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Separation and recovery of magnesium and calcium from simulated desulfurization wastewater in power plant

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ABSTRACT

The method of using CO_2 for separation and recovery of calcium and magnesium from desulfurization wastewater was studied, and the optimum conditions of the two-stage process were explored. In the first stage, CO_2 was used for the separation of calcium and magnesium in the desulfurization wastewater, 80% of the calcium in the desulfurization wastewater can be precipitated. The optimum temperature for the process was 30°C; the optimum pH of calcium and magnesium separation was about 7.0. As for desulfurization wastewater with different contents of calcium and magnesium, the efficiency of calcium and magnesium separation was different. When the concentration ratio of calcium and magnesium was more than 1:4, the separation efficiency could basically meet the requirements of subsequent wastewater treatment. In the second stage, NaOH was added for magnesium recovery, the content of $Mg(OH)_2$ in the precipitate could reach 85%. The purity of magnesium in the precipitates increased rapidly before pH reached 10, and stabilized at pH 11.0. Under the optimal conditions, the removal rate of calcium and magnesium could reach 90% and 85%, respectively. This research results provide experimental reference and theoretical basis for the use of CO_2 for the recovery of calcium and magnesium in desulfurization wastewater.

Keywords: Magnesium recovery; Desulfurization wastewater; Zero liquid discharge

1. Introduction

The zero-liquid discharge (ZLD) of desulfurization wastewater has been widely concerned in these years, thanks to the promulgation of "guideline on available technologies of pollution prevention and control for thermal power plant" in China and the release of the latest US EPA desulphurization wastewater discharge standards. The increasingly stringent environmental regulations have made the desulfurization of wastewater treatment even more challenging. Unlike other wastewater in power plant, desulfurization wastewater has high content of suspended solids, high total dissolved solid (TDS), and many kinds of heavy metals such as mercury, arsenic, selenium and so on [1]. Cl^- and heavy metals in the desulfurization wastewater come from coal. Heavy metals carried by the flue gas are washed down in the desulfurization process and accumulated in the desulfurization slurry.

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Limestone contributes most of the Mg^{2+} in the wastewater. Limestone contains 5%–46% magnesium carbonate (depending on the type and origin of limestone), and they enter the limestone slurry in the mixing process occurring in the ball mill [2].

At present, the ZLD technologies for desulfurization wastewater can be divided by evaporation and membrane concentration treatment. The evaporation technologies mainly include flue spray evaporation, bypass flue evaporation, mechanical atomization evaporation, etc. Evaporation technologies are the most widely used ZLD technologies, in which the pollutants are separated from the solution in the form of solid, to prevent water pollution, are now widely used in desulfurization wastewater zero discharge technology. However, the changes of temperature and concentration in the evaporation processes may lead to the precipitate of calcium and magnesium, tending to scale in the nozzle and the flue wall [3], threatening the safe operation of equipment or even leading to the cracking of flue duct [4]. Therefore, the control of calcium and magnesium concentration in wastewater is important to the application of evaporation technologies. The biggest advantage of membrane concentration technology is the good water quality of the effluent, most of which can be reused. However, during the treatment processes of membrane concentration, the solution is continuously concentrated, and the calcium and magnesium salts are precipitated and deposited on the surface of the membrane, causing the rapid drop in membrane flux and even shortening the membrane life [5]. Membrane fouling caused by the precipitation of magnesium hydroxide and calcium sulfate, calcium carbonate and other factors seriously affect membrane flux and membrane running time, which restricts the application of membrane in water treatment [6–9].

The content of calcium and magnesium in the desulfurization wastewater is about 5,000–12,000 mg/L, but fluctuates greatly because the water and limestone used in the flue gas desulphurization (FGD) system varies a lot, and. When limestone with higher magnesium content is used, the content of magnesium ions in the waste water is high, affecting subsequent equipment. However, if the magnesium in desulfurization wastewater can be recycled, it can benefit the power plants both in environment and economic. Magnesium hydrate is widely used in fire-fighting, paper-making and medical applications [10,11]. In the traditional methods for the softening of wastewater, alkali is added to accelerate the precipitates of calcium and magnesium [12], which consumes large amount of chemicals and generates a large amount of sludge [13]. Surfactant modified bentonite was used by Kadir et al [14] to soften wastewater and a removal rate of 66.67% for calcium and magnesium was reached. In Tofighy and Mohammadi [15] research, the use of carbon nanotubes to adsorb calcium and magnesium was studied. Arugula et al [16] put forward of the enzyme-catalyzed glucose binding electrochemical method, and the hardness could be removed by 80%; the initial hardness range of 1,000 mg/L. The researches on water softening technologies mentioned above were effective and mature. However, taking the bad water quality of desulfurization wastewater and the operation cost into account, cheaper and easier technologies are needed for the softening of desulfurization wastewater. Farmanbordar et al. [17] used CO_2 from flue gas to adjust the wastewater pH to remove the calcium ions, and the removal efficiency reached 50%. The flue gas in power plants contains 15% of CO_2, enough for the removal of calcium ions and the recovery of magnesium hydroxide.

In view of the problems such as incomplete hardness removal, high cost and high requirements in water quality in the existing desulfurization wastewater treatment technologies, a new method of using CO_2 to recover calcium and magnesium in the desulfurization wastewater is put forward. The feasibility, economic and environmental benefits of the technology are verified. The applicable scope of calcium and magnesium recovery by carbonation method is proved in this paper; furthermore, the optimized test conditions are obtained, providing valuable reference for industrial application.

2. Experiments

2.1. Experimental materials

Experiments were designed according to the treatment process above, mainly divided into calcium and magnesium separation and magnesium recovery. The first phase was calcium and magnesium separation. A thermostat magnetic stirrer (DF-101S thermostat magnetic stirrer, Gongyi City, Yu Hua Instrument Co., Ltd.) was used to control the reaction temperature; simulated desulfurization wastewater was prepared in accordance with the composition of real desulfurization wastewater; 15 vol% CO_2 was blew in, with a mass flow meter controlling the gas flow rate; the industrial online pH meter (Luheng biological DG160 industrial pH detector, Hangzhou Luheng Biological Technology Co., Ltd.) was used for the real-time determination of solution pH. Buchner funnel and air pump (SHD-Ⅲ type circulating water-type vacuum pump, Baoding High-tech Zone Sunshine Science and Education Instrument Factory) are used to filter precipitates.

