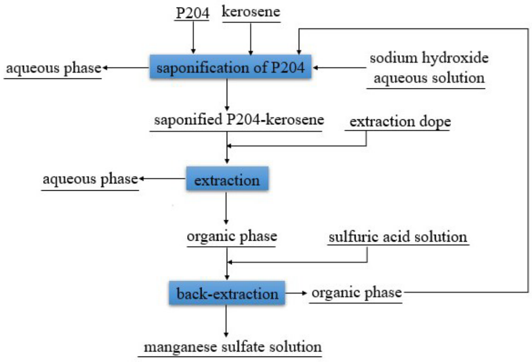

Fig. 1 (a) Process flow chart of extraction process of manganese sulfate purification solution

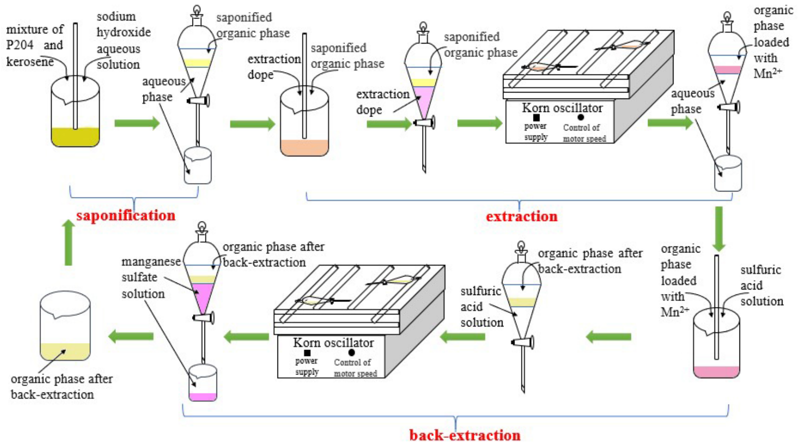

Fig.1 (b) Process flow chart of manganese sulfate purification liquid extraction equipment

Results: Extraction

Effect of Saponification Rate of P204 on Manganese Extraction

Different saponification rates of P204 had different influences on the extraction efficiency of manganese. Firstly, different volumes of P204 were saponified at different saponification rates. Next, a pressure leaching purification solution containing Mn^{2+} was extracted using P204 (with different saponification rates). The content of Mn^{2+} in the raffinate was determined and the manganese extraction rate was calculated. Other experimental conditions were as follows: the phase ratio (O/A) was 1:1, the concentration of P204 was 40%, the extraction temperature was 25℃, the extraction stage was level 1, and the extraction time was 5 min. The test results are shown in Fig. 2.

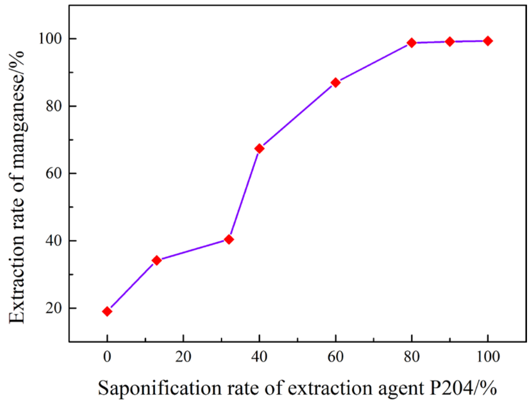

Fig. 2 Effect of the P204 saponification rate on the extraction of manganese

It can be seen from Fig. 2, that when the P204 saponification rate was 0%, the manganese extraction rate was only 19.05%. When the P204 saponification rate was 80%, the manganese extraction rate increased to 98.79%, after which there was no obvious increase in the manganese extraction rate as the P204 saponification rate increased further. The results shown that excellent manganese extraction could be obtained with a P204 saponification rate of 80%.

Determination of Saturation Capacity of P204 Extracted Manganese

Before the extraction experiment, the saturation capacity of manganese in its organic phase was measured, at different concentrations of P204. The experiment was conducted at 25℃, and the ratio of organic phase to the aqueous phase (O/A) was 1:1. The extraction was repeated several times until the concentration of manganese ions in the aqueous phase no longer changed [18]. The aqueous phase resulted in a purification solution for leaching manganese sulfate solution under pressure, the manganese ion concentration being 21.20g/L. The test results are shown in Fig. 3.

