

# A novel method to remove $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ impurities from manganese sulfate solution

Zefang CHENLI<sup>1, a</sup>, Fang LIAN<sup>1, b</sup> and Laijun MA<sup>1, c</sup>

<sup>1</sup> School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, P.R. China

<sup>a</sup>994149337@qq.com, <sup>b</sup>lianfang@mater.ustb.edu.cn, <sup>c</sup>malj4@163.com

**Keywords:** Manganese sulfate; Purification; Barium fluoride; Recovery

**Abstract.** Presently, the preparation of high pure manganese sulfate solution shows a long and complex process with low efficiency from the low grade manganese ore. The complete removal of calcium and magnesium ions coordinating with high recovery rate of manganese becomes one of the challenges for the conventional preparation of manganese sulfate. In the paper, the general removal methods of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  including crystallization, electrolysis, extraction and chemical precipitation were reviewed at first. Moreover, a novel approach was proposed herein with the aid of theoretical calculation, in which  $\text{Ba}(\text{OH})_2$  was used to adjust the pH value of manganese sulfate solution and  $\text{BaF}_2$  was used to completely remove  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The initial experimental results show that the calcium and magnesium removal rate reached 95.11% and 97.93%, respectively, and the recovery rate of manganese keeps 96%, which shows the prospect of industrial application.

## Introduction

With the development of energy and electronic materials, the demand of the manganese product with high purity is growing significantly such as battery grade manganese sulfate. Moreover, manganese sulfate is also the intermediate products for the other high pure manganese compounds and manganese salt [1]. So far, manganese sulfate usually prepared from the low grade manganese ore through leaching by sulfuric acid and subsequent purifying of the leach liquor. With a constant decrease of manganese ore grade, the complex mineral composition results in cumbersome purification process and low economic benefit. A large amount of manganese residual was abandoned, which causes the waste of manganese resources and the potential contamination to the environment. Furthermore, in the purification process  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  are easy to form saturated solution and generate crystal, which leads to pipe blockage. So The complete removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  coordinating with high manganese recovery rate in purification is of great importance to improve the economic and environmental benefit. In the paper, the commonly accepted removal methods of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  will be compared at first, including crystallization, electrolysis and extraction and chemical precipitation method. And with the aid of the theoretical calculation analysis, a novel approach was proposed, i.e.,  $\text{Ba}(\text{OH})_2$  was employed to adjust the pH value of manganese sulfate solution for avoiding the introduction of new impurity, and then  $\text{BaF}_2$  was applied for removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The recovery rate of manganese and effect of the impurity removal were characterized via chemical titration and ICP test, respectively.

## State-of-the-art of purification technology for Ca and Mg removal from manganese sulfate solution

### Crystallization

Based on the precipitation-solution equilibrium for insoluble balance system, the addition of the ions cause the fluctuation of the balance and change the solubility of the insoluble electrolyte such as the dissociation equilibrium of the weak electrolyte solution [2]. Benrath V A. [3] studied the effect of  $\text{MgSO}_4$  and  $\text{MnSO}_4$  on their solubility, which shows that the solubility of the substance will reduce with the increasing of the solubility of the other substance. Helen E.Farrah [4] also studied the

solubility of  $\text{CaSO}_4$  in  $\text{MnSO}_4$  solution, in which it is found that when the temperature is lower than  $80^\circ\text{C}$ , the solubility of  $\text{CaSO}_4$  increases with increased concentration of sulfuric acid solution, but decreases with increased concentration of manganese ions. Therefore, it is feasible theoretically to decrease the solubility of  $\text{CaSO}_4$  and  $\text{MgSO}_4$  by increasing the concentration of  $\text{MnSO}_4$  in solution, which provide a route to removal of magnesium and calcium. But unfortunately the purification should be repeated for the manganese sulfate solution with high concentration of magnesium and calcium, which leads to a sharp decrease of manganese recovery rate. Moreover,  $\text{MnSO}_4$  and  $\text{MgSO}_4$  will generate eutectic or mixed crystal, which contribute to the fluctuation of the solubility of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Initially, our research group has tried to improve the manganese concentration by adding some manganese sulfate in manganese ore leaching solution in order to reduce the relative concentration of calcium and magnesium impurity. But the experimental results show that the concentration of calcium and magnesium ions did not significantly reduced, which indicated that the crystallization method to remove calcium and magnesium ions from manganese sulfate should be further optimized.