The EDTA standard solution (Tianjin Kermel standard solution. 0.01022 mol/L, 0.1012 mol/L); polyacrylamide AR (Aladdin); chrome black T AR (Tianjin Kemel Chemical Reagent Co., Ltd.); sodium hydroxide AR (Tianjin Tianbei Chemical Reagent Factory); anhydrous sodium carbonate AR (Tianjin Sailboat Chemical Reagent Technology Co., Ltd.); absolute ethanol AR (Tianjin Sailboat Chemical Reagent Technology Co., Ltd.); magnesium chloride AR (Tianjin Guangfu Science and Technology Development Co., Ltd.); calcium hydroxide AR (Tianjin Guangfu Fine Chemical Research Institute); triethanolamine AR (Tianjin Beichen Founder Reagent Factory); potassium chloride AR (Tianjin Beichen Founder Reagent Factory); ammonia water AR (Yongfei Chemical Plant); calcium reagent IND (Tianjin Huadong Reagent Factory); CO_2/N_2 15% (Baoding Warwick Gas Technology Co., Ltd.); deionized water (self-made).

2.2. Experimental methods

The treatment process for desulfurization wastewater using CO_2 is shown in Fig. 1. The desulfurization wastewater was sent into the tank, and as the traditional method of removing heavy metal ions, then $Ca(OH)_2$ was

added to adjust solution pH to 9 and which could reduce costs; the precipitate in the bottom was separated with a plate-and-frame filter press and the supernatant was sent into the carbonation tower. In the carbonation tower, the carbon dioxide in flue gas was blown into tower, the solution pH changed to 7, then the precipitate in the bottom was sent back to the desulfurization tower for calcium recovery, the supernatant was transported to the caustic tower; NaOH was used to adjust the pH of solution in the caustic tower and $Mg(OH)_2$ was separated by plate-and-frame filter press when the pH reached 11; the supernatant could be recycled to the desulfurization tower after simple treatment.

Related principles are introduced as follows.

(1) Heavy metals removal using $Ca(OH)_2$

$Ca(OH)_2$ is added to the desulfurization wastewater to adjust the pH to about 9, removing most of the heavy metals, suspended solids, SO_4^{2-} and other substances in the desulfurization wastewater. The reactions occurring in this process are shown in Eqs. (1) and (2).

$$M^{2+} + Ca(OH)_2 \rightarrow M(OH)_2\downarrow + Ca^{2+} \quad (1)$$

$$Ca^{2+} + SO_4^{2} \rightarrow CaSO_4 \quad (2)$$

where M represents heavy metal ions.

(2) Separations of calcium and magnesium using CO_2

After the treatment in step (1), CO_2 is blown into the desulfurization wastewater to lower the pH of the solution, and the calcium ions in the wastewater are precipitated as $CaCO_3$ and separated from the solution. After filtration, the precipitate mainly consists of $CaCO_3$, and the precipitate is returned to the desulfurization tower for recycling, and the supernatant liquid is processed in the next step for further treatment. The reactions involved in this process are shown in Eqs. (3), (4) and (5).

$$CO_2 + H_2O \rightarrow CO_3^{2-} + 2H^+ \quad (3)$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO3\downarrow \quad (4)$$

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3\downarrow \quad (5)$$

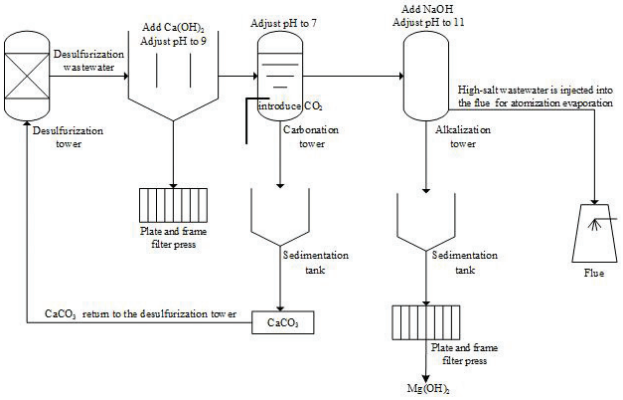

Fig. 1. Two-step treatment process for desulfurization wastewater softening.

(3) Magnesium recovery

After the treatment of steps of (1) and (2), alkali is added to the supernatant after the filtration in (2) to increase the pH of the solution, and the magnesium in the solution is recycled. The obtained precipitate mainly consist of $Mg(OH)_2$. The reactions occur in this process are shown in Eqs. (6) and (7).

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow \quad (6)$$

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2\downarrow \quad (7)$$

The solubility product K_{sp} of $Ca(OH)_2$ is 1.3×10^{-5} [18], and the K_{sp} of $Mg(OH)_2$ is 1.8×10^{-11} [18]. Obviously, $Mg(OH)_2$ precipitates first.

The chemical process schematic diagram is shown in Fig. 2.

Calcium and magnesium ion concentrations in the solution were measured using EDTA titration method (GB/T 15452–2009).

The calculations of calcium precipitating ratio η_{Ca}, magnesium precipitating ratio η_{Mg}, and calcium-magnesium precipitating molar ratio $\frac{N_{Ca}}{N_{Mg}}$ list as follows.

$$\eta_{Ca} = \frac{\frac{(V_1/1000)cM_1}{V_0/1000} - \frac{(V_2/1000)cM_1}{V/1000}}{\frac{(V_1/1000)cM_1}{V_0/1000}} \quad (8)$$

Eq. (8) is simplified as

$$\eta_{Ca} = \frac{\frac{V_1}{V_0} - \frac{V_2}{V}}{\frac{V_1}{V_0}} \quad (9)$$

$$\eta_{Mg} = \frac{\frac{(V_3/1000 - V_1/1000)cM_2}{V_0/1000} - \frac{(V_4/1000 - V_2/1000)cM_2}{V/1000}}{\frac{(V_3/1000 - V_1/1000)cM_2}{V_0/1000}} \quad (10)$$

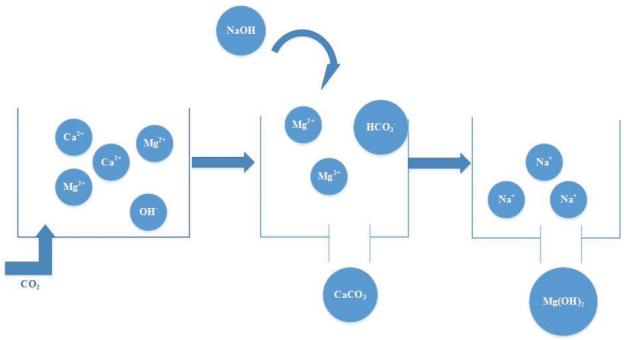

Fig. 2. Schematic of chemical separation principle.

