



Efficient preparation of magnesium bicarbonate from magnesium sulfate solution and saponification-extraction for rare earth separation

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Abstract: To realize the recycling of magnesium sulfate wastewater in the hydrometallurgy and separation process of Baotou mixed rare earth (RE) concentrate, the research on preparation of magnesium bicarbonate ($\text{Mg}(\text{HCO}_3)_2$) solution from magnesium sulfate solution by CO_2 carbonation, extraction separation and transformation of RE sulfate solution by saponified HDEHP was investigated. The key influencing factors and carbonation mechanism in the preparation of $\text{Mg}(\text{HCO}_3)_2$, and the distribution of RE, calcium and magnesium elements in the saponification extraction were systematically studied. The results show that the conversion of $\text{Mg}(\text{HCO}_3)_2$ during carbonation is inhibited by calcium sulfate, but promoted by increasing the concentration of magnesium sulfate and decreasing the carbonation temperature. Under the optimized conditions, $\text{Mg}(\text{HCO}_3)_2$ solution with impurities (such as Fe, Al and Si) of less than 15 mg/L is prepared stably and efficiently, and the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ is more than 95%. After multi-stage cascade extraction of RE sulfate solution, the RE extraction recovery is greater than 99.5%. Calcium sulfate crystals do not precipitate during the process, and the raffinate phase is magnesium sulfate solution that is used for the preparation of $\text{Mg}(\text{HCO}_3)_2$ solution.

Key words: carbonation; magnesium bicarbonate; rare earth sulfate solution; saponification extraction; calcium sulfate

1 Introduction

Rare earth elements (REEs) exhibit excellent physical and chemical properties such as magnetism, light, electricity and catalysis due to their unique 4f sublayer electronic structure [1–8]. REEs are known as “modern industrial vitamins” and “treasure house of new materials in the 21st century”. At present, REEs are mainly extracted and separated from RE minerals. Typical RE minerals include bastnaesite, monazite, xenotime and its mixed minerals, as well as ion-adsorption RE minerals [9–11]. Baotou Bayan Obo RE ore of

China is the largest light RE reserve in the world. It is mainly a mixture of bastnaesite and monazite, which is recognized as a refractory ore in the world. ZHANG et al [12] and WANG et al [13] successfully developed the classical process of sulfuric acid roasting for treating Bayan Obo RE concentrate. The process has been widely used in large-scale industrial production of mineral-type RE ores such as Bayan Obo RE concentrate in China (more than 90% of Bayan Obo RE concentrate is treated by this process) and the monazite from Mount Weld in Australia.

Researchers have studied the process optimization and improvement of the sulphuric acid

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roasting for the treatment of RE minerals distributed in the world. DEMOL et al [14] used monazite concentrate from placer deposits in Australia as raw material to study the effect of different roasting temperatures on the decomposition process of sulfuric acid roasting. SADRI et al [15] studied the decomposition process of monazite concentrate in Iran by sulfuric acid roasting method, and improved the recovery rates of cerium, lanthanum, neodymium and thorium by optimizing the temperature, time and mass ratio of sulfuric acid to monazite concentrate. CHEN et al [16] studied the leaching kinetics of RE, iron and phosphorus in sulphuric acid system, and reduced solid waste by improving the selective leaching efficiency of REEs. HUANG et al [17] studied the extraction behavior of REEs with HDEHP and HEH/EHP mixed extractants in sulfuric acid system and found a positive synergistic effect. CHENG et al [18] derived the minimum extraction amount in the extraction and separation process of two components of REEs based on the mass balance and extraction balance, which provided a basis for the design of extraction process. KUANG et al [19] synthesized a new extraction agent and applied it to the selective extraction of Ce(IV) in sulfuric acid system. WANG et al [20] described a novel process for conducting the extraction and recovery of cerium, fluorine, and thorium from a bastnaesite sulfuric leaching solution using HEH(EHP) as the solvent.

At present, magnesium oxide powder is usually used to adjust acidity or saponify organic phase in the extraction transformation and separation of RE sulfate solution. However, some bottleneck problems need to be solved urgently. For example, the solid–liquid reaction speed is slow, impurities such as aluminum and iron are extracted and enriched, and magnesium sulfate wastewater containing supersaturated calcium sulfate is easy to scale and difficult to recycle. In view of the above issues, HUANG et al [21–26] developed and applied the original technology of saponification extraction and separation of REEs with $\text{Mg}(\text{HCO}_3)_2$ solution in the chlorination system, and on this basis, proposed a new process of hydrometallurgy and separation for the treatment of mineral-type RE concentrate with $\text{Mg}(\text{HCO}_3)_2$ solution in the

sulfuric acid system [27,28]. Since the existent form, reaction mechanism and behavior of RE, magnesium and calcium ions in sulfuric acid system are more complex than those in chlorination system, it is necessary to solve the problems of efficient preparation of $\text{Mg}(\text{HCO}_3)_2$ in sulfuric acid system and directional regulation of element distribution in extraction process.

In this work, the effects of calcium sulfate, additives, slurry concentration and temperature on the preparation of $\text{Mg}(\text{HCO}_3)_2$ in sulfuric acid system were studied, and the carbonation mechanism of efficient transformation of $\text{Mg}(\text{HCO}_3)_2$ was clearly revealed. In addition, the control conditions for efficient conversion of pure $\text{Mg}(\text{HCO}_3)_2$ were obtained, and the saponification extraction and separation transformation technology of $\text{Mg}(\text{HCO}_3)_2$ solution in RE sulfate solution was studied. The distribution law of REEs, calcium and magnesium elements under the extraction equilibrium condition was investigated, and then the scale formation of calcium sulfate was eliminated by element directional regulation. The separation and efficient extraction transformation of REEs from calcium and magnesium were realized.