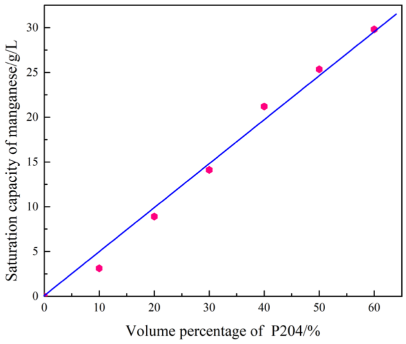

Fig. 3 Saturation capacity of manganese in the organic phase

Based on Fig. 3, the content of manganese in the organic phase increased linearly with P204 concentration—that is, each 10% concentration of P204 could extract 5 g/L of manganese—indicating that the extractant P204 could stabilize the complexation of manganese ions, that is, the number of molecules of P204 complex extractant per manganese ion was stable. However, it was found that phase separation in the manganese extraction test process was slow when the volume fraction of P204 was greater than 50%. Consequently, the volume fraction of P204 was set to be 20%–40% in the extraction test process in this study.

Effect of Extraction Phase Ratio (O/A) on Manganese Extraction

The extraction phase ratio (O/A) is the volume ratio of the P204-kerosene mixture to the extracted purified solution containing manganese via pressure leaching, and was used to examine the maximum extraction capacity of different extractant concentrations. We set the extraction phase ratio to be 1:2, 1:1, 2:1 and 3:1, respectively, to examine the effect of the extraction phase ratio on the extraction of manganese. Other experimental conditions were as follows: the concentration of P204 was 40%, the saponification rate was 80%, the extraction equilibrium time was 5 min, the extraction temperature was 25°C, and the extraction stage of was level 1. The test results are shown in Fig. 4.

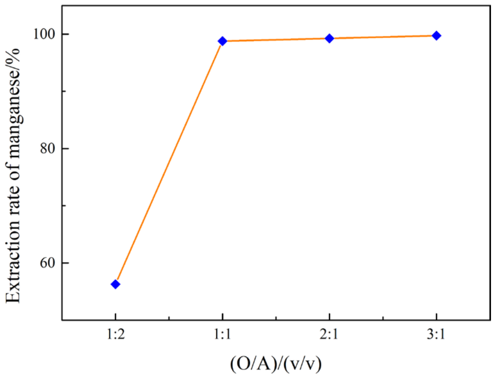

Fig. 4 Effect of extraction phase ratio on the extraction of manganese

It can be seen from the Fig. 4, that when the phase ratio of (O/A) was 1:2, the extraction rate of manganese was just 56.29%, as the manganese content in the purification solution exceeded the extraction capacity of the P204-kerosene solution. However, the extraction rate reached more than 98% when the extraction phase ratio was more than 1:1, although the extraction efficiency was not significantly increased by further increases in the extraction phase ratio. Theoretically, the extraction rate should increase with increasing phase ratio, but the increasing phase ratio also increases the use of the extraction agent P204, leading to increasing production costs [19]. After full consideration, the extraction phase ratio (O/A) was set to be 1:1.

Effect of Extractant Concentration on Manganese Extraction

We investigated the effects of different P204 concentrations on the extraction rate of manganese. Consequently, we set the P204 concentration to be 20, 30, 35, and 40%, respectively. Other experimental conditions were as follows: the P204 saponification rate was 80%, the extraction equilibrium time was 5 min, the phase ratio (O/A) was 1:1, the extraction temperature was 25°C, and the extraction stage was level 1. The test results are shown in Fig. 5.

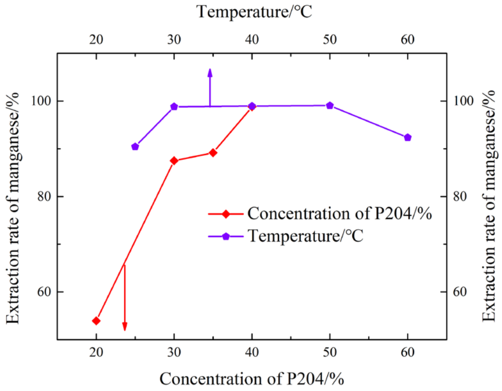

Fig. 5 Effect of extractant concentration and temperature on extraction of manganese

It can be seen from Fig. 5 (red line), that when the concentration of P204 was 20%, the extraction rate of manganese was just 53.93%. However, when the concentration of P204 increased to 35%, the extraction rate increased to 89.15%. Similarly, when the concentration was 40%, the extraction rate rose to 98.79%. On the basis of the above results, it was more than reasonable to set the concentration of extraction agent P204 to be 40%.

