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# Separation of manganese from calcium and magnesium in sulfate solutions via carbonate precipitation

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**Abstract:** The separation of manganese from sulfate solutions containing 14.59 g/L $Mn^{2+}$, 1.89 g/L $Mg^{2+}$ and 1.54 g/L $Ca^{2+}$ was preformed successfully by carbonate precipitation. The results of thermodynamic analysis and tests indicate that carbonate precipitation holds better selectivity for manganese over magnesium than hydroxide precipitation and the feeding method is the most critical factor for minimizing the co-precipitation of calcium and magnesium. Furthermore, with adding $MnSO_4$ solution to $NH_4HCO_3$ solution, the effects of the initial $NH_4HCO_3$ concentration, $NH_4HCO_3$ amount, solution pH value, reaction temperature and time on carbonate precipitation were evaluated and the optimum precipitation conditions were obtained. Under the optimum conditions, the precipitation rates of $Mn^{2+}$, $Ca^{2+}$ and $Mg^{2+}$ are 99.75%, 5.62% and 1.43%, respectively. Moreover, the prepared manganese carbonate was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) equipped with energy-dispersive X-ray spectroscopy (EDX). The results demonstrate that the product can be indexed to the rhombohedral structure of $MnCO_3$.

**Key words:** carbonate precipitation; separation; manganese; calcium; magnesium

## 1 Introduction

Manganese sulfate solutions derived from the hydrometallurgical process of low-grade manganese ore usually contain a certain amount of calcium and magnesium ions, which affect the subsequent recovery of manganese. Generally, it is difficult to remove calcium and magnesium ions from the $MnSO_4$ solutions, because the chemical properties of $Ca^{2+}$ and $Mg^{2+}$ are similar to those of $Mn^{2+}$. Till now, there are mainly three purification methods of $Ca^{2+}$ and $Mg^{2+}$ including variable temperature crystallization, chemical precipitation and solvent extraction. Each method has its own advantages and disadvantages. Variable temperature crystallization of manganese sulfate solutions is simple and easy to operate, but difficult to avoid the formation of the mixed crystal of $MnSO_4$ and $MgSO_4$ [1−3]. Chemical precipitation method is of great significance in the purification process of manganese solutions. For instance, fluoride, oxalate, phosphate and carbonate are used as precipitants of calcium and magnesium ions [4−7]. Especially, fluorides such as $MnF_2$ and $NH_4F$ are widely used because the solubility product constants of $CaF_2$ and $MgF_2$ are far lower than that of $MnF_2$ at 25 °C [8]. However, fluorination precipitation method cannot evade the drawbacks of difficult sedimentation, strong corrosion and environmental pollution. Solvent extraction can be used to separate manganese selectively from other metals and avoid above drawbacks of fluorides, but the reagent costs may limit its application for the removal of calcium and magnesium ions from manganese-bearing solutions [9−11]. Therefore, in view of today’s economic and environmental concerns, chemical precipitation method using green reagents will be a future trend in the purification processes of manganese solutions.

In recent years, studies on separation and recovery of manganese from solutions containing one or more metals such as iron, cobalt, nickel, zinc, copper, calcium and magnesium have been carried out by hydroxide precipitation, carbonate precipitation or oxidative precipitation [12−17]. Hydroxide precipitation alone is easy to cause co-precipitation of manganese and

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magnesium due to its poor selectivity. Oxidative precipitation with $SO_2/O_2$ (air) is highly selective for the recovery of manganese ions in the form of $Mn_2O_3$ or $MnO_2$, but the disadvantages of this approach are the need for very precise feed control and the use of toxic and corrosive $SO_2$ gas. As for carbonate precipitation, previous research reported the separation of manganese and magnesium ions utilizing ammonia solution and carbon dioxide or ammonium bicarbonate [18]. More recently, PAKARINEN and PAATERO [19] also reported that carbonate precipitation is a fast and effective approach for manganese recovery and iron separation from sulfate solutions, with $Na_2CO_3$ or combined $CaCO_3$ and $O_2$ (air) oxidation due to their relatively low prices, good filtration and leaching properties. However, to the best of our knowledge, carbonate precipitation method has not been investigated intensively for the synthesis of $MnCO_3$ associated with the removal of calcium and magnesium ions.

In this study, ammonium bicarbonate was used to precipitate manganese ions for the preparation of manganese carbonate product while calcium and magnesium ions remained in solution. Then, the remaining solution could be used to produce ammonium sulfate fertilizer containing calcium and magnesium. Moreover, the obtained manganese carbonate is a profitable product, which can be widely used for the production of manganese zinc magnetic ferrite, non-ferrous alloys, paints, fertilizers, dietary additives, welding electrodes and other manganese compounds [20,21]. The aim of this work was to investigate the selectivity for manganese over calcium and magnesium by carbonate precipitation and effects of several experimental variables such as the initial concentration of $NH_4HCO_3$, solution pH value, feeding methods, $NH_4HCO_3$ amount, reaction temperature and time on carbonate precipitation. Then, the optimum experimental conditions for the synthesis of manganese carbonate and minimizing co-precipitation of calcium and magnesium were determined.