2 Experimental

2.1 Materials

Magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), calcium oxide (CaO) and calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were analytically pure and produced by Sinopharm group. The CO_2 gas used in this study was industrial grade and derived from gas center of General Research Institute for Nonferrous Metals. HDEHP was purchased from Shanghai Laias Chemical Co., Ltd. (purity>99%), and was diluted with sulfonated kerosene at volume ratio of about 1:1 to obtain 1.5 mol/L extractants. The RE sulfate solution was provided by Gansu Rare Earth New Materials Co., Ltd. The main chemical composition is listed in Table 1.

Table 1 Main chemical composition of RE sulfate solution (g/L)

La_2O_3	CeO_2	Pr_6O_{11}	Nd_2O_3	MgO	CaO
5.18	8.40	0.56	1.36	8.79	0.80

2.2 Experimental procedures

(1) Preparation of $\text{Mg}(\text{HCO}_3)_2$ solution in sulfuric acid system

Calcium oxide reacted with water to obtain calcium hydroxide slurry (Reaction temperature was controlled by thermostatic water bath to 80 °C). Magnesium sulfate solution obtained by dissolving $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in water was used for alkali conversion reaction with the calcium hydroxide slurry. Then, the mixed slurry was carbonized by CO_2 in a carbonation reactor(self-made). Finally, $\text{Mg}(\text{HCO}_3)_2$ solution in sulfuric acid system and solid carbonation slag were obtained by solid–liquid separation.

(2) Saponification of HDEHP extractant with $\text{Mg}(\text{HCO}_3)_2$ solution and extraction of REEs

$\text{Mg}(\text{HCO}_3)_2$ solution was used to saponify the extractant (HDEHP) to obtain the organic phase loaded Mg^{2+} , aqueous phase and CO_2 gas. Then, a cascade extraction experiment was carried out with the organic phase loaded Mg^{2+} and the RE sulfate solution. Under a certain volume ratio of organic to aqueous phase, the mixture was placed in a constant temperature (25 °C) oscillator and shaken at 200 r/min for 5 min, and then it was taken out and stood for phase separation. The organic phase and aqueous phase (magnesium sulfate solution) were obtained after equilibrium extraction.

2.3 Analysis and characterization

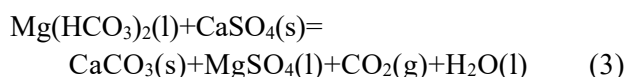
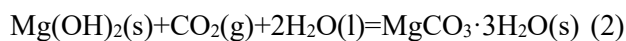
The concentration of $\text{Mg}(\text{HCO}_3)_2$ was determined by acid–base titration. $\text{Mg}(\text{HCO}_3)_2$ conversion rate was defined as the molar ratio of HCO_3^- in $\text{Mg}(\text{HCO}_3)_2$ solution to alkalinity in slurry, which was determined by acid–base titration method. The contents of REEs, Ca and Mg elements in aqueous and organic phases were analyzed by ICP-OES (Optima 8300, Perkin-Elmer). The phase structure of carbonized solid slag was determined by XRD (X 'Pert PRO MPD), and the morphology of the sample was characterized by SEM (TM3000).

3 Results and discussion

3.1 Efficient preparation of $\text{Mg}(\text{HCO}_3)_2$ solution in sulfuric acid system

Magnesium sulfate solution reacts with calcium hydroxide to form a mixed slurry containing magnesium hydroxide and calcium

sulfate. The carbonation reaction is a complex reaction involving solid, liquid and gas phases. The main reaction is shown in Eq. (1). In addition, some side reactions such as Eqs. (2) and (3) may occur during the carbonation reaction.



3.1.1 Effect of calcium sulfate on carbonation process

According to Eq. (3), the side reactions between CaSO_4 and $\text{Mg}(\text{HCO}_3)_2$ solution may occur, thus the effect of molar ratio of calcium sulfate to magnesium hydroxide ($n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$) on the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ was investigated, and the results are shown in Fig. 1. The magnesium hydroxide slurry with the concentration of 8 g/L MgO is used, and the reaction temperature is 25 °C in this experiment.

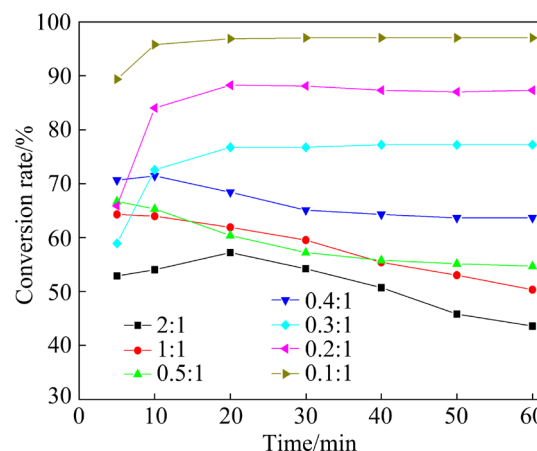


Fig. 1 Effect of $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ on $\text{Mg}(\text{HCO}_3)_2$ conversion rate (Magnesium hydroxide slurry concentration of 8 g/L MgO, and reaction temperature of 25 °C)

From Fig. 1, when $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ is less than 0.3:1, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ increases gradually with the increase of the carbonation time and tends to be stable at above 80% after 30 min. When the $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ is higher than 0.3:1, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ reaches the maximum at the initial stage of carbonation, and then decreases with the increase of carbonation time. In addition, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ continues to

decrease as the $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ continues to increase. When $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ is 1:1, $\text{Mg}(\text{HCO}_3)_2$ conversion rate is only about 50% after carbonation for 60 min. This phenomenon is explained by the fact that Ca^{2+} ions are released from the solid calcium sulfate, and the generated $\text{Mg}(\text{HCO}_3)_2$ will continue to react with the free Ca^{2+} ions to form calcium carbonate and magnesium sulfate, resulting in a lower concentration of $\text{Mg}(\text{HCO}_3)_2$. Side reactions are exacerbated due to the increase of free Ca^{2+} ions in the system.