Eq. (10) is simplified as

$$\eta_{Mg} = \frac{\frac{(V_3 - V_1)}{V_0} - \frac{(V_4 - V_2)}{V}}{\frac{(V_3 - V_1)}{V_0}} \tag{11}$$

$$\frac{N_{Ca}}{N_{Mg}} = \frac{\frac{(V_1/1000)c}{V_0/1000} - \frac{(V_2/1000)c}{V/1000}}{\frac{(V_3/1000 - V_1/1000)c}{V_0/1000} - \frac{(V_4/1000 - V_2/1000)c}{V/1000}} \tag{12}$$

Eq. (12) is simplified as

$$\frac{N_{Ca}}{N_{Mg}} = \frac{\frac{V_1}{V_0} - \frac{V_2}{V}}{\frac{(V_3 - V_1)}{V_0} - \frac{(V_4 - V_2)}{V}} \tag{13}$$

$$P_{Mg} = \frac{\frac{(V_3/1000 - V_1/1000)cM_2}{V_0/1000} - \frac{(V_4/1000 - V_2/1000)cM_2}{V/1000}}{\frac{(V_3/1000 - V_1/1000)cM_2}{V_0/1000} - \frac{(V_4/1000 - V_2/1000)cM_2}{\frac{V}{1000}} + \frac{(V_1/1000)cM_1}{V_0/1000} - \frac{(V_2/1000)cM_1}{V/1000}} \tag{14}$$

Eq. (14) is simplified as

$$P_{Mg} = \frac{\frac{(V_3 - V_1)M_2}{V_0} - \frac{(V_4 - V_2)M_2}{V}}{\frac{(V_3 - V_1)M_2}{V_0} - \frac{(V_4 - V_2)M_2}{V} + \frac{V_1 M_1}{V_0} - \frac{V_2 M_1}{V}} \tag{15}$$

where η_{Ca} represents calcium precipitation rate; η_{Mg} represents magnesium precipitation rate; P_{Mg} represents the purity of magnesium; V_1 represents volume of EDTA standard titration solution consumed in the titration process of total Ca, mL; V_2 represents volume of EDTA standard titration solution consumed in the titration process of remained Ca, mL; V_3 represents volume of EDTA standard titration solution consumed in the titration process of total Ca and Mg, mL; V_4 represents volume of EDTA standard titration solution consumed in the titration process of remained Ca and Mg, mL; c represents the concentration of EDTA standard titration solution, mol/L; V_0 represents volume of the sample solution consumed in the titration process of total Ca and total Ca and Mg, mL; V represents volume of the sample solution consumed in the titration process of remained Ca and remained Ca and Mg, mL; M_1 represents molar mass of Ca, g/mol (M_1 = 40.08); M_2 represents molar mass of Mg, g/mol (M_2 = 24.31).

3. Results and discussions

3.1. Effect of pH on calcium and magnesium separations

In order to explore the impact of pH on the separations of calcium and magnesium, simulated desulfurization wastewater at different concentration was carbonized. The concentration ratio of calcium and magnesium in simulated desulphurization wastewater was in accordance with the concentration ratio of calcium to magnesium in the actual desulfurization wastewater of a factory. In addition, we had experimented with different molar ratios of wastewater, which also paved the way for the following.

The pH of the solution was monitored during carbonization process; water temperature was controlled at 20°C; the flow rate of CO_2 was kept at 0.6 L/min by flow meter.

Simulated desulfurization wastewater with calcium-magnesium molar ratio at 1:4, 1:1, 3:2 were listed in Table 1. Samples were taken for measurement at pH 9.0, 8.5, 8.0, 7.5, 7.0 and 6.0.

For simulated desulfurization wastewater with calcium-magnesium molar ratio at 1:4, calcium and magnesium content in the supernatant was compared with the content in original solution. The calcium and magnesium precipitation rate curve over time obtained is shown in Fig. 3.

In order to show the effect of calcium and magnesium separations more intuitively, the relationship between calcium-magnesium precipitating molar ratio, time and pH is shown in Fig. 4.

Then the high calcium and low magnesium simulated desulfurization wastewater with the molar ratio of Ca and Mg of about 1:1 was studied. The change of calcium-magnesium precipitating molar ratio with pH was obtained as shown in Fig. 5.

Table 1
Calcium and magnesium concentrations in simulated wastewater samples

Molar ratio of calcium to Magnesium	Concentration of Ca^{2+} (mg/L)	Concentration of Mg^{2+} (mg/L)
1:1	5,313.49	3,247.43
1:4	2,271.41	5,166.36
3:2	11,722.1	4,895.75

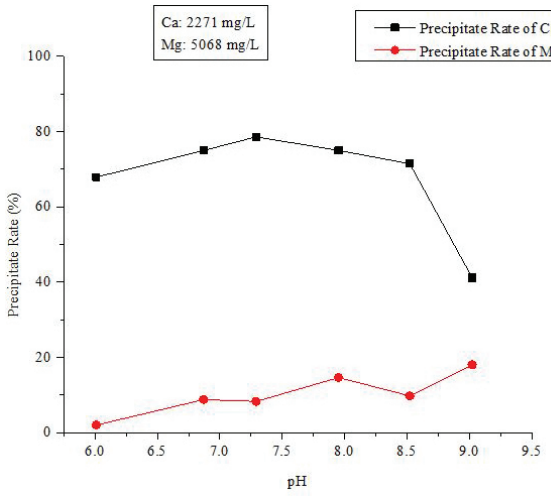

Fig. 3. Calcium and magnesium precipitation rate curve with pH (1:4 calcium and magnesium molar ratio).

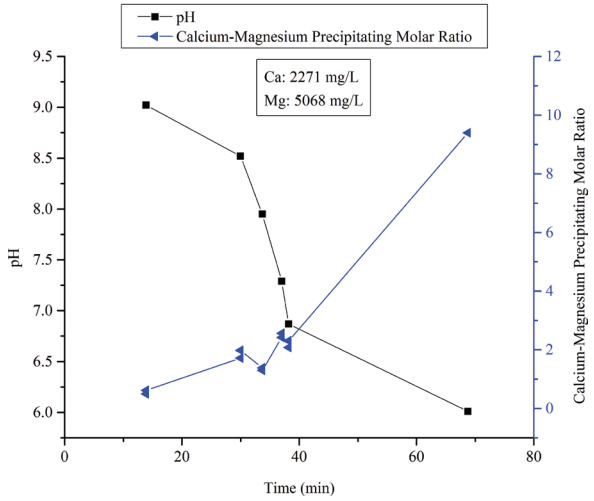

Fig. 4. Calcium-magnesium precipitating molar ratio in simulated wastewater with calcium-magnesium content at 1:4.

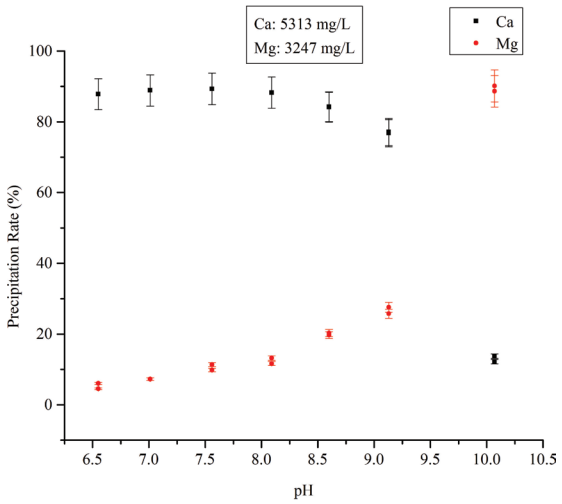

Fig. 5. Calcium and magnesium precipitation rate curve with changes in pH (1:1 calcium and magnesium molar ratio).