Effect of Extraction Temperature on Manganese Extraction

The experimental conditions were as follows: the organic phase of P204 was 40% and of sulfonated kerosene, 60%, the extraction phase ratio (O/A) was 1:1, the extraction equilibrium time was 5 min, the extraction equilibrium pH was 5–6, and the P204 saponification rate was 80%. The experimental results are shown in Fig. 5.

It can be seen from Fig. 5 (violet line) that with the increasing extraction temperature, the manganese extraction rate increased initially before decreasing slowly. When the extraction temperature was between 30°C and 50°C, the extraction rate was better. However, when the extraction temperature was higher than 50°C, the extraction rate showed a downward trend. Since the ambient temperature was rarely greater than 40°C, although the extraction rate increased slightly after the increase in temperature, the volatilization of the organic phase increased too, resulting in an increase in the consumption of extractant. Therefore, the optimal manganese extraction temperature was set to be 30–40°C.

Effect of Extraction Equilibrium pH on Manganese Extraction

The experimental conditions were as follows: the organic phase of P204 was 40% and of sulfonated kerosene, 60%, the extraction phase ratio (O/A) was 1:1, the extraction equilibrium time was 5 min, the extraction temperature was 25°C, the P204 saponification rate was 80%. During the test, different volumes of sulfuric acid solution and sodium hydroxide solution were added to control the terminal pH value. The test results are shown in Fig. 6.

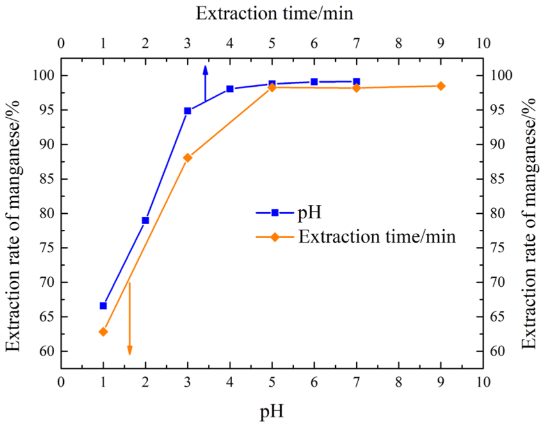

Fig. 6 Effect of pH and extraction time on extraction of manganese

It can be seen from Fig. 6 (blue line) that the extraction equilibrium pH exhibited a significant influence on the manganese extraction rate, the manganese extraction rate increasing with increasing extraction equilibrium pH. When the pH of the solution was maintained at more than 3 during the extraction process, the extraction rate of manganese was greater than 94.88%, the concentration of manganese ions in the raffinate being less than 1.085g/L. When the extraction equilibria pH was greater than 4, the manganese extraction rate increased slightly and when it was approximately 5, practically all of the manganese ions in the solution were extracted. Consequently, the pH of the purified manganese sulfate solution was set to be the most suitable extraction equilibrium pH.

Effect of Extraction Equilibrium Time on Manganese Extraction

The extraction equilibrium time also has an important effect on the extraction efficiency of manganese, and the appropriate extractant should be efficient and fast. In this experiment, the extraction times were set to be 1, 3, 5, 7 and 9min, respectively, to examine the influence of the extraction equilibrium time on the manganese extraction rate. Other experimental conditions were as follows: the organic phase of P204 was 40% and of sulfonated kerosene, 60%, the extraction phase ratio (O/A) was 1:1, the extraction equilibrium pH was 5–6, the extraction temperature was 30°C, and the P204 saponification rate was 80%. The test results are shown in Fig. 6.