In addition, the change of Ca^{2+} ion concentration during carbonation was investigated, as shown in Fig. 2. The concentration of Ca^{2+} ions in the solution increases gradually with the increase of $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$. When $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ is greater than 1, the Ca^{2+} ion concentration in the solution exceeds 1 g/L CaO due to the dissolution equilibrium of the system containing solid calcium sulfate, which is consistent with the change of Ca^{2+} ion concentration.

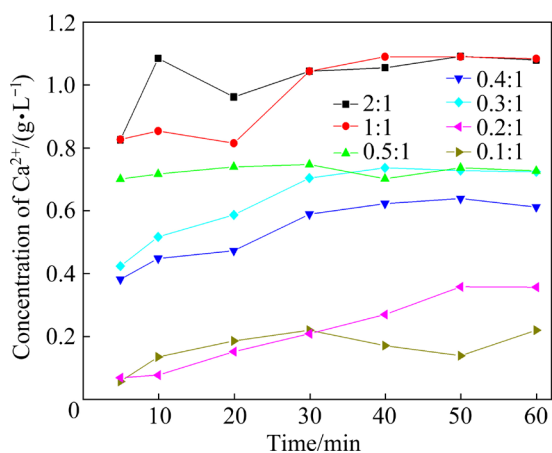


Fig. 2 Change of Ca^{2+} ion concentration in carbonation process at different $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)$ ratios (Magnesium hydroxide slurry concentration of 8 g/L MgO, and reaction temperature of 25 °C)

3.1.2 Effect of additive on carbonation process

Calcium hydroxide slurry reacts with magnesium sulfate solution to form magnesium hydroxide and calcium sulfate mixed slurry. According to the above experimental results, if carbon dioxide gas is directly injected into the system for carbonation reaction, it is difficult to achieve efficient preparation of $\text{Mg}(\text{HCO}_3)_2$ solution due to the side reactions between $\text{Mg}(\text{HCO}_3)_2$ solution and calcium sulfate. The dissociation of calcium sulfate can be inhibited due

to the addition of large amounts of sulfate to the system, resulting in the reduction of calcium ions in the solution and the weakening of side reactions. Based on this principle, magnesium sulfate was added to the mixed slurry after alkali conversion, and the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ at different molar ratios of magnesium sulfate to magnesium hydroxide ($n(\text{MgSO}_4):n(\text{Mg}(\text{OH})_2)$) is obtained, as shown in Fig. 3.

As can be seen from Fig. 3, after alkali conversion, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ increases due to the addition of magnesium sulfate in the slurry. When the $n(\text{MgSO}_4):n(\text{Mg}(\text{OH})_2)$ increases to 1:1, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ rapidly increases from about 50% to more than 95% after carbonation for 30 min. Thus, the dissociation of calcium sulfate is inhibited by the addition of sulfate, and the main reaction of carbonation takes place smoothly. With the increase of magnesium sulfate, the carbonation rate decreases slightly. The reason is that the viscosity of the solution increases due to addition of excessive magnesium sulfate in the system, which is not conducive to the diffusion of CO_2 gas and the carbonization reaction, resulting in the reduction of the conversion rate of $\text{Mg}(\text{HCO}_3)_2$. However, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ still remained above 90%, indicating that the concentration balance of HCO_3^- , Ca^{2+} and SO_4^{2-} in the solution was reached at this time.

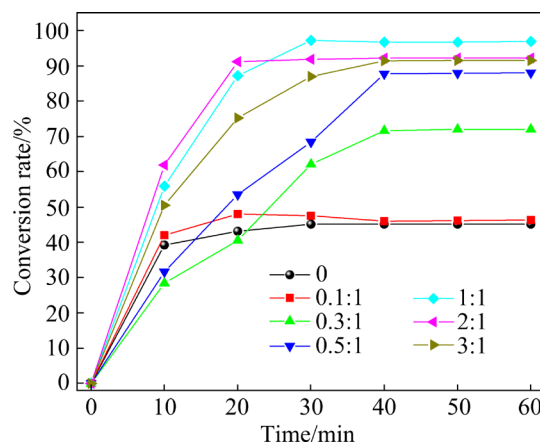


Fig. 3 Effect of $n(\text{MgSO}_4):n(\text{Mg}(\text{OH})_2)$ ratio on $\text{Mg}(\text{HCO}_3)_2$ conversion rate (Magnesium hydroxide slurry concentration of 8 g/L MgO, reaction temperature of 25 °C, and $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2)=1:1$)

Therefore, it is beneficial to adding proper amount of magnesium sulfate into the slurry after alkali conversion. On the one hand, the conversion

rate and the concentration of $\text{Mg}(\text{HCO}_3)_2$ are improved, and it saves costs and realizes full utilization of resources. On the other hand, it can ensure the continuous circulation of magnesium sulfate. According to the experimental results, the best carbonation effect is achieved when the $n(\text{MgSO}_4):n(\text{Mg}(\text{OH})_2)$ ratio is 1:1. In order to further understand the conversion process of each ion in the carbonation process, the change of the concentrations of each ion during the carbonation is investigated, as shown in Fig. 4.

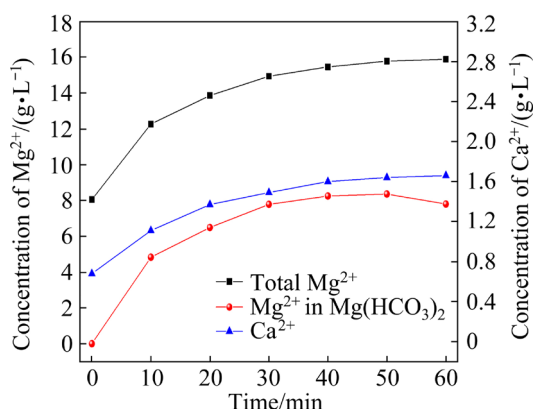


Fig. 4 Variation of ion concentration during carbonation (Magnesium hydroxide slurry concentration of 8 g/L MgO , reaction temperature of 25 °C, and $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2):n(\text{MgSO}_4)=1:1:1$)

As can be seen from Fig. 4, the concentration of $\text{Mg}(\text{HCO}_3)_2$, total Mg^{2+} ions and Ca^{2+} ions in the system increase with the increase of carbonation time. This phenomenon is caused by the gradual transformation of solid magnesium hydroxide into $\text{Mg}(\text{HCO}_3)_2$ solution with the carbonation time, resulting in the increasing concentration of $\text{Mg}(\text{HCO}_3)_2$ and Mg^{2+} ions in the solution, and then tends to be stable. In addition, as the concentration of $\text{Mg}(\text{HCO}_3)_2$ solution increases, the solubility of CaSO_4 increases until the dissociation of CaSO_4 reaches equilibrium, which leads to the increase of Ca^{2+} ion concentration.