The change of calcium-magnesium precipitating molar ratio and pH over time is shown in Fig. 6.

The high calcium and high magnesium simulated desulfurization wastewater with the molar ratio of Ca and Mg at about 3:2 was studied, too. Due to the high calcium and magnesium content, the required amount of CO_2 was larger. In order to shorten the experiment time, the flow rate was changed to 2.67 L/min. (Here the CO_2 flow rate was not discussed as a variable, instead, the flow rate of CO_2 was just appropriately increased. This was because the larger the flow rate of CO_2, the greater the precipitation rate of calcium. These conclusions can be found in the literature [19]. Thus the experiment conclusion will not be influenced by appropriate increase of the rate of CO_2) When the pH was 9.0, 8.0, 7.0, 6.0, the change of calcium and magnesium precipitation rate with the pH is shown in Fig. 7.

The precipitate rate was calculated and converted to calcium-magnesium precipitating molar ratio, as shown in Fig. 8.

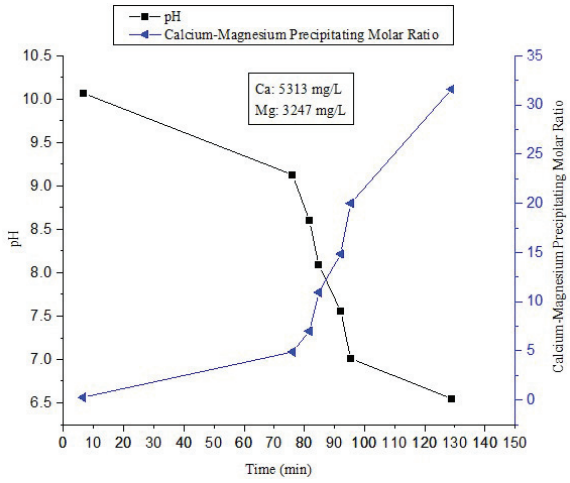

Fig. 6. Change of calcium-magnesium precipitating molar ratio and pH over time (1:1 calcium-magnesium molar ratio).

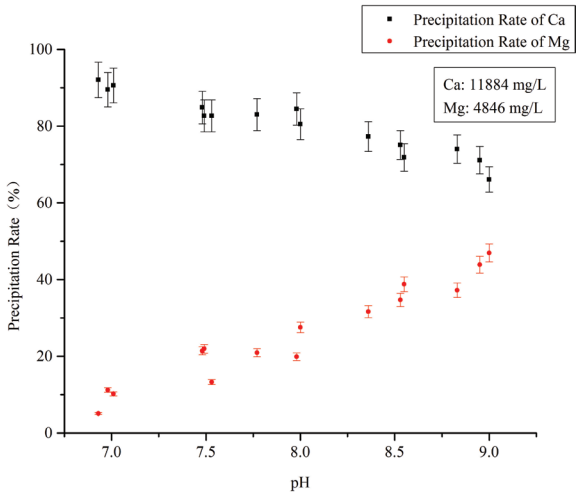

Fig. 7. Change trend of calcium and magnesium precipitation with pH (3:2 calcium-magnesium molar ratio).

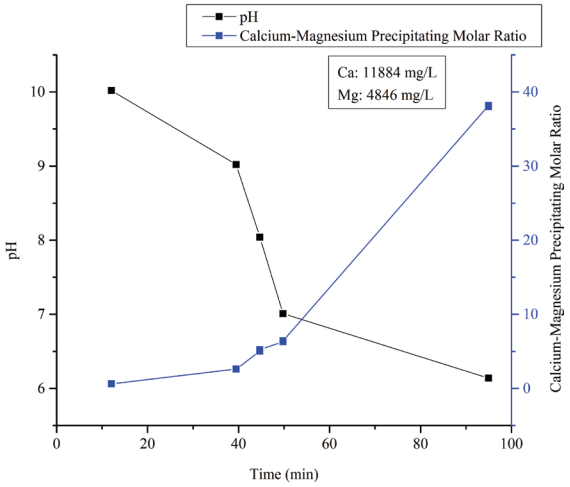

Fig. 8. Change of calcium-magnesium precipitating molar ratio and pH over time (calcium and magnesium molar ratio of 3:2).

As can be seen in Figs. 3, 5 and 7, at higher pH, Mg precipitated more and Ca precipitated less. As pH decreased, precipitate rate of Mg decreased while precipitate rate of Ca increased. This experimental phenomenon was consistent with literature [20]. Finally the precipitate rate of Ca was settled at 60% to 80%. In the first stage, at high pH, hydroxide precipitate is generated. $Mg(OH)_2$ precipitates first as the K_{sp} of $Ca(OH)_2$ is 1.3×10^{-5} and the K_{sp} of $Mg(OH)_2$ is 1.8×10^{-11}. With the continuous blowing in of CO_2, the pH decreased gradually. In the second stage, the precipitation of hydroxide gradually changed to $CaCO_3$ and $MgCO_3$. The K_{sp} of $CaCO_3$ is 8.7×10^{-9} [21] and K_{sp} of $MgCO_3$ is 2.6×10^{-5} [18] at room temperature. So the precipitate is gradually transformed into $CaCO_3$ first, resulting in an increase in the precipitation rate of Ca, and decrease in Mg precipitation. When $CaCO_3$ is completely precipitated, that is, the third stage, it doesn't make much sense if the pH continues to decrease. Therefore, the key to calcium and magnesium separation by carbonization is to control the pH in the second stage.

When the molar ratio of calcium to magnesium increased to 1:1, the change trend of precipitation rate was generally the same. But the overall precipitation rate of calcium was increased to about 80%, which was significantly higher than that of 60%–80% in Fig. 3. This is due to the change in the calcium-magnesium molar ratio, from 1:4 to 1:1. The increase of the molar ratio of calcium and magnesium leads to more Ca^{2+} reacting with the CO_3^{2-} to precipitate in the early stage, replacing Mg^{2+}, thus increasing the total precipitation rate of calcium. It can be concluded that the content proportion of calcium and magnesium have certain impact on the separation effect.

When the molar ratio of calcium to magnesium increased to 3:2, the overall trend of calcium and magnesium precipitation rate remains unchanged. Due to the high content of calcium and magnesium in the solution, makes it easier to react with CO_2. Therefore, the precipitation rate of calcium and magnesium is significantly higher than the former two solutions.