It can be seen from Fig. 6 (orange line) that the manganese extraction rate increased with the increasing extraction equilibrium time. However, when the extraction equilibrium time exceeded 5 min, the manganese extraction rate did not change significantly. Considering potential errors in the test process and test results, it was considered that the manganese extraction rate exhibited practically no difference. During the extraction process, if the oscillation time was too long, the organic and the aqueous phase would form an emulsion, making phase separation difficult [20]. Knowing that a long extraction equilibrium time in industrial production would reduce production efficiency, and the fact that full mixing of the organic and aqueous phases had been completely realized after an extraction time of 5 min, it was clear that extraction equilibrium had been reached. Consequently, the extraction equilibrium time was set to be 5 min.

Drawing of Extraction Isotherm and Determination of Extraction Stage

A curve indicating the change of metal concentration in the organic phase and the aqueous phase is generally referred to as an extraction (or back-extraction) isotherm [21]. The position of the isotherm is related to the concentration of the extractant, the shape of the isotherm changing with changes of the extraction system—that is, the location of the extraction isotherm for the same extractant with different concentrations changes, but it shape remains much the same.

There are two methods for drawing extraction isotherms [22]:

(1) The determination of phase radio method: here, the concentration of the organic phase, the concentration of the feed solution, the extraction temperature, and the extraction equilibrium pH used during the test must remain the same. Due to differences in the phase ratio, the pH after extraction equilibrium may be different. In this case, it may be necessary to adjust the equilibrium pH with acid or alkali and then re-contact until the pH of the raffinate of each sample is the same. Based on the specified phase ratio, the organic and the aqueous phase are loaded into the separation funnel, and then oscillated on the Kane oscillator to equilibrium—that is, where the pH of the raffinate phase ratio can be measured directly, with the pH being constant as the criterion. After phase separation, the metal content is analyzed in the two phases, making sure to avoid entrainment before sampling and analysis. The aqueous phase analysis sample should be filtered to remove the entrained organic phase. After the loaded organic phase is washed with distilled water, the separated phase is discharged, and the metal content in the organic phase can be analyzed after separation by centrifuge.

(2) In this method, first determine an appropriate phase ratio, the organic and the aqueous phases in this phase ratio reacting and reaching an equilibrium. Then, after two phase separations to release the aqueous phase, different volume of organic and aqueous phase can be analysed for their metal content. Next, based on the original phase ratio, a new aqueous phase is added to the separator funnel to react with the remaining organic phase. When the two phases reach equilibrium again, a sample analysis can be conducted as before. This process is repeated several times until the metal load in the

organic phase reaches saturation, the extraction equilibrium pH being maintained each time. Finally, the extraction isotherm can be plotted by plotting the analysis results of each group on a graph with the concentration of the aqueous phase metal on the X-axis and the concentration of the organic phase metal on the Y-axis.

If there is still a large volume of extractant in the raffinate after the first extraction stage, it would be necessary to conduct multi-stage extraction treatment to achieve the maximum extractant extraction. After the optimized selection of a series of factors, such as the saponification rate of the P204-kerosene extraction system, the extraction equilibrium time, the extraction phase ratio, the concentration of P204, the extraction temperature, and the extraction equilibrium pH, an extraction isotherm could be under the following conditions: the organic phase consisted of 40% P204 and 60% sulfonated kerosene, the phase ratio (O/A) was 1:1, the pH of the solution was between 5 and 6, the extraction equilibrium time was 5 min, the extraction temperature was 30°C, and the saponification rate was 80%. The simplest method to estimate the number of extraction stages required for multi-stage extraction is the McCabe-Thiele diagram method. The extraction isotherm of manganese drawn based the test results is shown in Fig. 7.

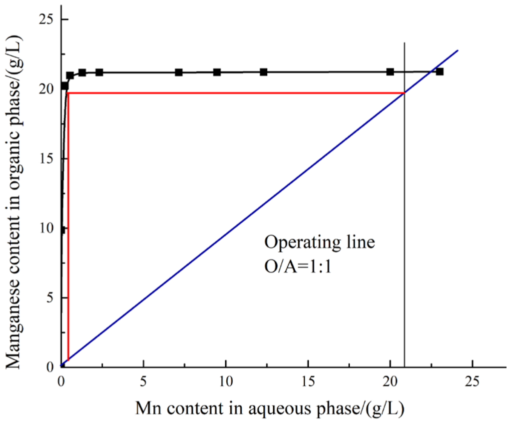

Fig. 7 Manganese extraction isotherm using P204

It can be seen from Fig. 7 that for the manganese sulfate purification solution with a manganese ion concentration of 21.20g/l under pressure leaching, using the organic phase—which was 40% of P204 and 60% of sulfonated kerosene—and where O/A was 1, the manganese extraction rate could reach more than 95%, the concentration of manganese ions in the raffinate being less than 1g/L, to achieve the maximum recovery of Mn2+. However, an increasing number of extraction stages would undoubtedly increase industrial production costs. Consequently, the extraction stage for this experiment was set to be level 1.