Yuan Mingliang [5] analysed the  $\text{MnSO}_4\text{-MgSO}_4\text{-H}_2\text{O}$  phase diagram proposed by Benrath. The residual manganese sulfate in solution was controlled to be 5% by adjusting the evaporation capacity of water. Li Xuanhai [6] studied the effects of the concentration of the feeding liquid, operating temperature, keeping time and stirring intensity on the crystallization rate of manganese sulfate in high temperature crystallization methode. It is found that when the temperature is below  $27^\circ\text{C}$ , the solubility of manganese sulfate increases with the increase of temperature, while it will gradually decrease with an increase of temperature above  $27^\circ\text{C}$ , especially higher than  $100^\circ\text{C}$ . The solubility curves of manganese sulfate at high temperature are shown in Fig.1. In cases, precipitate at high temperature occurs for the manganese sulfate solution with low concentration of Mn, which suggests a new way to purification with saving energy and reducing consumption.

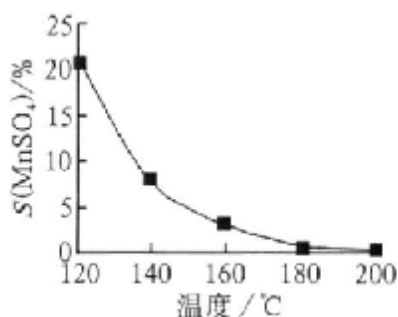


Fig.1 The temperature-dependence curve of  $\text{MnSO}_4$  solubility

## Electrolysis

Manganese sulfate solution with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  impurities is electrolyzed and is transformed into anodic product (manganese oxide) or cathode product [7] (electrolytic manganese metal), and then the as-obtained product is washed and dissolved in sulfuric acid, finally further removal of calcium and magnesium is performed to prepare manganese sulfate solution with high purity. In the comparison, anode product method can significantly improve the current efficiency and reduce energy consumption than Cathode product method, the calcium and magnesium content can be reduced to  $3.0\mu\text{g/g}$ . However, electrolysis method to prepare high purity manganese sulfate presents long process flow, low efficiency and high energy consumption. And high concentration of heavy metals and calcium and magnesium impurities in manganese sulfate solution will reduce the hydrogen evolution potential and lessens the purity of the electrolytic products.

## Chemical precipitation

Some chemical agents are used to precipitate with calcium and magnesium ions, which is based on the principle of the different ionic compound with varieties of solubility in the solution. The difficulty of the process is to ensure that the precipitation agent and the precipitate rarely react with or absorb the manganese ions.

Chen Lijuan [8] employed  $\text{MnF}_2$  to remove Ca and Mg, and the removal rates of Ca and Mg impurities were 97% and 98.3%, respectively. Bao Xinjun [9] has done the process optimization. The optimal technical parameter and procedure is as follows: the  $\text{MnSO}_4$  solution concentration is increased to 600g/L, the amount of  $\text{MnF}_2$  addition is 1.2 times of the theoretical one.  $\text{MnF}_2$  was added into the solution by the separated two lots at 90°C. The Experimental results show that the precipitation rate of  $\text{Ca}^{2+}$  is higher than 95%, and the precipitation rate of  $\text{Mg}^{2+}$  reach 87.04%. Moreover, it is feasible to use  $\text{MnF}_2$  as the precipitant to remove Ca and Mg from Manganese sulfate solution due to its pH value close to the one of manganese sulfate solution. Li Junqi [10] used chelating agent to precipitate calcium and magnesium ions as  $\text{MgY}$  and  $\text{CaY}$  (Y is chelating agent ion), respectively. The purification depends on the stirring intensity, pH value, the amount of chelating agent and the different of adding ways. While, Zheng Wenjun [11] used  $\text{NH}_4\text{F}$  to remove Ca and Mg ions before the carbonized treatment of the solution. The results showed that the residual Ca reaches 1 mg/L, but the concentration of  $\text{Mg}^{2+}$  had a little change before and after the carbonized treatment. It indicated that most of magnesium ions did not participate in the precipitation reaction and still kept in the mother liquor. Therefore, it is necessary to further optimize the conditions of carbonization in order to prepare manganese sulfate with high purity.