As can be seen from Figs. 4, 6 and 8, with the continuous introduction of CO_2, pH gradually decreased, and the calcium-magnesium molar ratio gradually increased. Before reaching 9.0, pH declined slowly, and the decline accelerated between 9.0 and 7.0, and then slowed again after pH dropped below 7.0. This is because when CO_2 is blown in the wastewater, the reaction formula (3) is initially performed in the wastewater. At this period, the concentration of CO_3^{2-} in the wastewater is very small and does not reach the K_{sp} of $CaCO_3$ and $MgCO_3$. There is no precipitation of $CaCO_3$ and $MgCO_3$. With the CO_2 keeps blowing in the concentration of CO_3^{2-} in waste water increases to form the solubility product of $CaCO_3$ and $MgCO_3$. As shown in Eqs. (4) and (5), the precipitation of $CaCO_3$ and $MgCO_3$ begins. Based on the balance movement principle, Eq. (3) moves to the right. The concentration of H^+ in wastewater increases and the pH decreases rapidly. When the waste water becomes neutral, the CO_2 continues to blow in, and the solution is acidic. Calcium and magnesium will not form precipitation again. When Ca^{2+} precipitation is complete, the trend of balance moving to the right in Eq. (3) becomes smaller, and the pH decreases slowly.

But compared with Fig. 4 (Fig. 8 is not mentioned here because the flow rate of CO_2 in Fig. 8 has been changed), the pH of the 1:1 solution need more time to decrease than that in the 1:4 solution. The high calcium and low magnesium wastewater is harder to be carbonized, because the higher the concentration of Ca^{2+} is, the more CO_3^{2-} is consumed, the longer the reaction time will be. And the time needed to carbonize the low calcium and high magnesium wastewater is shorter, while the actual desulfurization wastewater has a composition closer to that of low calcium and high magnesium solution.

In order to minimize the error caused by various experimental factors, the results of multiple experiments are summarized to obtain the diagram of pH and calcium-magnesium precipitating molar ratio, as shown in Fig. 9.

As can be seen from Fig. 9, at pH 8–10, calcium-magnesium precipitating molar ratio changes little. Because when CO_2 is blown in the wastewater at the previous stage, both calcium and magnesium form deposits. When the pH drops to about 7, precipitating molar ratio begins to grow rapidly. This is because magnesium carbonate is no longer precipitated. However, no more significant increase occurs if the pH continues to decrease. Therefore, in order to achieve better separation effect of calcium and magnesium, the optimum pH condition for the carbonation process is 7, and it is not meaningful to continue lowering the pH.

3.2. *Effect of different calcium and magnesium concentrations on the separation of calcium and magnesium*

In practical desulphurization wastewater, the proportion of calcium and magnesium varies. This is also mentioned above. The following research was carried out to determine the proportion of calcium and magnesium suitable for the process of calcium and magnesium recovery. The concentration of calcium and magnesium in each water sample is shown in Table 1 (The data is the same as above). Based on the experiments in section 3.1, the relevant data is used to plot Fig. 10.

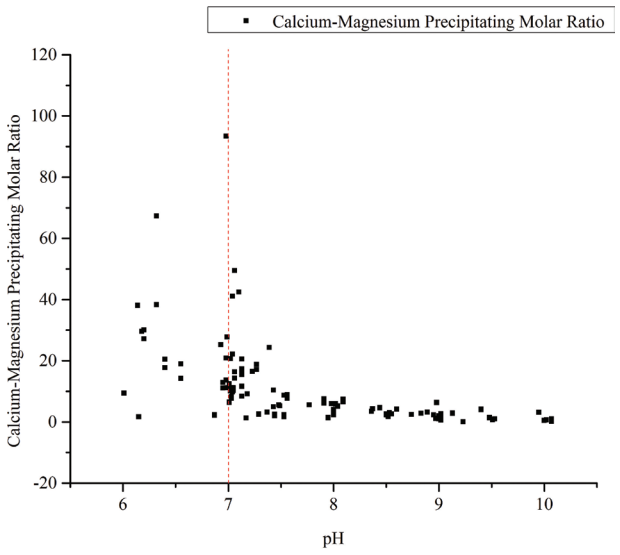

Fig. 9. Change of calcium-magnesium precipitating molar ratio with pH.

As can be seen from Fig. 10, calcium-magnesium precipitating molar ratio was influenced by calcium-magnesium molar ratio. The calcium-magnesium precipitating molar ratio in the 1:1 solution was the highest and the change was relatively flat. The change in the 3:2 solutions was gentle. The calcium-magnesium precipitating molar ratio of Ca and Mg precipitated in 1:4 was the lowest, that was, and the worst separation effect and this ratio were closest to the concentrations of calcium and magnesium desulfurization wastewater. Because when the molar ratio of calcium and magnesium in wastewater are higher, Ca^{2+} is easier to combine with CO_3^{2-} to form precipitation, and calcium and magnesium separation is more thorough. When the molar ratio of calcium to magnesium in wastewater is relatively low, the CO_2 initially injected is easy to combine with Mg^{2+} to form magnesium carbonate precipitation, which may lead to incomplete Ca^{2+} precipitation, resulting in poor separation effect of calcium and magnesium.

As mentioned above, when the calcium-magnesium molar ratio is 1:4, the separation effect is the worst. However, it can be seen from Fig. 10 that at 1:4, the precipitation rate of calcium is still over 70% while the magnesium precipitation rate is below 20%. The separation of calcium and magnesium can basically meet the requirements for the treatment of desulfurization wastewater.

The effect of calcium and magnesium separation decreases with the increase of the content of magnesium ions in the wastewater. Therefore, the technology works best in wastewater containing high calcium and low magnesium, and can basically meet the requirements when the calcium-magnesium molar ratio is not less than 1:4. If the ratio continues to decrease, the follow-up recovery of magnesium product purity may be difficult to achieve the industry standard. Industrial grade $Mg(OH)_2$ qualified product quality fraction (purity of magnesium product mentioned in this experiment) is not less than 92% according to HG/T 3607–2007. But the molar ratio in most of the desulfurization wastewater is higher than 1:4.

3.3. Effect of water temperature on calcium and magnesium separation

In order to explore the effect of water temperature on the separation of calcium and magnesium, the temperature of the simulated desulfurization slurry was controlled at 10°C, 20°C, 30°C, 40°C and 50°C with a thermostatic magnetic stirrer. When the pH dropped to 7, calcium-magnesium precipitation molar ratio was measured and calculated. The relationship between the temperature and calcium-magnesium precipitation molar ratio is obtained, as shown in Fig. 11.

