

# *Study on the Acidification Process to Prepare Industrial Grade Manganese Sulfate with Low Ca<sup>2+</sup> Content*

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**Abstract:** Manganese sulfate is an important chemical raw materials, which is always prepared by sulfuric acid leaching of manganese ore stone. The impurities in ore shall enter into the solution and product along with manganese, especially calcium and magnesium impurities. Solubility determinations of calcium in water and acid solution have been carried out from 303.15K to 373.15K. The calcium solubility increased with the addition of sulfate acid. The data also increased with the increase of temperature until 353.15-363.15K, then the values decreased after the peak. A new method to remove Ca<sup>2+</sup> impurity has been raised on base of the fundamental data. The removal ratio of Ca<sup>2+</sup> impurity was as high as 59%. Purity of manganese sulfate was higher than the industry standard.

## 1. Introduction

Manganese sulfate[1-3] is a significant precursor for the preparation of other manganese compounds, which are widely used in energy, medicine, fertilizer, feed, food, paper, catalyst and other industries. There are different uses depending on the purity of the manganese sulfate product. Manganese is a trace element essential to plants, animals and human, even a useful trace element for medium of microbes. It can usually be supplemented from the soils and the feed for plants and animals, respectively. Manganese sulfate can be manufactured through the reaction between manganese dioxide and sulfur dioxide or between potassium permanganate with sodium hydrogen sulfate and hydrogen peroxide. In the industry, the manganese sulfate is always obtained from manganese ore stone[4-8]. Firstly, manganese sulfate can be extracted into a leaching solution by sulfuric acid leaching process. Then, manganese sulfate raw material can be prepared through a process of evaporation crystallization. However, the impurities in ore will be leached out and precipitated along with manganese during the above processes, causing negative influences on the manganese sulfate electrolysis and the subsequent product preparation.

In recent years, electronic chemistry has developed rapidly. Manganese sulfate has get more attention as the main raw material of producing electronic chemicals such as electrolytic manganese, manganese dioxide and the manganese oxide, lithium cobalt nickel manganese oxide ternary positive electrode materials and lithium manganese oxide anode materials. As a result, high requirements have been put forward for the quality of manganese sulfate, especially for the content of impurities in manganese sulfate[9]. According to the literatures, the main impurity elements in manganese sulfate solution are calcium, magnesium, potassium, sodium, aluminum, heavy metal, etc.

Potassium and sodium impurities are always removed using precipitation or extraction method[10]. In the former method,  $K^+$  and  $Na^+$  can react with  $Fe^{3+}$  to form sodium jarosite and jarosite precipitation, respectively. In the later one, stable complexes are obtained between  $Mn^{2+}$  and complexing agent in the extractant. Both these  $K^+$  and  $Na^+$  impurities removal technologies are mature. Heavy metals impurities removal methods are mainly include manganese powder replacement, sulfide precipitation and adsorption method. As a kind of strong reducing agents, manganese can replace the heavy metals in the manganese sulfate solution. Insoluble heavy metals sulfides will generate by adding soluble sulfide[11]. Adsorption method uses heavy metal ions adsorbing material to adsorb and remove heavy metal ions. Relevant technologies have been successfully applied in industrial production. Magnesium and calcium are the main impurities in manganese leaching liquid. Crystallization, chemical precipitation, solvent extraction are the most commonly used methods. However, the properties of  $Ca^{2+}$  and  $Mg^{2+}$  are similar to  $Mn^{2+}$ , so it's difficult to decrease the  $Ca^{2+}$  and  $Mg^{2+}$  contents to the standard of high purity manganese sulfate. Fluorination precipitation and solvent extraction are the main removal methods for  $Ca^{2+}$  and  $Mg^{2+}$ [12]. Although removal effects are obvious, the high cost and new impurity doping restricted their development. Therefore, it is very necessary to develop a removal universally applicable process of  $Ca^{2+}$  and  $Mg^{2+}$  impurities.

