The Efficient Removal of Calcium and Magnesium Ions from Industrial Manganese Sulfate Solution through the Integrated Application of Concentrated Sulfuric Acid and Ethanol

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Abstract: In the process of preparing high-purity MnSO4 from industrial MnSO4 solution, it is difficult to remove Ca2+ and Mg2+ due to their closely similar properties. In this study, thermodynamic software simulation and experimental procedures were combined to remove Ca2+ and Mg2+ from industrial MnSO4 solution to obtain high-purity MnSO4. The simulation model was applied to predict the trend of the crystallization of different ions in the solution upon the addition of H2SO4, which revealed that, at a volume ratio of H2SO4 to MnSO4 solution of more than 0.2, MnSO4 started to crystallize and precipitate. The experimental results further verified the simulation results, and the yield of MnSO4 increased with the increasing ratio of H2SO4 while the removal rate of Ca2+ and Mg2+ decreased gradually. Keeping the economic aspect in mind, the 0.3 ratio of H2SO4 was selected at which the yield of MnSO4 reached 99.44%. The removal rate of Ca2+ and Mg2+ by recrystallization reached 99.68% and 99.17% respectively after six consecutive cycles. The recrystallized sample was washed twice with anhydrous ethanol (volume ratio of ethanol to MnSO4 reached the battery grade requirements with the final yield as high as 80.54%. This study provides important guideline information for the purification of MnSO4·H2O from industrial MnSO4 solution via a cost-effective, simple and facile approach.

Keywords: OLI Stream Analyzer; high-purity MnSO4; recrystallization; Ca2+ and Mg2+ removal

1. Introduction

MnSO4, as a base manganese salt, is used in the preparation of various advanced manganese-based alloys and products [1-4]. The front drive system of the positive tri-vumirate of a battery’s material (Ni-Cobalt Manganese Acid Lithium) requires high-purity MnSO4, where the major impurities include potassium, sodium, calcium and magnesium (the sum of the concentration of calcium and magnesium impurities is ≤0.05%) [5,6]. In order to obtain these high-quality manganese-based materials for use in batteries, the purity of manganese-based raw materials must be solved first. Therefore, the deep decontamination of MnSO4 solution for producing high-grade materials to be used in lithium-ion batteries has become a research hotspot [7].

Among the many impurities like K+, Na+, Ca2+ and Mg2+, the chemical properties of manganese are closely similar to the calcium and magnesium present in MnSO4 solu-
tion, and hence it becomes very tough to prepare MnSO₄ for meeting the requirements of high-purity MnSO₄ via traditional decontamination methods [8,9]. In addition, Ca²⁺ and Mg²⁺ have a great impact on many subsequent processes, and in the electrolytic manganese phase, they affect the current efficiency of electrolysis and the purity of electrolytic manganese products. The traditional methods for the removal of Ca²⁺ and Mg²⁺ in MnSO₄ solution mainly include chemical precipitation [10,11], recrystallization [12,13], fluoridation [14], extraction [15–17], and electrolysis [18]. Recrystallization includes evaporative concentration, high temperature and pressure crystallization [19–21], where it uses MnSO₄ solubility, which shows a sharp decrease at temperatures of over 100 °C, and the MnSO₄ crystals are obtained by heating the solution in the high-pressure reactor. This process is very stringent on the material and quality requirements of the equipment, otherwise it can affect the normal safe operation of the system [22,23]. The fluoride method uses the difference between the solubilities between manganese fluoride, calcium fluoride and magnesium fluoride, and the decontamination of Ca²⁺ and Mg²⁺ [24]. However, this method introduces Na⁺, NH₄⁺ and F⁻ as impurities while removing Ca²⁺ and Mg²⁺, and high-purity MnSO₄ needs to be treated with extractors and adsorbents for their removal. In addition, the waste liquid and residue produced by this process contains hazardous F⁻ which requires further purification processes. The extraction method utilizes the difference in solubilities of Mn²⁺ and the impurity ions (K⁺, Na⁺, Ca²⁺ and Mg²⁺) in different extractants for effective separation [25], but the product purity and recovery rate obtained by this method is low. Electrolysis uses the difference in the rate of precipitation of manganese ions and impurity ions in manganese sulfate leaching solution, though it generates hydrogen, which poses a safety hazard.