As can be seen from Fig. 11, if the temperature was lower than 30°C, the calcium-magnesium precipitating molar ratio was greatly influenced by temperature. At 10°C, the calcium-magnesium precipitating molar ratio was the largest and decreased at 20°C. After reaching 30°C, calcium-magnesium precipitating molar ratio tended to be gentle, and less affected by temperature. It can be concluded that lower temperature contributes to better separation effect for calcium and magnesium. This is due to the great influence of temperature on gas-liquid mass transfer of CO_2 during the carbonization process. At low temperature, more CO_2 dissolves in the water, accelerating the reaction of CO_2 and $Ca(OH)_2$, to achieve better calcium Magnesium separation effect; when the temperature is higher than 30°C, high temperature is not conducive to the mass transfer of CO_2, thus affecting the separation of calcium and magnesium. Desulfurization wastewater temperature is usually at 50°C–60°C. Therefore, in the actual treatment process, the wastewater should be cooled naturally before entering the carbonization process. If the cooling temperature is too low, the problem of cold source is difficult to solve. Therefore, we chose to carry out the carbonization experiment at 30°C. At this point, the effect of temperature on the calcium and magnesium separation is not great.

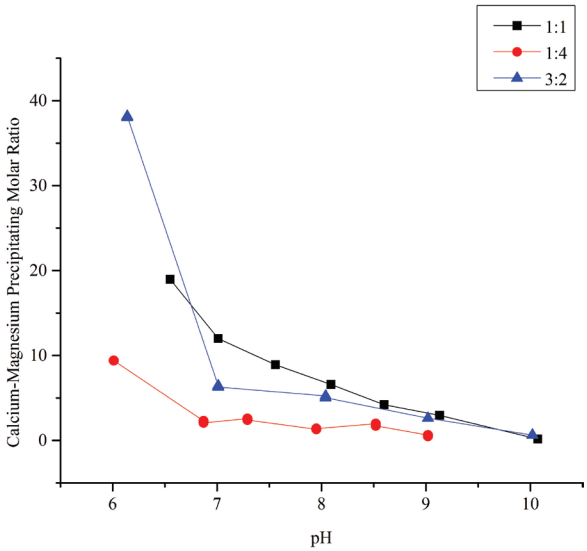

Fig. 10. Molar ratio of Ca and Mg precipitates in different concentrations of desulfurization wastewater varied with pH.

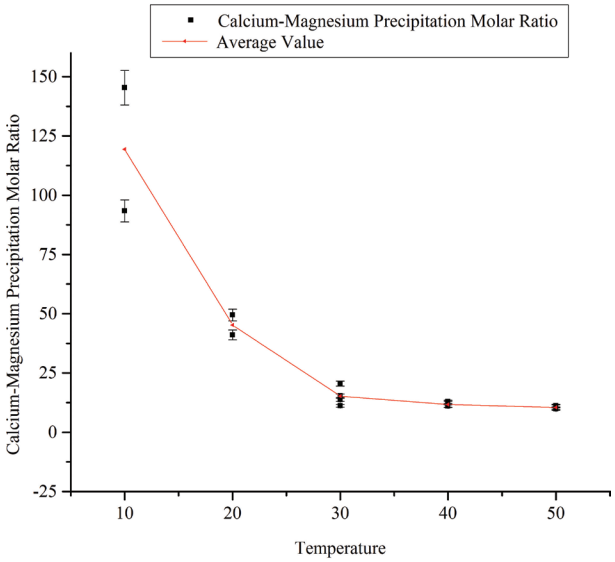

Fig. 11. Calcium-magnesium precipitation molar ratio with temperature.

3.4. Effect of different agents on magnesium recovery

After calcium and magnesium separation stage, the calcium precipitate was returned to the desulfurization tower for reuse, and the supernatant was sent into the next tower. Lye was added to adjust the pH, for the precipitation of magnesium, with a frame filter press to separate the magnesium hydroxide.

In order to verify the effect of different lye proportion on the precipitation of Mg, five kinds of lyes were prepared (the concentration of each lye is listed in Table 2). The lye was added into the solution respectively to adjust pH to 11; then the solution was filtered to titrate the calcium and magnesium content in the solution. The obtained calcium-magnesium precipitating molar ratio is shown in Fig. 12.

As can be seen from Fig. 12, a change in the proportion of lye had impact on the calcium-magnesium precipitating molar ratio. For the solution added with B lye (ie, 1 mol/L NaOH solution), the lowest calcium-magnesium precipitating molar ratio was obtained, with the highest magnesium purity. With the increase of sodium carbonate concentration, the calcium-magnesium precipitating molar ratio gradually increased, and the purity of magnesium decreased obviously. From the perspective of magnesium purity, pure NaOH should be chosen as the lye.

In order to analyze the precipitation and crystallization conditions of different lye from the microscopic point of view, the precipitate formed from the alkaline solution of B and C is taken and dried to carry out the SEM characterization to obtain Fig. 13.

Table 2
Components of lye

Percentage	Concentration of Na_2CO_3 (mol/L)	Concentration of NaOH (mol/L)
A	1	0
B	0	1
C (1:2)	0.33	0.67
D (1:1)	0.5	0.5
E (2:1)	0.67	0.33

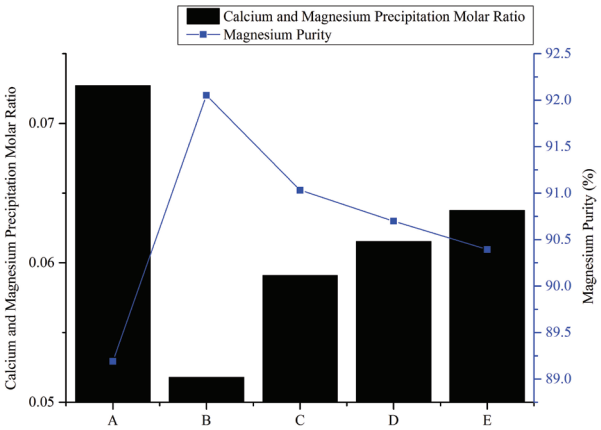

Fig. 12. Effect of different lye on calcium and magnesium precipitation molar ratio.

It can be seen from the SEM characterization that the precipitates formed by the addition of pure NaOH lye have uniform particle size and better crystallization effect. Such precipitate is easier to filter in the actual production process and the product particle size is better. When mixed lye is added, the particles in precipitate are not uniform, with amorphous crystals, and may have difficulty in dehydration process. This is caused by the addition of different kinds of alkali, which results in different kinds of precipitation. Different sizes of sediment may cause inconvenience to subsequent processing. Therefore, pure NaOH is the best choice for recovery process, both in yield and in precipitation condition of magnesium.

3.5. Effect of pH on recovery of magnesium

Based on the above experiment, during the process of recovering magnesium, the pH value of the desulphurization wastewater after adding different amounts of alkali is different, and the recovery and purity of magnesium obtained are also different. In order to study the optimum dosage for maximum magnesium recovery, the pH value was adjusted by controlling the amount of dosage, and the recovery rate and purity of magnesium at each pH value were obtained. Finally, the optimal dosage was gotten.