In this work, the acidification process has been put forward to decrease the content of  $Ca^{2+}$  impurity in manganese sulfate product. The calcium sulfate solubility behavior in acid manganese sulfate solution has been observed at different temperatures. According to the basic data, sulfuric acid was used to decrease the calcium impurity concentration in the manganese sulfate product prepared by evaporation crystallization from leaching solution.

## 2. Experimental Section

### 2.1. Materials

Leaching solution of manganese ore was supplied by Daxin manganese ore branch of CITIC Dameng Mixing Industries Co., Ltd. The contents of  $Mn^{2+}$ ,  $Ca^{2+}$  and  $Mg^{2+}$  were 140200mg/L, 2459mg/L and 420mg/L, respectively, determined by inductively coupled plasma emission spectrometer(ICP, Ultima Expert, France). Concentrated sulfuric acid (mass fraction is 98.08%) used in the experiments was purchased from Taicanghushi reagent co., LTD. Calcium sulfate and manganese sulfate are obtained from Tianjin Guangfu fine chemical industry research institute, with purity greater than 99.0%.

### 2.2. Solubility Measurements of Calcium Sulfate

The static method[13-16] was used to determine the solubility of calcium sulfate. An excess of calcium sulfate was added into water and sulfuric acid solution with different concentration in jacketed glass flasks. A heating and cooling bath (type F12, Julabo Technology (Beijing) Co., Ltd., China, temperature stability  $\pm 0.05$  K) was applied to control the temperature of the solution. The

solution was stirred continuously for 6 hours. Then the suspension was settled down after the solid-liquid equilibrium was reached. The upper clear solution sample was filtered through a 0.2  $\mu\text{m}$  PTFE filter, weighted and dried in a vacuum drying oven at 323.15 K.

### 2.3. Preparation of Manganese Sulfate

The manganese sulfate has been prepared by evaporation of the manganese ore leaching solution at 375.15K. Different amounts of sulfuric acid were added during the process. The washing process has also been investigated according to the basic solubility data. The contents of  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in manganese sulfate product were determined by the inductively coupled plasma emission spectrometer. The influence of sulfuric acid on the crystallization of manganese sulfate and washing performance was observed systematically.

## 3. Results and Discussion

### 3.1. Solubility of Calcium Sulfate

The solubility data of  $\text{Ca}^{2+}$  in the given solutions at different temperatures are listed in Table1 and plotted in Figure 1. It can be seen that, the solubility of  $\text{Ca}^{2+}$  decreased with the increasing temperature. The influence of sulfuric acid on the solubility was remarkable: the data were larger than those in the absence of acid. Besides, the solubility raised with the temperature until the maximum value at 363.15K, 353.15K and 353.15K in the presence of  $\text{H}_2\text{SO}_4$  concentration of 3%, 5% and 7%, respectively. The data were in agreement with literature values[17]. Furthermore, except 363.15K, the solubility increased with the increasing of acid concentration at a given temperature. At 363.15K, the order of solubility changed due to the different solubility peaks.

Table 1: The solubility data of  $\text{Ca}^{2+}$  in the given solutions at different temperatures.

T/K	C( $\text{Ca}^{2+}$ )/%			
	C( $\text{H}_2\text{SO}_4$ )=0	C( $\text{H}_2\text{SO}_4$ )= 3%	C( $\text{H}_2\text{SO}_4$ )= 5%	C( $\text{H}_2\text{SO}_4$ )= 7%
303.15	0.060	0.075	0.079	0.081
313.15	0.058	0.092	0.095	0.095
323.15	0.058	0.100	0.106	0.110
333.15	0.057	0.123	0.138	0.145
343.15	0.050	0.15	0.165	0.178
353.15	0.051	0.192	0.213	0.231
363.15	0.049	0.228	0.185	0.135
373.15	0.045	0.120	0.128	0.132