In view of the aforementioned shortcomings of traditional MnSO₄ purification processes, and to maintain the sustainable exploitation of resources and the perspective of economic development, it is particularly important to study, develop and apply new processes for the generation of high-purity MnSO₄. Thus, this study applies the approach of variation in the solubility–product constant (Kₛₚ) of Mn²⁺, and Ca²⁺ and Mg²⁺ in the water–H₂SO₄ system for the preparation of high-purity MnSO₄·H₂O at room temperature [26,27]. The impurity ions are removed by repeated recrystallization, and the H₂SO₄ remaining on the surface is washed with ethanol, with the high-purity MnSO₄·H₂O obtained after drying. Compared with the traditional synthesis method, this method is cost- and energy-effective and simplified with reduced mechanical requirements, while maintaining sustainable and green development approaches by effectively utilizing waste and environmentally friendly materials for the production of high-purity MnSO₄·H₂O.

2. Experimental Section

2.1. Materials and Equipment

The concentration of various ions in the MnSO₄ leaching solution (CITIC Dameng Mining Industries Limited Chongzuo Branch, Nanning, Guangxi, China) used in this work is shown in Table 1 (pH = 2.8). The H₂SO₄ used in this experiment was obtained from Chengdu Kelong chemical reagent factory, China. Ethanol was provided by Guangdong Guanghua Sci-Tech Co., Ltd., Guangzhou China. The constant-temperature magnetic heating mixer was provided by Gongyi Yuhua Instrument Co., Ltd. Ethanol was recovered via a rotary evaporator (EYELA-1300D-WB, Tokyo Japan), while solution pH was tested via a pH meter provided by Shanghai San-Xin Instrumentation, China.

| Ion | Mn (g/L) | Mg (mg/L) | Ca (mg/L) | Na (mg/L) | K (mg/L) | Ni (mg/L) | Co (mg/L) | Zn (mg/L) |
|-----|----------|-----------|-----------|-----------|----------|-----------|-----------|-----------|
| Concentration | 139.20 ± 1.24 | 1726.39 ± 39.51 | 544.95 ± 8.99 | 93.11 ± 9.13 | 23.62 ± 6.91 | 236.87 ± 6.88 | 64.20 ± 1.02 | 48.20 ± 7.94 |
2.2. Simulation Software and Methods

OLI Stream Analyzer predicted the system phase equilibrium and crystallization thermodynamic process of complex chemical mixtures in aqueous systems. Different pH values, temperature and pressure could be adjusted according to experimental requirements, and the solute saturation point, precipitation point, acid-base titration curve and thermodynamic properties of the components and their dependence relationships could be simulated and predicted. The ratio of $H_2SO_4$ to the crystallization trend of different components and the change of $MnSO_4 \cdot H_2O$ yield with temperature were calculated by the software OLI Stream Analyzer version 3.1.

2.3. Preparation of High-Purity $MnSO_4 \cdot H_2O$

High-purity $MnSO_4 \cdot H_2O$ was prepared by $H_2SO_4$ in coordination with ethanol, and this preparation process is shown in Figure 1. Firstly, 50 mL of $MnSO_4$ solution was taken in a beaker at room temperature, and 15 mL of $H_2SO_4$ was slowly added to it under continuous stirring. When the crystals were completely precipitated, stirring was stopped and the crystals were separated from the solution. The obtained crystals were re-dissolved with 30 mL deionized water, and then 15 mL $H_2SO_4$ was slowly added to completely precipitate the crystals. This process was repeated 6 times. Secondly, the filtered $MnSO_4$ crystals were washed with 50 mL of ethanol in two steps to remove $H_2SO_4$ on the surface, and ethanol was recycled through the rotary evaporator. Finally, the $MnSO_4$ crystals were dried at 120 $^\circ$C for 6 h to obtain high-purity $MnSO_4 \cdot H_2O$.