Results: Back-extraction

The back-extraction solution was prepared with analytically pure H2SO4 and distilled water, the volume fraction of P204 in the loaded organic phase was 40%, containing 20.44 g/L of manganese.

Effect of Back-Extraction Acidity on Manganese Back-Extraction Rate

The experimental conditions were as follows: the volume fraction of P204 in the loaded organic phase was 40%, the back-extraction phase ratio (O/A) was 2:1, the back-extraction temperature was 25°C, and the mixing time of the back-extraction was 3 min. We examined the changes in the back-extraction rate of manganese under different back-extraction acidity. The test results are shown in Fig. 8.

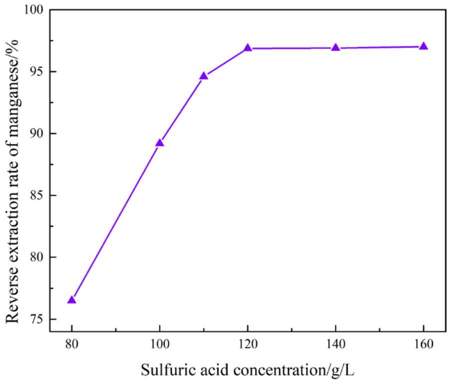

Fig. 8 The effect of the stripping solution acidity on the manganese back-extraction rate

It can be seen from Fig. 8, that with increasing sulfuric acid concentrations in the back-extraction solution, the manganese back-extraction rate exhibited an upward trend. Because the concentration of manganese ions in the low-concentration manganese sulfate solution treated using the extraction-back-extraction process had reached the needs of the electrolytic manganese, it could be sent to the electrolytic process as the new electrolytic solution, its pH remaining within the range of 6.5–7. Consequently, while ensuring different acid concentrations and back-extraction rates of manganese, a lower sulfuric acid concentration should be used for back-extraction as much as possible. In this experiment, the optimum acidity of the back-extraction process was 120g/L.

Effect of Back-Extraction Temperature on Manganese Back-Extraction Rate

The experimental conditions were as follows: the volume fraction of P204 in the loaded organic phase was 40%, the back-extraction phase ratio (O/A) was 2:1, the sulfuric acid concentration of the back-extraction solution was 120g/L, and the mixing time of the back-extraction was 3 min. We examined the variation of the manganese back-extraction rate under different back-extraction temperatures. The test results are shown in Fig. 9.

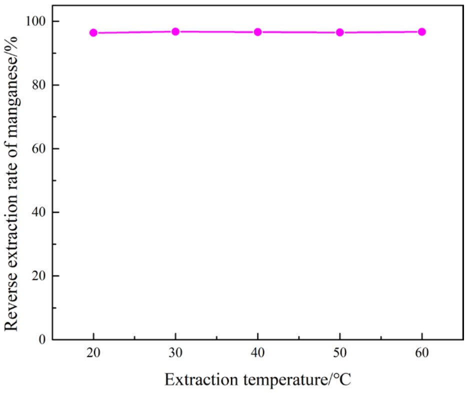

Fig. 9 The effect of temperature on the manganese back-extraction rate

It can be seen from Fig. 9, that with increasing back-extraction temperatures, the manganese back-extraction rate did not change significantly, so the temperature of back-extraction process could be selected to be 25°C.

Effect of Back-Extraction Mixing Time on Manganese Back-Extraction Rate

The experimental conditions were as follows: the volume fraction of P204 in the loaded organic phase was 40%, the back-extraction phase ratio (O/A) was 2:1, the sulfuric acid concentration of the back-extraction solution was 120g/L, and the back-extraction temperature was 25°C. We investigated the variation of the manganese back-extraction rate under different back-extraction mixing time. The results are shown in Fig. 10.