## 2 Theory

As we all know, there are two important dissociation equilibria between carbonic acid, bicarbonate ion and carbonate ion in the carbonate solution.

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+,\ K_1=10^{-6.38} \tag{1}$$

$$HCO_3^- \rightleftharpoons CO_3^{2-} + H^+,\ K_2=10^{-10.32} \tag{2}$$

where $K_1$ and $K_2$ are the first and second dissociation constants of carbonic acid at 25 °C, respectively [8]. Then, according to the relevant knowledge of solution chemistry, the mass balance of carbon element can be expressed by the following equations:

$$c(\mathrm{C})_\mathrm{t} = c(CO_3^{2-}) + c(HCO_3^-) + c(H_2CO_3) \tag{3}$$

$$c(\mathrm{C})_\mathrm{t} = c(CO_3^{2-}) \cdot \varPhi_\mathrm{c} \tag{4}$$

$$\varPhi_\mathrm{c} = 1 + 10^{\mathrm{p}K_2 - \mathrm{pH}} + 10^{\mathrm{p}K_1 + \mathrm{p}K_2 - 2\mathrm{pH}} \tag{5}$$

where $c(\mathrm{C})_\mathrm{t}$ represents the total concentration of carbon element in aqueous solution (mol/L), $c(CO_3^{2-})$, $c(HCO_3^-)$ and $c(H_2CO_3)$ are the concentrations of carbonate ion, bicarbonate ion and carbonic acid, respectively, (mol/L), $\varPhi_\mathrm{c}$ is the coefficient of total concentration of carbon element in the system and its value can be calculated by Eq. (5), $\mathrm{p}K_1$ and $\mathrm{p}K_2$ are the negative logarithms of $K_1$ and $K_2$, respectively [22].

On one hand, the carbonate precipitation of divalent metal ions and the solubility product constant of related carbonate salts can be expressed by the following equations:

$$Me^{2+} + CO_3^{2-} \rightleftharpoons MeCO_3 \tag{6}$$

$$K_{\mathrm{sp,MeCO_3}} = c(Me^{2+}) \cdot c(CO_3^{2-}) \tag{7}$$

$$\lg c(Me^{2+}) = \lg K_{\mathrm{sp,MeCO_3}} - \lg c(CO_3^{2-}) \tag{8}$$

where $c(Me^{2+})$ represents the concentration of divalent metal ion such as $Ca^{2+}$, $Mg^{2+}$ or $Mn^{2+}$ (mol/L); $K_{\mathrm{sp,MeCO_3}}$ refers to the solubility product constant of $CaCO_3$, $MgCO_3$ or $MnCO_3$.

Applying Eqs. (4) and (5), and $\mathrm{p}K_1$ and $\mathrm{p}K_2$ values to Eq. (8), the relationship between equilibrium concentrations of divalent metal ions and the pH value in aqueous solution can be presented as follows:

$$\begin{aligned}\lg c(Me^{2+}) = {} & \lg K_{\mathrm{sp,MeCO_3}} + \\ & \lg(1 + 10^{10.32-\mathrm{pH}} + 10^{16.70-2\mathrm{pH}}) - \lg c(\mathrm{C})_\mathrm{t}\end{aligned} \tag{9}$$

where the $K_\mathrm{sp}$ values of $CaCO_3$, $MgCO_3$ and $MnCO_3$ are $10^{-8.54}$, $10^{-5.17}$ and $10^{-10.63}$, respectively [8].

On the other hand, hydroxide precipitation of divalent metal ions may occur with the solution pH value increasing according to the following equations:

$$Me^{2+} + 2OH^- \rightleftharpoons Me(OH)_2 \tag{10}$$

$$\lg c(Me^{2+}) = \lg K_{\mathrm{sp,Me(OH)_2}} + 2\mathrm{p}K_\mathrm{W} - 2\mathrm{pH} \tag{11}$$

where the $K_\mathrm{sp}$ values of $Ca(OH)_2$, $Mg(OH)_2$ and $Mn(OH)_2$ are $10^{-5.26}$, $10^{-11.25}$ and $10^{-12.72}$, respectively [8], $\mathrm{p}K_\mathrm{W}$ refers to the negative logarithm of the ionic activity product constant of water and its value is 14 at 25 °C.

## 3 Experimental

### 3.1 Materials

The main material of experiments was manganese sulfate solution obtained by acid leaching of low-grade