![Figure 1. Preparation flow chart of $MnSO_4 \cdot H_2O$ crystals.](image)

2.4. Characterization

X-ray powder diffraction (XRD, Rigaku MiniFlex 600, Japan) was used to analyze the crystal phase structure of $MnSO_4 \cdot H_2O$ in scanning range of 10–70 $^\circ$ (2$\theta$) at a rate of 5 $^\circ$/min under Fe-K$\alpha$ as anode target, 40 kV and 15 mA conditions. The sample was digested with 5% HCl. The concentrations of various metal ions in manganese sulphate leaching solution and filtrate were measured by inductively coupled plasma atomic emission spectroscopy (ICPS-7510, Shimadzu, Japan) and atomic absorption spectrophotometer (AA-7000, Shimadzu, Japan), respectively.

3. Results and Discussions

3.1. Simulation Results of OLI Stream Analyzer Software

The density of the industrial $MnSO_4$ solution used in this experiment was $1.3127 \pm 0.0004$ g/cm$^3$, and the density calculated by the OLI Stream Analyzer software was $1.2982$ g/cm$^3$, hence it could be concluded that the OLI Stream Analyzer software could be used to simulate and calculate the industrial $MnSO_4$ solution. The software was used to calculate the scaling trend and yield changes of different components of industrial
MnSO\textsubscript{4} solution with the addition ratio of H\textsubscript{2}SO\textsubscript{4}. As shown in Figure 2A, the scaling trend of MnSO\textsubscript{4}·H\textsubscript{2}O, CaSO\textsubscript{4} and MgSO\textsubscript{4}·H\textsubscript{2}O increased with the increasing ratio of H\textsubscript{2}SO\textsubscript{4}. When the ratio of H\textsubscript{2}SO\textsubscript{4} reached 6% and 10%, the scaling trend of MnSO\textsubscript{4}·H\textsubscript{2}O and CaSO\textsubscript{4} in the solution reached 1 [28], which indicated that MnSO\textsubscript{4}·H\textsubscript{2}O and CaSO\textsubscript{4} were saturated and had reached the precipitation condition. In contrast, the MgSO\textsubscript{4}·H\textsubscript{2}O crystal does not match the precipitation condition. In a temperature range of 25–85 °C, the change trend of MnSO\textsubscript{4}·H\textsubscript{2}O yield with the ratio of H\textsubscript{2}SO\textsubscript{4} is shown in Figure 2B. The yield of MnSO\textsubscript{4}·H\textsubscript{2}O increased with the increasing ratio of H\textsubscript{2}SO\textsubscript{4}, and was sensitive to temperature change when the ratio of H\textsubscript{2}SO\textsubscript{4} was less than 26%, the main reason for this was that the solubility of manganese sulfate decreased with the increase of temperature at 25–85 °C, which led to the increase of crystallization yield. However, when the H\textsubscript{2}SO\textsubscript{4} concentration was high and the ratio exceeded 26%, the MnSO\textsubscript{4}·H\textsubscript{2}O saturation increased. Under the condition of a ratio of 30% H\textsubscript{2}SO\textsubscript{4}, the solution degree of MnSO\textsubscript{4}·H\textsubscript{2}O increased with the increase in temperature, which led to a slight change in the crystallization yield. Therefore, when the ratio of H\textsubscript{2}SO\textsubscript{4} was 30%, the maximum yield of MnSO\textsubscript{4}·H\textsubscript{2}O was 82.2% at 25 °C.