Chemical precipitation method to remove Ca and Mg impurities shows the advantages of simple operation, short duration, and high removal effectivity of calcium and magnesium ions. But few attention is attracted to the manganese recovery rate in the purification process. In our paper, chemical precipitation method was considered to obtain the complete removal of calcium and magnesium ions coordinating with high recovery rate of manganese, and the process parameters were optimized with the aid of the theoretical calculation analysis.

#### Extraction

Liu Honggang [12] reported the extraction method i.e. the roasting-leaching-P507 extracting to remove calcium and magnesium ions from GuangXi low grade manganese ore. The results showed that the extraction rates of Mg and Ca were 72.06% and 48.97% respectively, and the lost rate of Mn was 6.35% when 30% P507 and 70% sulfonated kerosene were mixed as extraction agen. Moreover, it avoids the problems in the traditional fluoride precipitation method. But the purity of the production can not meet the requirements of battery grade manganese sulfate.

#### Study of a novel method to remove Ca and Mg by $\text{BaF}_2$

In the paper,  $\text{BaF}_2$  was employed as a precipitating agent to remove Ca and Mg from manganese sulfate solution. The appropriate reaction conditions was determined through theoretical calculation using system ionization and dissolution equilibrium to ensure the high recovery rate of manganese. The concentration of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the manganese sulfate solution is shown in Table 1.

Table 1 The concentration of Ca and Mg in the manganese sulfate solution		
Impurity ions	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$
concentration/[mmol/L]	3.354	16.658

The impurity ions of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  can be precipitated by fluoride, and their fluoride precipitation in the solution reaches the dissolution equilibrium as shown in Eq. 1-4.



To ensure that the  $Mn^{2+}$  does not react with the precipitation, the residual F<sup>-</sup> in solution should not precipitate in the form of  $MnF_2$  as by-product. Since  $MnF_2$  saturation concentration in water is 1.05g/100g, the equilibrium concentration of F<sup>-</sup> can be obtained as  $[F^-]_{aq}=0.284\text{mol/L}$  according to the Eq. 4. In this case, considering the solubility product constant of  $CaF_2$  and  $MgF_2$ [13], the equilibrium concentrations in solution were calculated and shown in Table 2.

Table 2 The theoretical removal rate of Ca and Mg		
Impurity ions	$Ca^{2+}$	$Mg^{2+}$
Equilibrium concentration[ mol/L]	$3.35 \times 10^{-10}$	$8.06 \times 10^{-8}$
Removal rate %	99.999990	99.999516

The concentration of F<sup>+</sup> required for precipitation is:

$$[F^-]_s = \sum n^*([M^{n+}] - [M^{n+}]^0) = 0.040\text{mol/L} \quad (5)$$

The F<sup>+</sup> is easy to hydrolyze in the water as shown in Eq. 6. So part of the fluorine is ready for the precipitation of calcium and magnesium, and the other part maintains the equilibrium of ions in the solution. The concentration of F<sup>+</sup> except for precipitation is represented as  $\Delta[F^-]$  as shown in Eq. 8.



$$K = [H^+] \cdot [F^-] / [HF] \quad (7)$$

$$\Delta[F^-] = [F^-]_{aq} + [HF] \quad (8)$$

$$\Delta[F^-] = [F^-]_{aq} + [H^+][F^-]/K = 0.284 \times (1 + 10^{\text{pH}+3.17}) \quad (9)$$

According to Eq. 5 and Eq. 9, the concentration of fluoride ion for the system was calculated to guarantee the removal of Ca and Mg under different pH value and shown in Table 3.