The simulation wastewater with Ca^{2+} content of 2,271.41 mg/L and Mg^{2+} content of 5,166.36 mg/L was prepared. The temperature of water sample was kept constant at 30°C with constant temperature magnetic stirrer, the flow of CO_2 gas was maintained at 0.6 L/min, the solution was carbonated to pH 7.39. The solution was filtered, and 1 mol/L NaOH was added to adjust pH. At pH of 9, 10, 11, 12 and 13, certain amount of solution was filtered to measure the concentration of calcium and magnesium, and the calcium-magnesium precipitating molar ratio was calculated. The change of calcium-magnesium precipitating molar ratio with pH is shown in Fig. 14.

As can be seen from Fig. 14 that the calcium-magnesium precipitating molar ratio decreased with the increasing pH. The larger the pH was, the higher the content of Mg in the precipitate would be. The calcium-magnesium precipitating molar ratio decreased obviously at about pH 10, and tended to be stable after the pH reached 11, indicating that there was almost no new precipitate. This is because after the alkali is added, the Mg^{2+} in the wastewater rapidly reacts with the alkali to form white precipitate. When the Mg^{2+} precipitate is completed, the molar ratio of calcium to magnesium will not change. Therefore, the pH of the magnesium recovery process can be adjusted to 11 and the amount of lye added is the optimal amount. This conclusion can be verified in document [21].

During the process of recovering magnesium with alkali, the pH can be adjusted to 10–11. The specific pH can be adjusted according to the purity of the magnesium product. But in order not to cause unnecessary waste of alkali, the maximum of pH should not exceed 11.

3.6. Effect of different flocculants on magnesium precipitation

Magnesium hydroxide precipitate is flocculent precipitation, which is difficult to be separated from the

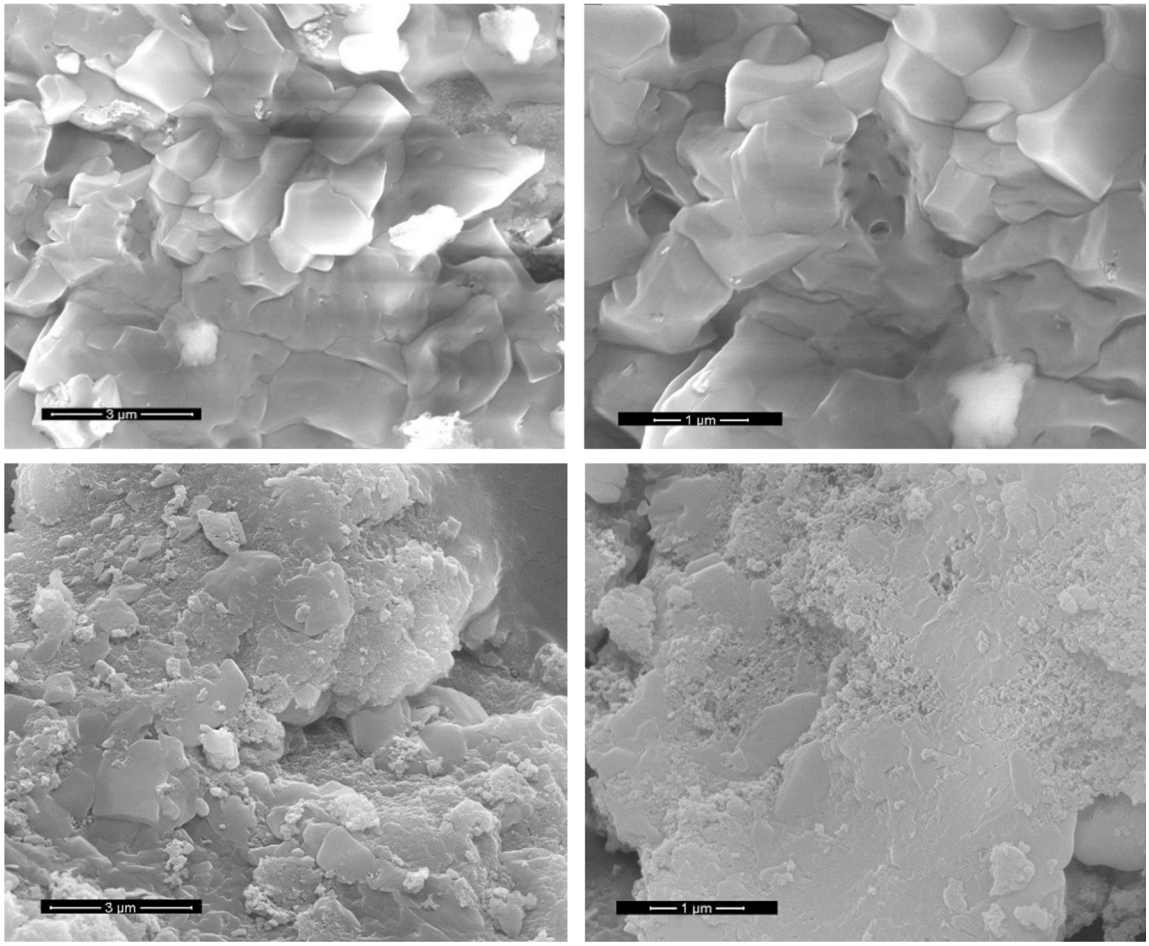

Fig. 13. SEM characterization of the precipitate produced by alkaline solution B (pure NaOH) (the upper) and alkaline solution C (Na_2CO_3: NaOH = 2:1) (the lower).

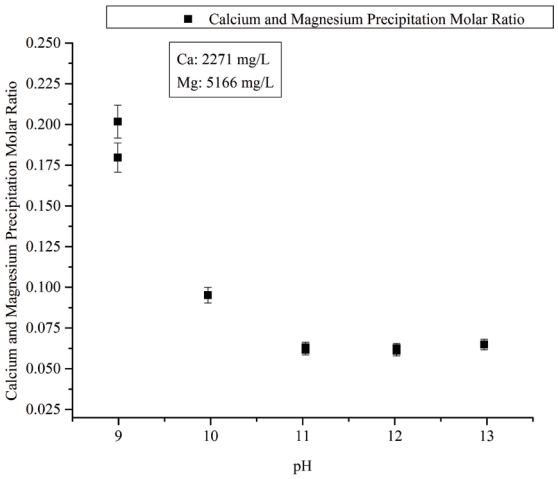

Fig. 14. Calcium and magnesium precipitation molar ratio with pH changes (NaOH).

solution in the actual process. Therefore, flocculants are needed to speed up the precipitation. Therefore, five different flocculants were used in this experiment, to compare its flocculation effect.

Different flocculants of 10g were added to 100mL solution respectively. The beakers from left to right in Fig. 15 were the samples added with PAC (polyaluminum chloride), nonionic PAM, PAM (AR), anionic PAM, cationic PAM solution, the right was the control group without any flocculants added.