![Figure 2. The scaling trend (A) of different components of industrial MnSO\textsubscript{4} solution with the addition ratio of H\textsubscript{2}SO\textsubscript{4} and MnSO\textsubscript{4}·H\textsubscript{2}O yield (B) in the temperature range of 25–85 °C.](image)

3.2. Calculated and Tested Yield of Different Components

Under the condition of 25 °C, in order to obtain the influence of H\textsubscript{2}SO\textsubscript{4} on the yield of different components (MnSO\textsubscript{4}·H\textsubscript{2}O, CaSO\textsubscript{4} and MgSO\textsubscript{4}·H\textsubscript{2}O), the comparison of the results of the calculations and tests were used to obtain the yield of different components of industrial MnSO\textsubscript{4} solution, with the addition of H\textsubscript{2}SO\textsubscript{4} in different ratios. As shown in Figure 3, the calculated and tested yield of MnSO\textsubscript{4}·H\textsubscript{2}O was very close to the change trend of the ratio of H\textsubscript{2}SO\textsubscript{4} and increased proportionally with increasing H\textsubscript{2}SO\textsubscript{4} ratio. When the ratio of H\textsubscript{2}SO\textsubscript{4} exceeded 30%, its increasing trend was not obvious. The calculated and tested yields were 82.2% and 86.6%, respectively, at a 30% H\textsubscript{2}SO\textsubscript{4} ratio. As the ratio of H\textsubscript{2}SO\textsubscript{4} increased, a wide gap appeared between the calculated and tested yield of CaSO\textsubscript{4}, which was mainly because the industrial MnSO\textsubscript{4} solution was laden with a high content of salt (the content of MnSO\textsubscript{4} exceeds 100 g/L) and the force between the ions was strengthened, which increases the solubility of CaSO\textsubscript{4} [19]. Hence, the actual amount of CaSO\textsubscript{4} precipitation was minimal, which was beneficial for the removal of Ca\textsuperscript{2+}. MgSO\textsubscript{4}·H\textsubscript{2}O precipitation was not generated in the simulation calculation, but MgSO\textsubscript{4}·H\textsubscript{2}O crystals were found in the actual test. This was because MnSO\textsubscript{4} and MgSO\textsubscript{4} in the solution were similar in structure and could form a mixed crystal system [29]. MgSO\textsubscript{4} could attach to the solid surface of MnSO\textsubscript{4}·H\textsubscript{2}O for the heterogeneous nucleation and in the actual crystallization process.
Figure 3. The calculated and tested yield of different components of industrial MnSO₄ solution with the addition ratio of H₂SO₄.

3.3. Determination of the Optimal Ratio of H₂SO₄

The change trend of the MnSO₄·H₂O yield and Ca²⁺, Mg²⁺ removal rate with the ratio of H₂SO₄ was explored in a range from 20–50%. As shown in Figure 4, the yield of MnSO₄·H₂O increased with increasing the ratio of H₂SO₄, while the change in the removal rate of Ca²⁺ and Mg²⁺ demonstrated the opposite trend. Considering the actual production cost and the results of the previous calculations, the optimal ratio of H₂SO₄ was determined to be 30% and at this ratio, the MnSO₄·H₂O crystal yield was 86.60%, and the removal rates of Ca²⁺ and Mg²⁺ were 65.25% and 70.91%, respectively.

Figure 4. The effect of H₂SO₄ ratio on MnSO₄·H₂O yield and Mg²⁺, Ca²⁺ removal rate.

