Evaporation-Cooling Coupling Method to Remove the Calcium and Magnesium Impurities in Leaching Solution of Manganese Ore

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Abstract. Calcium and magnesium impurities are the major impurities in the leaching solution of manganese ore, which will influence the produce of manganese sulfate. Solubility determinations of calcium sulfate, magnesium sulfate and manganese sulfate in water have been carried out from 273.15K to 373.15K. According to the basic data, a new method to remove Ca\(^{2+}\) and Mg\(^{2+}\) impurities in leaching solution has been put forward. The removal ratios of calcium and magnesium impurities could reach 48.5% and 39.2% using the new method, respectively.

Keywords: Manganese sulphate, Calcium impurity, Magnesium impurity, Crystallization.

1. Introduction
Manganese sulfate [1-3] is an important manganese salt chemical product, widely used in chemical industry, medicine, pesticide, coating, feed and many other fields. In inorganic industry, manganese sulfate is the basic raw material for the preparation of other manganese salts. In the medical industry, manganese is a necessary trace element in the human body. It exists in the pancreas, pituitary and bone as a component of various enzymes. It also participates in the hematopoietic process in the body to promote the oxidation of intracellular fat, and to prevent atherosclerosis. In agriculture, manganese sulfate is always regarded as a micronutrient fertilizer to promote the growth of crops and increase the yield by seed dipping, seed mixing, topdressing and leaf spraying. Besides, it is also a catalyst for plants to synthesize chlorophyll. In the coating industry, it is used to produce manganese linolate, drier and phosphating agent for metal products. In animal husbandry, manganese sulfate can be applied as feed additive to promote the development and fattening of livestock and poultry. In recent years, with the development of new energy lithium manganate battery technology, more and more attention has been paid to the production process of lithium manganate from high purity manganese sulfate. According to the uses, manganese sulfate products have been divided into several grades, and corresponding standards have different requirements on the content of impurities in products. The contents of various impurities are strictly required, especially for the grades of battery, medicine, food additives, feed additives. In industry, manganese sulfate is usually prepared from manganese ore stone [4-8], which contains calcium, magnesium, potassium, sodium, aluminum, heavy metal as impurities [9-11]. The process of preparation...
mainly includes reduction reaction, leaching, impurity removal, concentration and crystallization, etc. The key step of the preparation process of manganese sulfate is the removal process, directly determining the grade and market price of manganese sulfate products. Among metal impurities mentioned above, calcium and magnesium are the ones most difficulty to remove due to their similar properties to manganese. According to the literatures [12], calcium and magnesium impurities are always removed by high temperature crystallization, chemical precipitation or solvent extraction. In the high temperature crystallization process, the MgSO4 will be separated out above 393.15K. However, the use of this method is limited the experimental stage because of the high energy consumption and heavy loss of manganese sulfate. In the chemical precipitation method, fluoride is always used as a precipitant. The removal rate of calcium and magnesium impurities could reach more than 90%. But the fluorine remained in the system will cause great corrosion to the equipment, and also adversely affect the subsequent production processes. Finally, the development of solvent extraction is restricted the high price of extraction agent and complex post-processing. Therefore, it is necessary to develop a practical approach for Ca2+ and Mg2+ impurities removal.

In this work, the crystallization behavior of magnesium and calcium impurities has been investigated. Both evaporation crystallization and cooling crystallization have been studied to remove the magnesium and calcium impurities. According to the basic data, a cooling-evaporation coupling method was put forward to prepare industrial grade manganese sulfate product with low concentration of magnesium and calcium impurities.

2. Experimental Section

2.1. Materials
Leaching solution of manganese ore stone was provided by Daxin manganese ore branch of CITIC Dameng Mixing Industries Co., Ltd. Calcium sulfate, magnesium sulfate and manganese sulfate are obtained from Tianjin Guangfu fine chemical industry research institute, with purity greater than 99.0%. The metal composition of the solutions and products in this work were all determined by inductively coupled plasma emission spectrometer (ICP, Ultima Expert, France).

2.2. Crystallization experiments
Solubility of calcium sulfate, magnesium sulfate and manganese sulfate in water from 273.15K to 373.15K have been determined using a static method[13-16]. Based on these solubility data, the crystallization behaviors were explored. The cooling crystallization and evaporation experiments have been carried out. The cooling rate and evaporation rate were investigated systematically. The contents of Mn2+, Ca2+ and Mg2+ in manganese sulfate product and crystalline mother solution were determined by the inductively coupled plasma emission spectrometer. According to the results, a new method has been proposed to prepare manganese sulfate with low magnesium and calcium impurities. Then the process conditions were optimized. For convenience of control, the evaporation was conducted at 373.15K under negative pressure by a rotary evaporation instrument (type RC2, ICK, Germany). The cooling temperature was set as 275.15K, which was controlled by a heating and cooling bath (type F12, Julabo Technology (Beijing) Co., Ltd., China, temperature stability ±0.05 K).

3. Text Results and Discussion

3.1. Solubility results
The solubility data of calcium sulfate, magnesium sulfate and manganese sulfate in water at different temperatures were given in Table1 and plotted in Figure 1. It can be seen that, the solubility of these sulphates increased with the temperature rise until a certain temperature. After this point, the solubility began to decrease with the increasing of temperature. The corresponding temperatures of the maximum solubility for calcium sulfate, magnesium sulfate and manganese sulfate are 293.15K, 353.15K and 323.15K, respectively. Considering the process evaporation of leaching solution of manganese ore stone
to prepare the MnSO$_4$ product at 375.15K, most calcium impurity came from the crystallization of CaSO$_4$ due to the increasing temperature. While, the magnesium impurity was proposed to exist in the concentrated evaporation mother liquor. It can be seen from above that, the calcium and magnesium impurities will precipitate along with MnSO$_4$ during the evaporation process. Pretreatment to remove the impurities is essential.