As can be seen from Fig. 15, the effect of non-ionic PAM was the best; the precipitate could basically be filtered. After standing for 10 min, certain flocculation effect occurred in the five kinds of flocculants, in different rate. The PAC flocculant would cause discolouration of precipitation and affect the quality of sedimentation, which was not recommended in the actual production process. Effect of the four other flocculants: Nonionic PAM > PAM (AR) > Anionic PAM > Cationic PAM. Therefore, non-ionic PAM was usually used as flocculant to accelerate flocculation effect.

4. Product characterization and discussions

The sample solution before treatment and treated supernatant was evaporated to dryness for XRD characterization analysis, with dried precipitate obtained in the process. The diffraction pattern of the three samples verify the separation and recovery efficiency for calcium and

magnesium, XRD characterization analysis was performed for the water sample before treatment, the treated supernatant evaporated to dryness, and the precipitate obtained by diffraction pattern is shown in Fig. 16.

It can be seen from the XRD diffraction pattern that the initial water sample contained Ca and Mg compounds such as $MgCl_2{\cdot}6H_2O$ and $CaSO_4$; The precipitate obtained after magnesium recovery contained $Mg(OH)_2$; calcium and magnesium were not detected in the supernatant. The result indicates that the removal efficiency of this process is excellent and the obtained $Mg(OH)_2$ precipitate is in high purity. It can be used as an economical and efficient desulfurization wastewater softening technology.

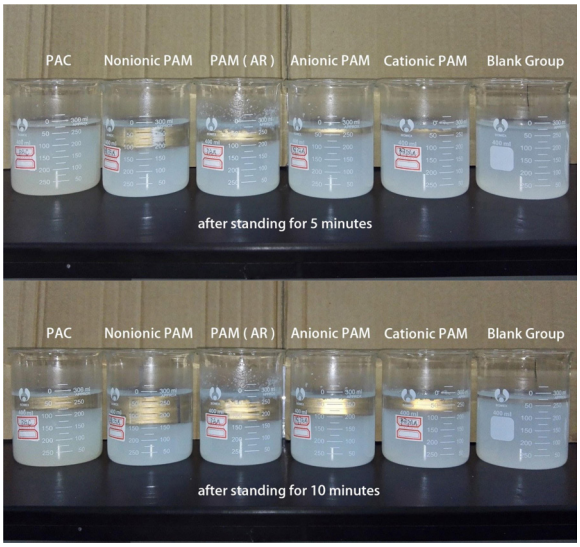

Fig. 15. Precipitation of six solutions after standing for 5 and 10 min.

In the laboratory-wide experiments, by calculating, the removal rates of calcium and magnesium can reach 80% and 90% respectively according to Eqs. (9) and (11), and the purity of magnesium hydroxide can reach 92% according to Eq. (15), which can fully meet the requirements of industrial magnesium hydroxide. The actual data show that although the calcium precipitation is not complete, the purity of magnesium can still meet the industrial requirements (industrial magnesium product purity requirements are referred to above). And the CO_2 required for pH adjustment is easy obtained from flue gas in power plants. The added $Ca(OH)_2$ and NaOH is at low prices, and the operation cost of the process is far lower than the existing power plant wastewater softening technologies. This experiment provides a theoretical reference for the recovery of calcium and magnesium in the desulfurization wastewater by carbonization. The experiment in the laboratory is successful, and pilot-scale experiment is needed in the next step, to verify its feasibility in actual production process.

5. Conclusions

In the first stage, the separation effect of calcium and magnesium in desulfurization wastewater by carbonation was good, and the precipitation rate of calcium could basically reach 80%. The optimum temperature condition for the carbonation was 30°C; the optimal pH of calcium and magnesium separation was about 7.0. The change of pH with time is related to the content of calcium and magnesium in the solution. The higher the content is, the slower the pH decrease. The separation effect is different for the desulfurization wastewater with different content of calcium and magnesium. The higher the content of magnesium is, the worse the separation effect is. When the ratio of calcium to magnesium is greater than 1:4, the effect of calcium and magnesium separation can basically meet the wastewater treatment requirements.

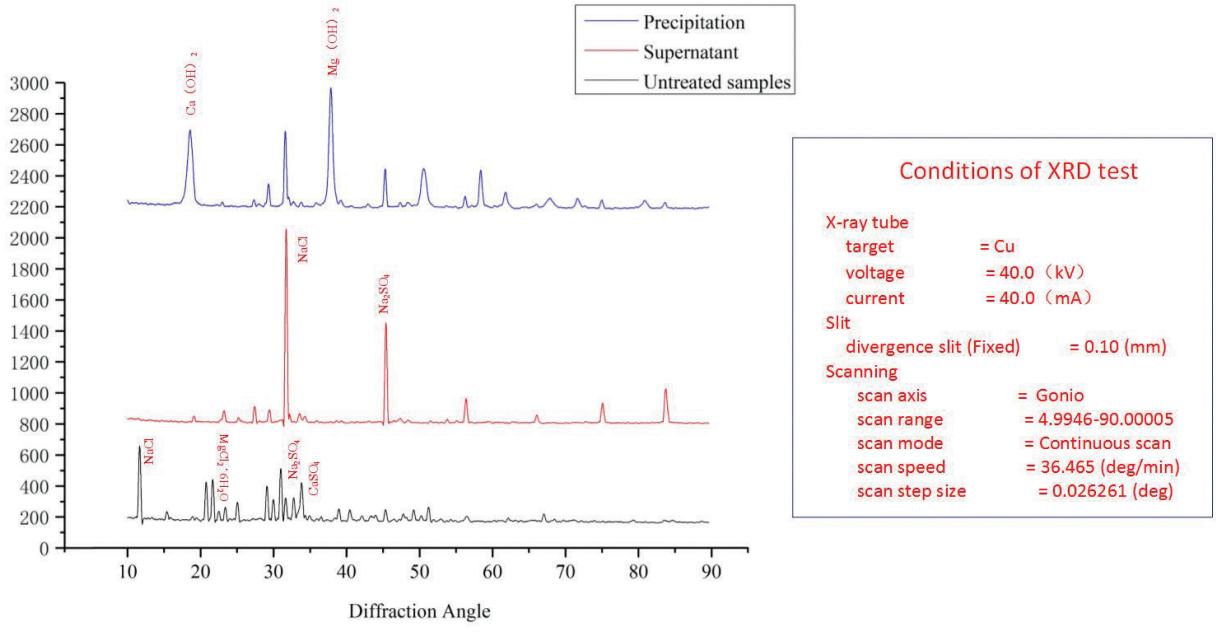

Fig. 16. XRD diffraction pattern.

In the second stage, lye was added to precipitate $Mg(OH)_2$ in the waste water, the purity of Mg was high, which could basically meet the industrial requirements. Pure NaOH is the best choice of lye to be added for pH adjustment. In the process of magnesium recovery, in order to separate the magnesium product, a certain amount of flocculant can be added to accelerate the precipitation. Among the PAM flocculants, the non-ionic PAM was the best choice.

Acknowledgment

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