3.4. Recrystallization Experiment

In order to obtain high-purity MnSO₄·H₂O crystals, it was necessary to perform recrystallization experiments on the obtained MnSO₄·H₂O. The ratio of H₂O and the
number of cycles in the recrystallization process had a great influence on the yield of 
\( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) and the removal rates of \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) \[30\]. The solubility of \( \text{MnSO}_4 \) at 25 °C was around 64.8 g/100 g \( \text{H}_2\text{O} \) \[31\], and hence the ratio of \( \text{H}_2\text{O} \) added (the volume ratio of \( \text{H}_2\text{O} \) to the original \( \text{MnSO}_4 \) solution) varied between 60–100%. As shown in Figure 5A, the yield of \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) decreased with an increase in the ratio of \( \text{H}_2\text{O} \) which was because the dissolution loss of \( \text{MnSO}_4 \) increased as the amount of water increased, and finally determined that 60% was the optimum ratio of \( \text{H}_2\text{O} \). It can be seen from Figure 5B that the yield of \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) decreased with the increase of the number of cycles, while the removal rate of \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) gradually increased. However, the yield of \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) changed marginally, and still reached 80.54% after six cycles. The residual content (wt.%) of \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) in \( \text{MgSO}_4 \cdot \text{H}_2\text{O} \) with different recrystallization cycles in Table 2 suggested that \( \text{Ca}^{2+} \) content attained the requirement (\( \leq 0.0050\)) after two cycles while \( \text{Mg}^{2+} \) needed six cycles to attain this requirement. The preparation of high-purity \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) crystals in this paper required a minimum of six cycles. During the experiment, excessive concentrated \( \text{H}_2\text{SO}_4 \) was recovered and used in industry to prepare \( \text{MnSO}_4 \) solution by leaching manganese ore. Therefore, the recycling of \( \text{H}_2\text{SO}_4 \) could effectively save immeasurable production costs. At present, compared with the traditional extraction method, this technology was not only simple in operation, lower in cost, and larger in production scale, but also through preliminary feasibility analysis, the annual economic benefits of using this technology were at least twice that of the traditional technology.

![Figure 5](image_url)

**Figure 5.** (A) The effect of \( \text{H}_2\text{O} \) ratio on \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) yield during recrystallization; (B) The effect of cycles on \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) yield and \( \text{Mg}^{2+}, \text{Ca}^{2+} \) removal rate.

**Table 2.** Residual content (wt.%) of \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) in \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) with different recrystallization cycles.

| Cycle Number | Mg/wt.% | Ca/wt.% |
|--------------|---------|---------|
| 1            | 0.11    | 0.042   |
| 2            | 0.062   | 0.0040  |
| 3            | 0.044   | 0.0030  |
| 4            | 0.016   | 0.0010  |
| 5            | 0.0078  | 0.00044 |
| 6            | 0.0031  | 0.00039 |

**3.5. Determination of the Optimal Ratio of Ethanol**

The final product obtained in this study were high-purity \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \) crystals, which needed to be dried. Figure 6A shows that when the filtered sample was dried at 120 °C for 6 h, the whole sample was still stuck together and there was lot of water on the surface. This was mainly because the system contained a large amount of \( \text{H}_2\text{SO}_4 \) covering the surface of the filtered sample, while its strong water absorption properties made it difficult to remove the water from the sample. The study found that the solubility of \( \text{MnSO}_4 \cdot \text{H}_2\text{O} \)
in ethanol was very small [32]. Therefore, ethanol was used to clean the H$_2$SO$_4$ covering the surface of the sample to obtain a dry sample, and part of the MgSO$_4$ impurity could be removed during the washing process. It can be seen from Figure 6B–F that the sample gradually became loose and dry as the ratio of ethanol increased (the volume ratio of ethanol to the original MnSO$_4$ solution). The sample gradually became loose and dry, and at 100% volume ratio of ethanol, loose and dry MnSO$_4$·H$_2$O crystals were obtained. Figure 7A shows that the yield of MnSO$_4$·H$_2$O crystals gradually decreased as the ratio of ethanol increased, which was because the increase in the ratio of ethanol led to an increase in dissolved MnSO$_4$ [33]. In addition, the MnSO$_4$ samples obtained with different ethanol ratios were placed in a laboratory environment, and the water absorption rate was explored to confirm the complete removal of H$_2$SO$_4$. As shown in Figure 7B, the water absorption rate of MnSO$_4$ samples obtained with different ethanol ratios increased with time while that of MnSO$_4$·H$_2$O crystals changed little with time at an ethanol ratio of 100% and 120%, respectively which proved that H$_2$SO$_4$ had been successfully removed. From these experiments, a 100% ethanol ratio was selected as the optimum value.

Figure 6. Sample photos of MnSO$_4$·H$_2$O after washing with different ethanol ratios: 0% (A), 40% (B), 60% (C), 80% (D), 100% (E) and 120% (F), and drying at 120 $^\circ$C for 6 h.