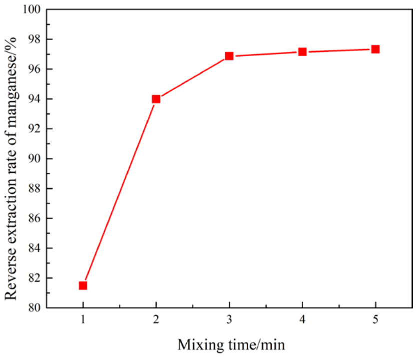

Fig. 10 The effect of mixing time on the manganese back-extraction rate

It can be seen from Fig. 10, that with the extension of the back-extraction mixing time, the manganese back-extraction rate increased. However, once the mixing time exceeded 3 min, there was no obvious change in the manganese back-extraction rate. This indicated that the back-extraction process was essentially balanced when the back-extraction mixing time was 3 min. To ensure the maximal manganese back-extraction rate, the optimal back-extraction mixing time was set to be 3 min.

Effect of Back-Extraction Phase Ratio on Manganese Back-Extraction Rate and Manganese Ion Concentration in Back-Extraction Solution

The experimental conditions were as follows: the volume fraction of P204 in the loaded organic phase was 40%, the back-extraction mixing time was 3 min, the concentration of sulfuric acid in the back-extraction solution was 120g/L, and the back-extraction temperature was 25℃. We examined the changes in the manganese back-extraction rate and the concentration of manganese ions in the back-extraction solution under different back-extraction phase ratios. The test results are shown in Fig. 11.

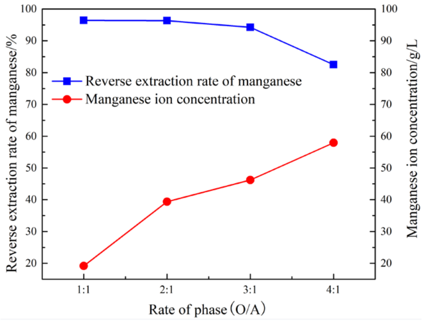

Fig. 11 The effect of phase ratio on the manganese back-extraction rate

It can be seen from Fig. 11, that with increasing back-extraction phase ratio (O/A), the manganese back-extraction rate exhibited a decreasing trend. However, the concentration of manganese ion in the back-extraction solution increased with increasing back-extraction phase ratio. Since the concentration of manganese ions in the new electrolytic solution in industrial production is required to be above 35g/L, to ensure a higher concentration of manganese ions and manganese back-extraction rate, the best back-extraction phase ratio (O/A) was considered to be between 2:1 and 3:1.

Determination of Back-Extraction Series

If there were still large volumes of unstripped manganese ions in the loaded organic phase after first stage back-extraction, it would be essential to conduct multi-stage back-extraction to achieve the maximum back-extraction of manganese. In this experiment, the number of back-extraction stages was selected to be 1, 2 and 3, respectively. The other experimental conditions were as follows: the volume fraction of P204 in the loaded organic phase was 40%, the back-extraction phase ratio (O/A) was 3:1, the back-extraction mixing time was 3 min, the sulfuric acid concentration of the back-extraction solution was 120g/L, and the back-extraction temperature was 25℃. The test results are shown in Table 2.

Table 2 The relationship of stripping stages and the manganese stripping rate.

Reverse extraction series	The concentration of manganese in the loaded organic phase (g/L)	Back-extraction rate of manganese (%)
1	0.57	96.9
2	trace amounts	100
3	trace amounts	100

It can be seen from Table 2, that through the optimal selection of a series of factors such as the concentration of sulfuric acid in the back-extraction solution, the contrast of the back-extraction solution, the mixing time and the temperature of the back-extraction process, the manganese recovery rate could reach 96.9% when the back-extraction stage was level 1, the maximum recovery of Mn2+ having been achieved. Increasing back-extraction series would undoubtedly increase the cost of industrial production, so the back-extraction stage was selected to be level 1[23].