Table 3 The theoretical F <sup>-</sup> concentration to remove Ca and Mg under different pH value							
PH	1.0	1.5	2.0	2.5	3.0	3.5	4.0
$[F^-][\text{mol/L}]$	42.331	13.608	4.525	1.652	0.744	0.457	0.366

Taking into account the operability and economical efficiency, the pH value of the solution is determined to be between 3 to 4. In the study,  $Ba(OH)_2$  was used to adjust the pH value of manganese sulfate solution, then  $BaF_2$  was introduced for the complete removal of Ca and Mg ions. It is important to note that  $Ba^{2+}$  will react with sulfuric acid, which appears in high concentration in the leaching solution. So the use of the precipitation agent can not bring the impurities to the system. Moreover, the precipitant of barium sulfate shows the large particles, which is easy to filter without side reaction. The experimental results showed that the removal rate of Mg and Ca reach 97.93% and 95.11% respectively, and the recovery rate of Mn is above 96%. The effect of temperature, stirring intensity and duration of the process will be further studied in our following work.

## Conclusion

The paper summarizes the generally accepted methods of removal of Ca and Mg for the high pure manganese sulfate. The chemical precipitation method has the advantages of simple operation, rapid response, and high removal efficiency of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Furthermore, a novel method is proposed to adjust the pH value using  $\text{Ba}(\text{OH})_2$  and completely remove of impurities using  $\text{BaF}_2$ . The process parameters such as the pH value and the amount of  $\text{BaF}_2$  were determined through the theoretical calculation analysis. The results show that the proposed method not only improves the removal rate of Mg and Ca 97.93% and 95.11% respectively, and also guarantees the high manganese recovery of more than 96%. The research indicates that it is feasible to realize the clean produce of high pure manganese sulfate from low grade manganese ore with short process, which promotes the sustainable development of the manganese resource industry. In our following work, we will focus on the process optimization to explore the efficient utilization of manganese resources.

## Acknowledgements

This work was financially supported by the National Science and Technology Pillar Program (2015BAB01B02).

## References

- [1] Tan Zhuzhong, Mei Guanggui, and Li Weijian. *Manganese metallurgy* [M]. Changsha: Central South University Press, 2004.
- [2] Zhong Guoqing, Zhu Yunyun. *Inorganic and Analytical Chemistry* [M]. Beijing: Science of Society, 2006.
- [3] Benrath V A. Uber mischkristalle in der vitriolreihe I [J]. Zeitschrift Furanorgaische und Allgemeine Chem emio, 1993, 216: 41~47.
- [4] Helen E.Farrah. Solubility of calcium sulfate salts in acidic man-ganese sulfate solutions from 30 to 105°C[J]. Hydrometallurgy, 2007, (86):13- 21.
- [5] Yuan Mingliang, Qiu Guanzhou. *An aqueous solution of manganese sulfate phase diagram of the principle of separation of magnesium sulfate crystallization* [J]. Journal of Central South University of Technology, 2003, 31(3): 212-214.
- [6] Li Xuanhai, Ji Dandan, and Su Haifeng. *Study on the production of manganese sulfate by high temperature crystallization method* [J]. Inorganic salt industry, 2010, 42(12): 16-19.
- [7] Chen Nanxiong, Liao Zanwei. *Effect of electrolyte composition on the production of electrolytic manganese metal* [J]. Manganese industry in China, 2008, 26(4): 5-8.
- [8] Chen Lijuan, Liu Dawei, Peng Tianjian, and etc. *Study on purification technology of manganese sulfate solution* [J]. Enterprise technology development, 2012, 31(4, 7): 128-129.
- [9] Bao Xinjun, Wang Zhijian, Liu Jibo, and etc. *Experimental study on the removal of calcium, magnesium and iron from the depth of industrial manganese sulfate* [J]. Mining and metallurgical engineering, 2013, 33(3): 90-93.
- [10] Li Junqi, Wang Hua, and Wu Fuzhong. *Study on the purification of manganese sulfate from desulfurization by-product* [J]. Chinese Journal of rare earths, 2004, 22(Album):529-533.
- [11] Zheng Wenjun, Shen Huiting, and Guo Kefei. *Experimental study on removal of impurities from manganese oxide ore slurry and preparation of products* [J]. Mining and metallurgical engineering, 2006, 26(1): 34-37.
- [12] Liu Honggang, Zhu Guocai. *Study on removal of calcium and magnesium by solvent extraction from leaching solution of manganese ore* [J]. Manganese industry in China, 2006, 26 (1): 37 - 34
- [13] Xia Yuyu, Zhu Yan, and Li Jie. *Handbook of chemistry laboratory* [M]. Beijing: Chemical Industry Press, 2015.