Figure 7. The effect of different ethanol ratios on the loss rate of MnSO$_4$·H$_2$O (A) and the water absorption rate of MnSO$_4$ (B).
3.6. High-Purity MnSO₄·H₂O Test Results

The MnSO₄·H₂O prepared in this study was tested with reference to the HG/T4823-2015 Manganese sulfate for battery materials; the ICP and AAS test results are shown in Table 3. It can be seen that the contents of all of the residual impurity ions had reached the test standards, especially those of Ca²⁺ and Mg²⁺ which were 0.002 wt% and 0.004 wt%, respectively, much lower than the test standards. In addition, the pH of the final product at (100 g/L, 25 °C) was 4.0, which was within the range of the standards (4.0–6.5) [4]. Furthermore, the experimental sample and commercial high-purity MnSO₄·H₂O crystals (99.99%) were analyzed by XRD. Figure 8 shows that the peak shapes of the two crystals were the same and consistent with the standard card (PDF# 81-0018 MnSO₄·H₂O), which further proved that the prepared product consisted of high-purity MnSO₄·H₂O crystals.

Table 3. Test standards and ICP/AAS results of high-purity MnSO₄·H₂O crystals.

| Inspected Item       | Standard Wt.% | Result Wt.% |
|----------------------|---------------|-------------|
| MnSO₄·H₂O            | ≥99           | 99.3        |
| Mn                   | ≥32           | 32.3        |
| Fe                   | ≤0.001        | 0.0005      |
| Zn                   | ≤0.001        | 0.004       |
| Cu                   | ≤0.001        | <0.001      |
| Pb                   | ≤0.001        | 0.0005      |
| Cd                   | ≤0.0005       | 0.0001      |
| K                    | ≤0.01         | <0.001      |
| Na                   | ≤0.01         | 0.002       |
| Ca                   | ≤0.01         | 0.002       |
| Mg                   | ≤0.01         | 0.004       |
| Ni                   | ≤0.005        | <0.001      |
| Co                   | ≤0.005        | 0.001       |
| insoluble residue    | ≤0.01         | 0.007       |
| pH (100 g/L, 25 °C)  | 4.0–6.5       | 4.0         |

Figure 8. XRD comparison between MnSO₄·H₂O crystals obtained in the experiment and commercial high-purity MnSO₄·H₂O crystals.
4. Conclusions

In this study, the OLI Stream Analyzer software was used to calculate the scaling trend of the industrial MnSO$_4$ solution and the MnSO$_4$$\cdot$H$_2$O yield at different temperatures with the ratio of H$_2$SO$_4$. The scaling trend revealed the reason why Ca$^{2+}$ and Mg$^{2+}$ could be separated. According to the MnSO$_4$·H$_2$O yield at different temperatures, the optimal temperature was determined to be 25 °C. In addition, the ratio of H$_2$SO$_4$ was explored through experimental comparative analysis and, combined with factors such as the yield of MnSO$_4$·H$_2$O crystals, the removal rate of Ca$^{2+}$ and Mg$^{2+}$, and the process cost, it was finally determined that the optimal volume ratio of H$_2$SO$_4$ was 30%. The optimal ratio of H$_2$O in the recrystallization experiment was 60%, which could effectively reduce the loss of MnSO$_4$·H$_2$O crystals and could better remove Ca$^{2+}$ and Mg$^{2+}$. After six cycles, the removal rates of Ca$^{2+}$ and Mg$^{2+}$ were 99.68% and 99.17%, respectively, and the yield of MnSO$_4$·H$_2$O crystals was 80.54%. The product was washed with ethanol, and the best volume ratio of ethanol was 100%. Finally, the product was tested and analyzed by XRD, ICP and AAS, and all the indicators of the sample met the requirements of high-purity MnSO$_4$·H$_2$O crystals. This study not only solved the problems of a low MnSO$_4$·H$_2$O crystals yield and complex processing in the recrystallization process, but also efficiently removed Ca$^{2+}$ and Mg$^{2+}$, which could be of great help in practical applications on the industrial-level production of high-purity MnSO$_4$·H$_2$O.

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