3.1.3 Effect of slurry concentration on carbonation process

$\text{Mg}(\text{HCO}_3)_2$ solution is a metastable solution with stable concentration region. The concentration of $\text{Mg}(\text{OH})_2$ slurry after alkali conversion will directly affect the concentration of $\text{Mg}(\text{HCO}_3)_2$ solution. Therefore, the effect of the concentration of $\text{Mg}(\text{OH})_2$ slurry after alkali conversion on the concentration and conversion rate of $\text{Mg}(\text{HCO}_3)_2$

solution prepared by the mixed slurry system is investigated, as shown in Figs. 5 and 6.

As can be seen from Fig. 5, when the concentration of magnesium hydroxide slurry is less than 14.0 g/L, the concentration of $\text{Mg}(\text{HCO}_3)_2$ is the highest after carbonization for 40–50 min, and the concentration of $\text{Mg}(\text{HCO}_3)_2$ increases with the increase of the concentration of magnesium hydroxide slurry. When the concentration of magnesium hydroxide slurry is 16.0 g/L, the maximum concentration of $\text{Mg}(\text{HCO}_3)_2$ reaches 11.8 g/L after carbonization for 30 min, and then decreases gradually with the increase of the carbonization time.

Figure 6 shows that the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ decreases gradually with the increase

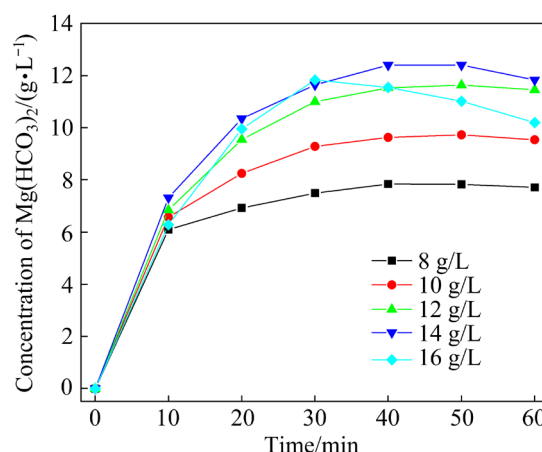


Fig. 5 Effect of magnesium hydroxide slurry concentration on $\text{Mg}(\text{HCO}_3)_2$ concentration (Reaction temperature of 25 °C, and $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2):n(\text{MgSO}_4)=1:1:1$)

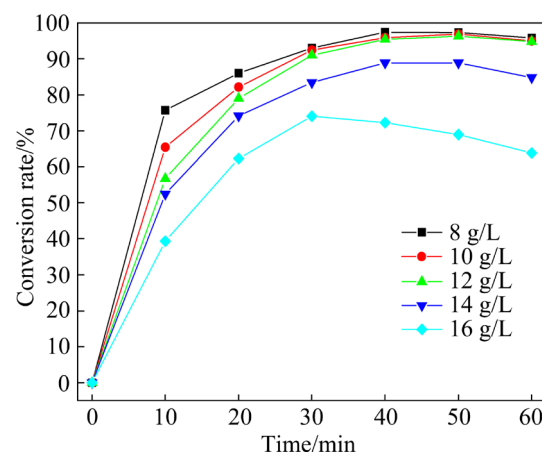


Fig. 6 Effect of magnesium hydroxide slurry concentration on $\text{Mg}(\text{HCO}_3)_2$ conversion rate (Reaction temperature of 25 °C, and $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2):n(\text{MgSO}_4)=1:1:1$)

of $\text{Mg}(\text{OH})_2$ slurry concentration. In other words, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ is low at high slurry concentration, and the highest carbonation rate is less than 75% at the slurry concentration of 16.0 g/L. According to the carbonation mechanism, when carbonation is carried out at a higher slurry concentration, a large amount of high-concentration $\text{Mg}(\text{HCO}_3)_2$ solution is locally generated, which reacts with the excessive OH^- ions dissociated from $\text{Mg}(\text{OH})_2$ before diffusion and degrades into solid hydrated magnesium carbonate. In addition, the stability of $\text{Mg}(\text{HCO}_3)_2$ at a higher concentration is poor in this complex system, which limits the efficient conversion of $\text{Mg}(\text{HCO}_3)_2$ at a higher slurry concentration.

3.1.4 Effect of temperature on carbonation process

Temperature plays an important role in the thermodynamics and kinetics of carbonation reaction. The effect of temperature on the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ is investigated, as shown in Fig. 7.