Determination of Back-Extraction Solution Composition

Under optimized extraction conditions—that is, with the volume fraction of P204 in the loaded organic phase being 40%, the back-extraction phase ratio (O/A) being 3:1, the mixing time of the back-extraction being 3 min, the sulfuric acid concentration of the back-extraction solution being 120g/L, the temperature of the back-extraction being 25°C, and the back-extraction stage being level 1—the chemical composition of the manganese sulfate back-extraction solution was obtained. The results are shown in Table 3.

Table 3 The chemical composition of the back-extraction solution.

Component	Mn	Fe	Al	Ca	Mg	Co	Ni	Cu
Content(g/L)	42.16	0.0003	0.00012	0.03	0.088	0.00014	0.00027	0.00005

It can be seen from Table 3, that the concentration of Mn2+ in the back-extraction solution had reached the manganese ion concentration range required by electrolytic manganese, and that the content of all impurities was lower than that of the extract solution, realizing the aim of deep impurity removal. Consequently, the solution could be sent to the electrolytic process for preparation of the electrolyte.

Conclusions

(1) We analyzed the basic experimental principles of extraction, back-extraction and saponification.

(2) The optimized extraction conditions of manganese from a manganese sulfate purification solution containing a manganese ion concentration of 21.20g/L under pressure were as follows: the saponification rate of P204 was 80%, the extraction phase ratio (O/A) was 1:1, the concentration of P204 was 40%, the extraction equilibrium pH was approximately 5.0, the extraction temperature was 30–40°C, the extraction equilibrium time was 5 min, and the extraction stage was level 1. Under these conditions, the extraction rate of manganese reached more than 95%, the concentration of manganese ions in the raffinate being less than 1g/L.

(3) To obtain higher manganese back-extraction rates and reach the required concentration range of manganese ions in electrolytic manganese, various factors affecting the manganese back-extraction rate were investigated. The optimum technological conditions for the back-extraction process were as follows: The back-extraction acidity was 120g/L, the back-extraction temperature was 25°C, the back-extraction mixing time was 3 min, the back-extraction phase ratio was 2:1–3:1, the back-extraction stage was level 1. The back-extraction process was conducted under these optimized conditions, achieving a manganese back-extraction rate of 96.9%, the concentration of manganese ions in the back-extraction solution being 42.16g/L (the concentration of other impurities reaching the requirements of electrolytic manganese).

Acknowledgments

This work was supported by the National Nature Science Foundation of China under Grant No. 51764007, and the National Key Laboratory Open Fund Project under Grant No. yy20160013.

Conflict of interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted.

References

[1] H.Y. Xie (2013) Study on the pressurized acid leaching purification extraction technology of complex low-grade manganese ore and manganese containing dust. Dissertation, Kunming University of Science and Technology.

[2] K. Wang, Q.W. Zhang, H.M. Hu, Y.C. Liu (2019) Efficient removal of iron (II) from manganese sulfate solution by using mechanically activated CaCO3. Hydrometallurgy 188: 169-173. DOI: 10.1016/j.hydromet.2019.07.003

[3] Y.S. Wang, L. Zeng, G.Q. Zhang, W.J. Guan, Z. Sun, D. Zhang, J.L. Qing (2019) A novel process on separation of manganese from calcium and magnesium using synergistic solvent extraction system. Hydrometallurgy 185:55-60. DOI: 10.1016/j.hydromet.2019.01.008

[4] T. Gigla, S. Djemal, K. Nana, L. Tinatin, G. David, B. Levan, S. Suladze, K. Izolda (2019) Novel hydro-electrometallurgical technology for simultaneous production of manganese metal, electrolytic manganese dioxide, and manganese sulfate monohydrate. Hydrometallurgy 186: 260-268. DOI: 10.1016/j.hydromet.2019.04.028

[5] X.P. Yu, J.J. Cui, C.L. Liu, F. Yuan, Y.F. Guo, T.L. Deng (2021) Separation of magnesium from high Mg/Li ratio brine by extraction with an organic system containing ionic liquid. Chemical Engineering Science 229: 116019. DOI: 10.1016/j.ces.2020.116019

[6] M.P. Elizalde, M.S. Rúa, B. Menoyo, A. Ocio (2018) Solvent extraction of copper from acidic chloride solutions with LIX 84. Hydrometallurgy 183:213-220. DOI: 10.1016/j.hydromet.2018.12.013