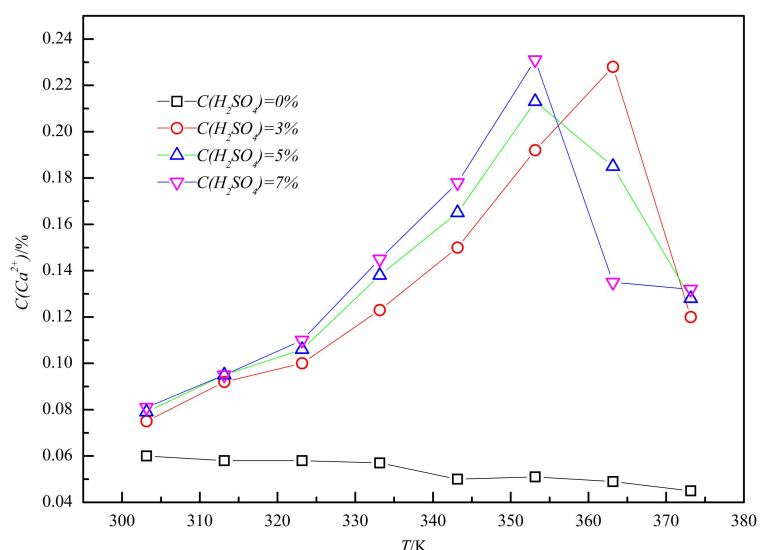


Figure 1: The solubility data of  $\text{Ca}^{2+}$  in the given solutions at different temperatures.

### 3.2. Optimization of Manganese Sulfate Preparation Process

The leaching solution of manganese ore was evaporated at 375.15K until the Baume degrees reached 50 degrees. Different amount of  $\text{H}_2\text{SO}_4$  have been added in the leaching solution. The results were listed in Table 2. It can be seen that, the concentrations of  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  decreased with the increasing of the addition amount of  $\text{H}_2\text{SO}_4$ . However, the concentration of  $\text{Mg}^{2+}$  raised, which can explain the decreasing of purity of manganese sulfate. When the concentration of  $\text{H}_2\text{SO}_4$  was lower than 7%, the purity of manganese sulfate could reach the industrial standard ( $\text{C}(\text{Mn}^{2+})=32\%$ ). In order to inspect the influence of acidification on the washing performance, saturated solution of manganese sulfate with 7%  $\text{H}_2\text{SO}_4$  has been prepared as washing solution. The product been washed was prepared from the leaching solution with 7% of  $\text{H}_2\text{SO}_4$ . According to the solubility value, the temperature was set at 353.15K to obtain the optimal dissolution of calcium. The data in Table 2 showed that, the  $\text{Ca}^{2+}$  impurity reduced to 308.6 ppm by a single washing process, 59% lower than the unwashed product (751 ppm). The content further decreased to 245.3 ppm after being washed twice. At the same time, the purity of product has been significantly improved. It is worth noting that the reduction of  $\text{Mg}^{2+}$  impurity was much less than that of  $\text{Ca}^{2+}$  impurity. This phenomenon could be attributed to the special solubility behavior of calcium sulfate in sulfuric acid solution.

Table 2: The contents of  $\text{Mn}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in manganese sulfate product obtained from evaporation.

	$\text{C}(\text{H}_2\text{SO}_4)/\%$	Washing times	Composition of product		
			$\text{C}(\text{Mn}^{2+})/\%$	$\text{C}(\text{Mg}^{2+})/\text{ppm}$	$\text{C}(\text{Ca}^{2+})/\text{ppm}$
Evaporation process	Leaching solution				
	5	0	32.4	1673	805
	7	0	32.1	1785	751
	15	0	29.5	1902	693
Washing process	washing solution				
	7	1	32.5	1585	308.6
	7	2	33.1	1349	245.3

## 4. Conclusions

The solubility of calcium sulfate in acid solution has been determined. The data indicated that the solubility of  $\text{Ca}^{2+}$  increased with the increase of temperature and sulfate acid concentration. The dissolution behavior was applied to purify the manganese sulfate products prepared from leaching solution of manganese ore. Remarkable effects was shown on the  $\text{Ca}^{2+}$  impurity removal. Relatively optimal preparation and cleaning processes have been inspected. The work in this article is greatly guiding significance for industrial production of manganese sulfate.

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