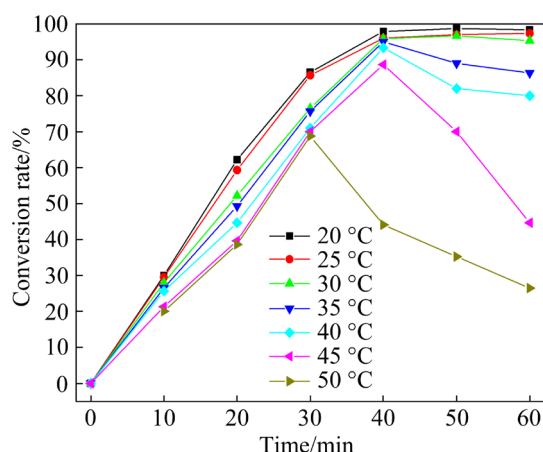


Fig. 7 Effect of carbonation temperature on $\text{Mg}(\text{HCO}_3)_2$ conversion rate (Magnesium hydroxide slurry concentration of 8 g/L MgO, and $n(\text{CaSO}_4):n(\text{Mg}(\text{OH})_2):n(\text{MgSO}_4)=1:1:1$)

From Fig. 7, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ decreases gradually with the increase of carbonation temperature. On the one hand, the solubility of CO_2 molecules in the solution decreases with the increase of temperature, leading to insufficient CO_2 in the system. In this case, the side reaction is easy to occur as shown in Eq. (2). On the other hand, the reaction shown in Eq. (1) is exothermic, while the reaction shown in Eq. (3) is endothermic, so the side reaction between $\text{Mg}(\text{HCO}_3)_2$ and CaSO_4 is more likely to occur at

high temperature, as shown in Eq. (3). In addition, from Fig. 7, the conversion rate of $\text{Mg}(\text{HCO}_3)_2$ decreases gradually with the carbonation time at the carbonation temperature of over 35 °C, and the trend of decline becomes more obvious with the increase of temperature. Thus, 35 °C is the critical point of temperature for the efficient conversion of $\text{Mg}(\text{HCO}_3)_2$. In order to prove the above analysis results, the carbonation slags obtained at 20 °C and different carbonation time are characterized by XRD and SEM, as shown in Figs. 8 and 9, and the analysis results of carbonation slags obtained at 50 °C are shown in Figs. 10 and 11.

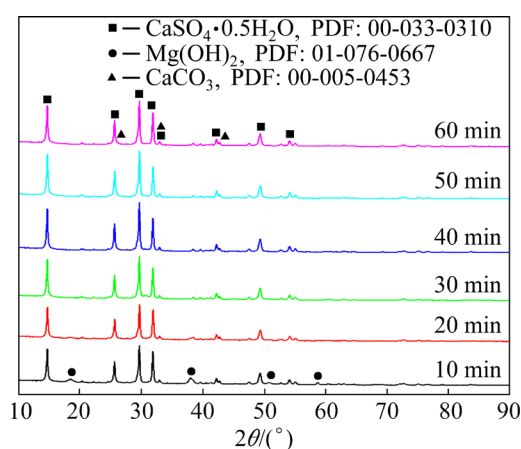


Fig. 8 XRD patterns of carbonation slag obtained at 20 °C for different carbonation time

From Fig. 8, it can be seen that under the condition of carbonation temperature of 20 °C and carbonation time of 10 min, the main phases of carbonation slag are $\text{Mg}(\text{OH})_2$ and CaSO_4 , and their microscopic morphology shows cluster shape and rod shape, respectively, as shown in Fig. 9. With the increase of carbonation time, the solid $\text{Mg}(\text{OH})_2$ in slurry is gradually transformed into $\text{Mg}(\text{HCO}_3)_2$, and the $\text{Mg}(\text{OH})_2$ in carbonation slag decreases simultaneously, which is consistent with the reduction of cluster particles in the carbonation slag obtained at 20 and 30 min. When the carbonation time is 40 min, the $\text{Mg}(\text{OH})_2$ phase disappears in the carbonation slag, because all of them are transformed into $\text{Mg}(\text{HCO}_3)_2$, no cluster particles are observed in the micromorphology, but trace amount of CaCO_3 is produced. As the carbonation time continues to extend, the phases in the system do not change significantly.

From Fig. 10, when the carbonation time is 10 min at 50 °C, the main phases and microstructure