[7] H. Srichandan, R.K. Mohapatra, P.K. Parhi, S. Mishra (2019) Bioleaching approach for extraction of metal values from secondary solid wastes: a critical review. Hydrometallurgy 189 (105122): 1-14. DOI: 10.1016/j.hydromet.2019.105122

[8] S. Piotr, B. Agnieszka, B. Henryk, G. Andrzej (2019) Quantitative evaluation and leaching behavior of cobalt immobilized in sulfur polymer concrete composites based on lignite fly ash, slag and phosphogypsum. Journal of Cleaner Production 222: 90-102. DOI: 10.1016/j.jclepro.2019.03.010

[9] L.M. Tan, H.P. Hu, J.M. Liao, C.X. Wang, C. Li (2014) Preparation of battery grade high purity manganese sulfate by solvent extraction. Nonferrous Metals (Extractive Metallurgy) (9): 62-65.

[10] T.T. He, L. Qian, J.X. Cui, H.F. Su (2018) Study on deep removal of calcium and magnesium from industrial manganese sulfate by fluorination. Nonferrous Metals (Extractive Metallurgy) (7): 1-4.

[11] F.Y. Chen, F. Wu (2012) Study on new technology of removing heavy metals in preparation of high purity manganese sulfate. China Manganese Industry 30(2): 26-28. DOI: 10.14101/j.cnki.issn.1002-4336.2012.02.009

[12] S. Yan, Y.R. Qiu (2014) Preparation of electronic grade manganese sulfate from leaching solution of ferromanganese slag. Transactions of Nonferrous Metals Society of China 24 (11): 3716–3721. DOI: 10.1016/S1003-6326(14)63520-2

[13] W.J. Yang, L.J. Zhu, X.J. Qu (2014) Study on removal of calcium and magnesium ions from leaching solution of poor pyrolusite by extraction. Journal of Hunan University (Natural Sciences) 41(12): 83–88.

[14] F.Z. Kong, J.Q. Li, S.H. Yang, L. Liu, P. Wang (2007) Study on Purification and impurity removal of manganese chloride aqueous solution. Journal of Guizhou University of Technology (Natural Science Edition) 36 (5): 28-31.

[15] Z.T. Xu, S.W.Gu, Dipak Rana, Takeshi Matsuura, Christopher Q.Lan (2021) Chemical precipitation enabled UF and MF filtration for lead removal. Journal of Water Process Engineering 41:101987. DOI: 10.1016/j.jwpe.2021.10198

[16] Q. Ye, G.H. Li, B.N. Deng, J. Luo, M.J. Rao, Z.W. Peng, Y.B. Zhang, T. Jiang (2019) Solvent extraction behavior of metal ions and selective separation Sc3+ in phosphoric acid medium using P204. Separation and Purification Technology 209: 175-181. DOI: 10.1016/j.seppur.2018.07.033

[17] Y.F. Shen, W.Y. Xue, W.Y. Niu (2008) Recovery of Co (II) and Ni (II) from hydrochloric acid solution of alloy scrap. Transactions of Nonferrous Metals Society of China 18 (5): 1262-1268. DOI: 10.1016/S1003-6326(08)60214-9

[18] X.H. Yu, G. Xie, D.J. Yang, Y.G. Li (2008) Extraction and separation of copper from high copper and high zinc sulfuric acid solution. Nonferrous Metals 60 (2): 51-54.

[19] C.Y. Wang, H.Y. Wang, P.H. Jiang, F. Yin, Y.Q. Chen (2006) Study on extraction separation of cobalt, manganese and iron by P204. Nonferrous Metals (Extractive Metallurgy) (5): 2-5.

[20] S.P. Liu, B. Li, C.L. Wang, X.P. Tang (2011) Experimental study on extraction separation of copper from copper zinc iron solution. Multipurpose Utilization of Mineral Resources (6): 16-19.

[21] G.H. Ye (2010) Study on new technology and mechanism of extracting V2O5 from vanadium bearing steel slag. Dissertation, Kunming University of Science and Technology.

[22] J.Y. Yang, D.X. Liu (1995) Extraction. Metallurgical Industry Press, Beijing.

[23] X.H. Yu (2008) Comprehensive recovery and utilization of complex copper, lead, zinc and silver polymetallic sulfide concentrate. Dissertation, Kunming University of Science and Technology.