### Table 1. The solubility data(C/%) of MnSO$_4$, MgSO$_4$, CaSO$_4$ in the water at different temperatures.

| T/K   | MnSO$_4$ | MgSO$_4$ | CaSO$_4$ |
|-------|----------|----------|----------|
| 273.15| 34.53    | 18.08    | 0.196    |
| 283.15| 37.41    | 21.89    | 0.215    |
| 293.15| 38.52    | 25.11    | 0.225    |
| 303.15| 38.49    | 27.54    | 0.232    |
| 313.15| 37.20    | 30.77    | 0.233    |
| 323.15| 36.13    | 33.05    | 0.228    |
| 333.15| 34.75    | 35.21    | 0.223    |
| 343.15| 33.61    | 35.44    | 0.22     |
| 353.15| 31.28    | 35.8     | 0.206    |
| 363.15| 28.92    | 34.55    | 0.179    |
| 373.15| 26.13    | 33.42    | 0.175    |

**Figure 1.** The solubility data of MnSO$_4$, MgSO$_4$, CaSO$_4$ in the water at different temperatures.

### 3.2. Removal experiments of calcium and magnesium impurities

According to the fundamental data, calcium impurity could be precipitated as CaSO$_4$ by raising temperature. And cooling crystallization is suitable for the removal of magnesium in the form of MgSO$_4$. Eight experiments have been carried out, and the results were shown in Table 2. For the evaporation crystallization, 2000mL leaching solution was evaporated at 373.15K in two steps. In the first step, the leaching solution (LS) was evaporated to oversaturated state. A small amount of product (P) precipitated, then the mother liquid (L) was evaporated to 50 baume degree. According to the results of experiment 1, 3 and 5, the calcium impurity mainly precipitated in the first step of the evaporation process. The removal rate of the calcium increased with the decrease of the evaporation rate. The maximum value was 48.5% when the evaporation rate was 5g H$_2$O/min. In the second step of evaporation (experiment 2 and 4), the calcium impurity in the manganese sulfate product was as low as 216ppm. While the magnesium impurity was concentrated after the removal of calcium. Cooling crystallization has been used to remove the magnesium impurity. The mother liquid of the evaporation experiment 3 (L3) was cooled down from 298.15K to 275.15K. It can be seen from the experiment 6, 7 and 8 that, the magnesium impurity precipitated during the cooling crystallization. By comparing the impurity consents
of L6, L7, L8 and L3, it showed that removal rate of the magnesium impurity could reach 39.2% when the cooling rate was 0.4K/min.

Table 2. The contents of Mn$^{2+}$, Ca$^{2+}$ and Mg$^{2+}$ in manganese sulfate product and mother liquid obtained from crystallization experiments

| experiment number | crystallization method | crystallization condition | sample | C/ppm |
|-------------------|------------------------|----------------------------|--------|-------|
|                   |                        | evaporation rate(g H$_2$O/min) | Leaching solution(LS) | Mn$^{2+}$ | Mg$^{2+}$ | Ca$^{2+}$ |
| 1                 | E of LS                | 9.5                         | P1     | 325066 | 1544 | 898 |
| 2                 | E of L1                | 5                           | L1     | 193620 | 5086 | 264 |
| 3                 | E of LS                | 5                           | P2     | 320533 | 2807 | 743 |
| 4                 | E of L3                | 5                           | L2     | 143200 | 6880 | 926 |
| 5                 | E of LS                | 3.5                         | P3     | 336200 | 866 | 1669 |
| 6                 | E of L3                | 3.5                         | L3     | 196320 | 5776 | 216 |
| 7                 | E of L3                | 0.8                         | P4     | 321066 | 2860 | 287 |
| 8                 | E of L3                | 0.2                         | L4     | 144510 | 6953 | 850 |
|                   |                        | cooling rate(K/min)         |        |        |        |        |
| 1                 | C of L3                | 0.8                         | P5     | 335989 | 887 | 1658 |
| 2                 | C of L3                | 0.4                         | L5     | 195036 | 5792 | 221 |
| 3                 | C of L3                | 0.4                         | P6     | 302233 | 6560 | 90 |
| 4                 | C of L3                | 0.4                         | L6     | 192400 | 3564 | 231 |
| 5                 | C of L3                | 0.2                         | P7     | 293210 | 8525 | 83 |
| 6                 | C of L3                | 0.2                         | L7     | 193202 | 3216 | 223 |
| 7                 | C of L3                | 0.2                         | P8     | 300918 | 7963 | 85 |
| 8                 | C of L3                | 0.2                         | L8     | 193202 | 3565 | 228 |

* E represents the evaporation crystallization, C represents the cooling crystallization, P is product, L is the mother liquid of crystallization.

4. Conclusion
The solubility data of calcium sulfate, magnesium sulfate and manganese sulfate in water at different temperatures have been determined. The solubility all raised with the temperature until the maximum value, then decreased with the increasing temperature. Basing on above fundamental data, a cooling-evaporation coupling method has been proposed to remove the magnesium and calcium impurities in leaching solution of manganese ore. Calcium impurity could be precipitated as CaSO$_4$ by raising temperature. And magnesium impurity was then removed by cooling crystallization. The contents of impurities were noticeably decreased by this method. The exploration in this work has important guiding significance for industrial production of manganese sulfate. Whereas, a part of manganese sulfate was precipitated during the cooling process. The post-processing for these intermediate products will be studied in our follow-up work.

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