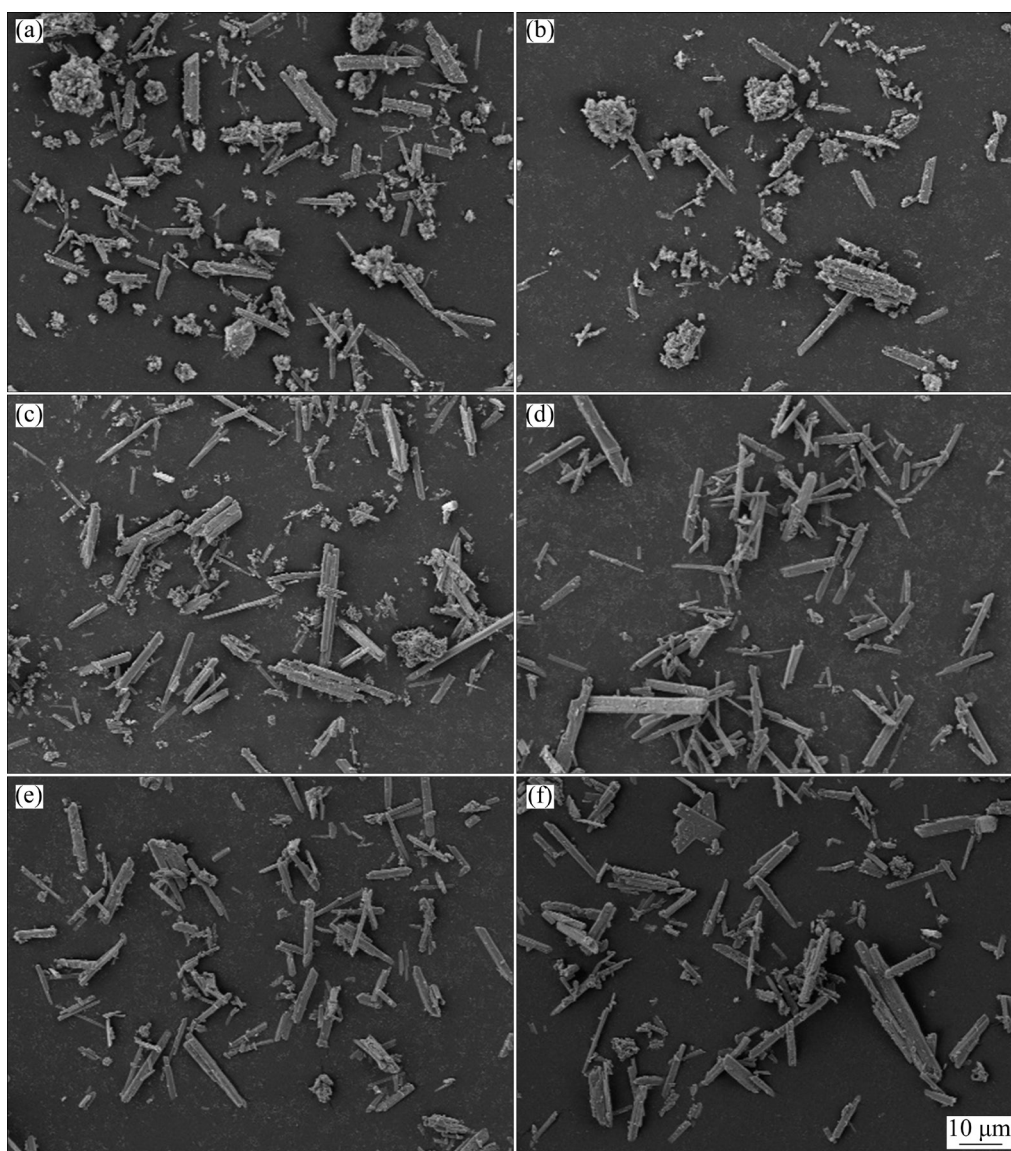


Fig. 9 SEM images of carbonation slag obtained at 20 °C for different carbonation time: (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min; (e) 50 min; (f) 60 min

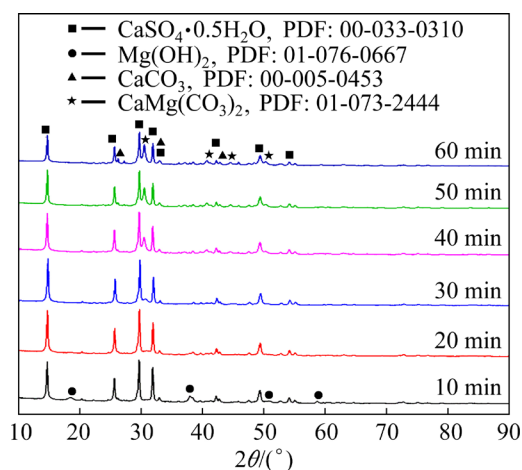


Fig. 10 XRD patterns of carbonation slag obtained at 50 °C for different carbonation time

of the carbonation slag are similar to those at 20 °C. The Mg(OH)_2 in the carbonation slag is reduced with the increase of carbonation time due to its transformation to $\text{Mg(HCO}_3)_2$. Therefore, the clusters of Mg(OH)_2 in the carbonation slag obtained after carbonation for 20 and 30 min gradually decrease, as shown in Fig. 11. After carbonation at 50 °C for 40 min, calcium and magnesium carbonate complex salt phase ($\text{CaMg(CO}_3)_2$) appears in the carbonation slag, and the cluster particles are also observed in the microstructure, which is significantly different from the phenomenon of carbonation temperature at 20 °C. With the extension of carbonation time, the diffraction peak strength of $\text{CaMg(CO}_3)_2$ in the

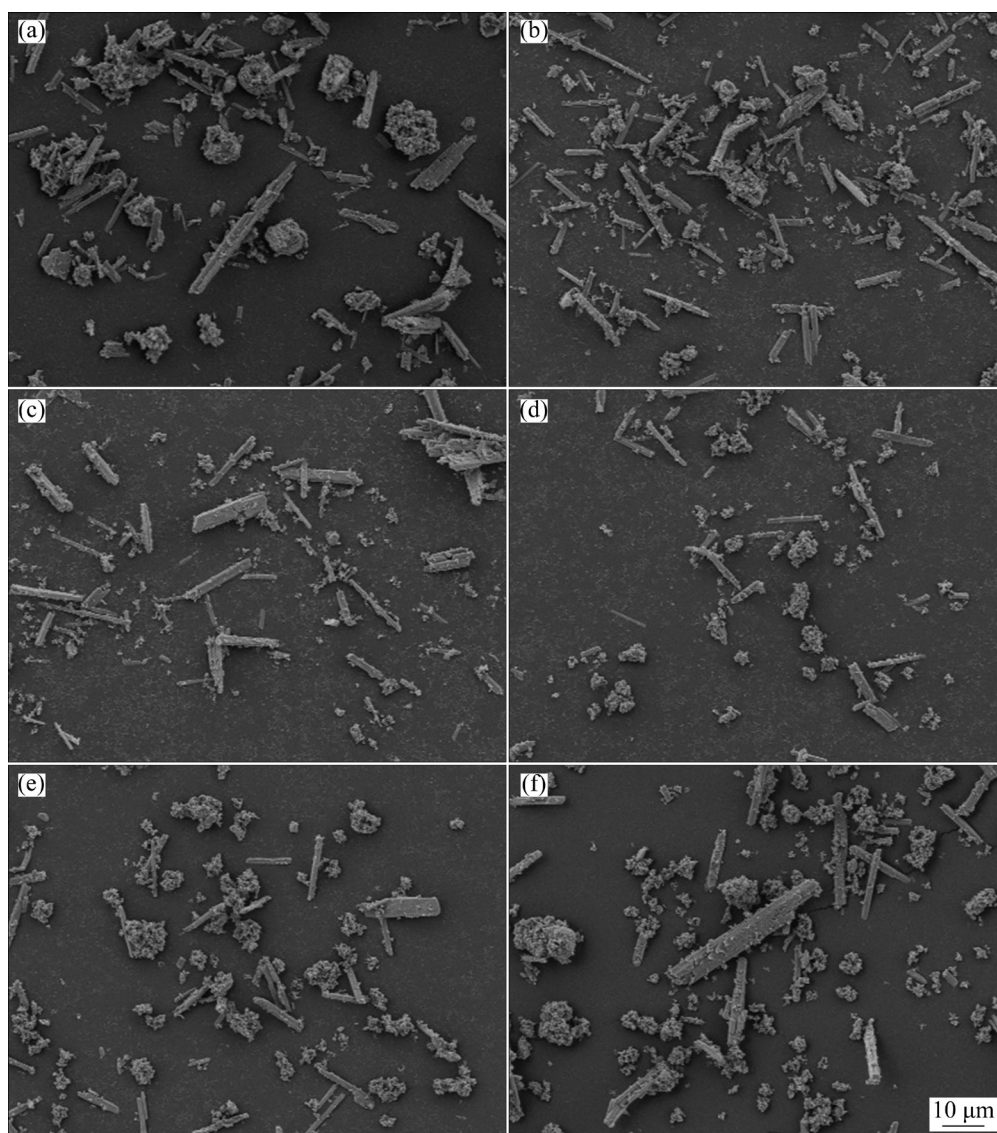


Fig. 11 SEM images of carbonation slag obtained at 50 °C for different carbonation time: (a) 10 min; (b) 20 min; (c) 30 min; (d) 40 min; (e) 50 min; (f) 60 min

carbonation slag gradually increases (Fig. 10), and the rod-like particles gradually decrease in the microstructure and the cluster particles increase, which can prove that the cluster particles are $\text{CaMg}(\text{CO}_3)_2$ (Fig. 11). Combined with the phenomenon of $\text{Mg}(\text{HCO}_3)_2$ conversion decreasing gradually as shown in Fig. 7, the side reaction between $\text{Mg}(\text{HCO}_3)_2$ and CaSO_4 at high temperature and the side reaction of $\text{Mg}(\text{HCO}_3)_2$ decomposed into MgCO_3 can be further verified.

Based on the above analysis, high temperature has adverse effects on the preparation of $\text{Mg}(\text{HCO}_3)_2$. The conversion rate of $\text{Mg}(\text{HCO}_3)_2$ can reach 95% by controlling reasonable carbonation time at the temperature of below 35 °C,

and the side reaction can be effectively avoided. Therefore, 35 °C is the critical temperature of carbonation reaction in this system.

3.1.5 Efficient preparation of $\text{Mg}(\text{HCO}_3)_2$ solution

Based on the effect law of the above key factors on the conversion rate of $\text{Mg}(\text{HCO}_3)_2$, the efficient and controllable preparation of $\text{Mg}(\text{HCO}_3)_2$ solution is realized in the appropriate carbonation conditions, and the specific performance parameters of $\text{Mg}(\text{HCO}_3)_2$ solution are shown in Table 2. The concentration of $\text{Mg}(\text{HCO}_3)_2$ solution reaches 8 g/L MgO, and the content of impurities (such as Fe, Al and Si) in the solution is less than 15 mg/L. The conversion rate of $\text{Mg}(\text{HCO}_3)_2$ is more than 95%, which can provide

reliable and high-quality raw materials for subsequent processes of saponification extraction and separation of REEs, and realize the recycling of magnesium sulfate wastewater.

3.2 $\text{Mg}(\text{HCO}_3)_2$ solution for saponification and extraction of REEs

HDEHP extractant is saponified by $\text{Mg}(\text{HCO}_3)_2$ solution, and a organic phase loading Mg^{2+} with saponification degree of 0.14 mol/L is obtained. Then, a 5-stage cascade extraction test is carried out by using the RE sulfate solution (A_0) and the organic phase loading Mg^{2+} (O_0) as raw

materials. Five separating funnels are used for simulation. The composition of raffinate aqueous phase (A_1) and loaded RE^{3+} organic phase (O_5) in two adjacent rows are consistent respectively, indicating that the extraction equilibrium has been achieved. The extraction equilibrium is achieved after extraction of 18 rows, and the samples at the 20th row are taken for analysis in this paper. The schematic diagram of cascade extraction of 5 stages is shown in Fig. 12, and the specific results are shown in Table 3. The process flowchart on saponification-extraction for rare earths separation by $\text{Mg}(\text{HCO}_3)_2$ is shown in Fig. 13.

Table 2 Parameters of $\text{Mg}(\text{HCO}_3)_2$ solution

$\text{Mg}(\text{HCO}_3)_2$ concentration/ ($\text{g}\cdot\text{L}^{-1}$)	$\text{Mg}(\text{HCO}_3)_2$ conversion rate/ %	Calcium ion concentration/ ($\text{g}\cdot\text{L}^{-1}$)	Iron ion concentration/ ($\text{mg}\cdot\text{L}^{-1}$)	Silicon ion concentration/ ($\text{mg}\cdot\text{L}^{-1}$)	Aluminum ion concentration/ ($\text{mg}\cdot\text{L}^{-1}$)
8	95.6	0.8	0.4	14.1	0.1

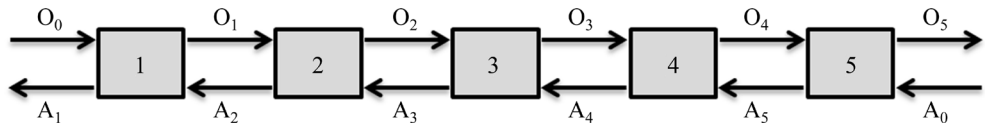


Fig. 12 Schematic diagram of cascade extraction of 5 stages

Table 3 Element content and distribution of organic phases and aqueous phases after cascade extraction

Sample	Concentration/($\text{g}\cdot\text{L}^{-1}$)			Acidity/($\text{mol}\cdot\text{L}^{-1}$)		Proportion/%		
	MgO	CaO	REO	H^+		MgO	CaO	REO
O_0	2.55	0.34	—	—		100	100	100
A_0	8.79	0.8	15.51	0.08				
A_1	11.33	0.83	0.06	0.23		99.9	72.8	0.4
A_2	8.98	1.27	0.84	0.31		79.2	111.4	5.4
O_2	0.15	0.58	1.61	—		1.3	50.9	10.4
A_4	8.84	0.98	3.36	0.28		78	86	21.7
O_4	0.14	0.42	6.86	—		1.2	36.8	44.2
O_5	0.12	0.32	15.45	—		1.1	28.1	99.6

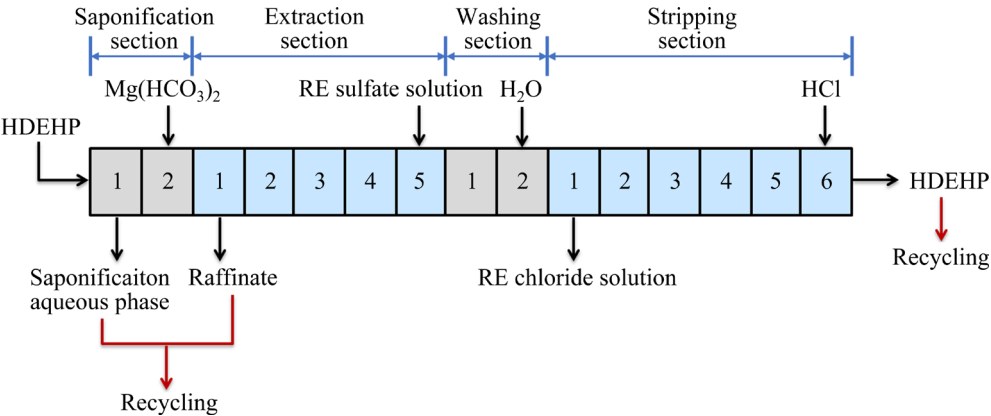


Fig. 13 Process flowchart on saponification-extraction for rare earths separation by $\text{Mg}(\text{HCO}_3)_2$

According to the data in Table 3, the distribution rules of RE, calcium and magnesium elements are different in the extraction process. As the extraction capacity of RE, calcium and magnesium in HDEHP system gradually weakens, most of the REEs are distributed in O₅. Therefore, REEs can achieve the complete extraction transformation and enter the subsequent extraction separation stage, and the extraction recovery of REEs can be calculated to be more than 99.5% according to the data of A₀ and A₁. In addition, the concentration of RE ions in aqueous and organic phases increases from Stages 1 to 5. All magnesium elements are almost distributed in A₁, that is, the magnesium sulfate wastewater after extraction transformation can be reused to prepare Mg(HCO₃)₂, so as to realize the recycling of magnesium sulfate. From Stage 1 to 5, the concentrations of Mg²⁺ ions in aqueous and organic phases decrease, and the concentration of Mg²⁺ ions of the first and second stages decreases greatly, and that of the latter stages decreases slightly. The extraction capacity of Ca²⁺ ions is between RE³⁺ and Mg²⁺ ions, so it is distributed in A₁ and O₅. The saponification degree can be effectively controlled by using Mg(HCO₃)₂ solution, and then the equilibrium acidity of aqueous phase can be precisely controlled to above 0.20 mol/L. The concentrations of Ca²⁺ ions in A₂ and A₄ are 1.27 and 0.98 g/L, respectively, which do not reach the saturation solubility of calcium sulfate in this system, thus no calcium sulfate crystal precipitation is generated. Therefore, Mg(HCO₃)₂ applied in saponification extraction of RE sulfate solution can effectively solve the problem of blocking the pipeline caused by calcium sulfate scaling, and realize the recycling of magnesium sulfate wastewater.

4 Conclusions

(1) By precisely controlling the carbonation process, Mg(HCO₃)₂ solution with the concentration of 8 g/L MgO is prepared by alkali conversion with magnesium sulfate solution and calcium oxide in sulfuric acid system. The conversion rate of Mg(HCO₃)₂ is more than 95%, and the content of Fe, Al, and Si impurities in the Mg(HCO₃)₂ solution is very low (less than 15 mg/L).

(2) During carbonation process, the formation

of Mg(HCO₃)₂ is inhibited due to the presence of calcium sulfate in the system, whereas this conversion process is facilitated by the addition of magnesium sulfate and reducing the carbonation temperature. The carbonation reaction at different temperatures is analyzed by XRD and SEM, and the carbonation mechanism is explained.

(3) The prepared Mg(HCO₃)₂ solution is applied in extraction separation and transformation of RE sulfate solution by saponified HDEHP. The balanced acidity of aqueous phase and the distribution of RE, calcium and magnesium elements can be effectively adjusted by controlling the saponification degree of organic phase. The extraction recovery of REEs exceeds 99.5%, and no calcium sulfate crystal is precipitated. The new technology proposed in this paper realizes the recycling of magnesium sulfate wastewater, and solves the issue of blocking the pipeline caused by calcium sulfate scaling.

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硫酸镁溶液高效制备碳酸氢镁及皂化萃取分离稀土

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摘 要: 为实现包头混合型稀土精矿冶炼分离过程中硫酸镁废水的循环利用, 开展硫酸镁溶液碱转制备氢氧化镁、CO₂ 碳化制备碳酸氢镁溶液, 以及硫酸稀土溶液的皂化 HDEHP 萃取分离转型技术研究。研究碳酸氢镁制备过程关键影响因素及碳化机理, 以及碳酸氢镁皂化萃取过程中稀土、钙、镁元素的分布规律。结果表明, 碳化过程中硫酸钙会抑制碳酸氢镁的转化, 而提高硫酸镁浓度和降低碳化温度均会促进碳酸氢镁的转化。在优化的工艺条件下, 实现碳酸氢镁溶液的稳定、高效制备, 碳酸氢镁转化率大于 95%, Fe、Al、Si 等杂质含量低于 15 mg/L; 硫酸稀土溶液经过多级串级萃取, 稀土萃取回收率大于 99.5%, 未出现硫酸钙结晶析出现象, 萃余水相为硫酸镁溶液, 循环用于制备碳酸氢镁溶液。

关键词: 碳化; 碳酸氢镁; 硫酸稀土溶液; 皂化萃取; 硫酸钙

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