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Softening of wastewater from wet flue gas desulfurization process based on internal airlift loop reactor (IALR)

Xiangxin Nie, Zongming Zheng*, Qiang Lu, Changqing Dong, Wu Qin, Tipeng Wang

National Engineering Laboratory for Biomass Power Generation Equipment, School of Renewable Energy, North China Electric Power University, Beijing 102206, China, Tel. +86-10-6177-1043; Fax: +86-10-6177-2030; emails: zmzheng@ncepu.edu.cn (Z. Zheng), xiangxinnie@126.com (X. Nie), qianglu@mail.ustc.edu.cn (Q. Lu), cqdong1@163.com (C. Dong), qinwugx@126.com (W. Qin), wtp_771210@163.com (T. Wang)

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ABSTRACT

The slurry discharge water from the flue gas desulfurization process in coal-fired power plant is rich in high salinity and chloride. The hardness may easily lead to scaling during the wastewater treatment. The internal airlift loop reactor based NaOH and CO_2 two-step approach is employed to investigate the softening of flue gas desulfurization wastewater treatment. NaOH is used to precipitate the dissolved magnesium in the first step. CO_2 is used to precipitate the dissolved calcium in the second step. The magnesium removal rate of 99% is obtained at the molar concentration ratio of NaOH and magnesium of 2.2 and aeration rate of 1 L min^{-1}. The optimized calcium removal condition is CO_2 concentration of 15% by volume, temperature of 30°C, initial pH of 12.8 and aeration gas rate of 7 L min^{-1}. The residual magnesium and calcium of 4.6 and 43.8 mg L^{-1} were detected in softening experiment with the coal-fired power plant flue gas desulfurization wastewater. The resultant $CaCO_3$ is the crystal calcite, which is a pure and regular flaky block and can be used as desulfurizer for wet flue gas desulfurization. This work provides the potential pretreatment solution for large scale flue gas desulfurization wastewater treatment.

Keywords: Coal-fired power plant; Scaling; Wastewater treatment; Internal airlift loop reactor; CO_2

1. Introduction

Sulfur oxide in the atmosphere, along with nitrogen oxide, could contribute to acid rain. It is the major precursor of fine particulate soot, or fine particulate matter. Emission of sulfur oxide may pose the significant health threat. Combustion of fuel containing sulfur in coal-fired power plants accounts for a large amount of sulfur oxide production. Flue gas desulfurization (FGD) is usually used to reduce the emission of sulfur dioxide. Among various FGD technologies, the wet scrubber technology is most popular due to its high efficiency and strong adaptability to feedstock coal. However, continuous operation of the system could lead to the accumulation of pollutant, such as chloride, fluorine, metals and other soluble component in the fly ash [1]. One approach to alleviating this negative influence is to discharge part of slurry when chloride content is 12,000–35,000 mg L^{-1} [2,3]. However, a large amount of FGD wastewater is produced during the discharge of slurry, which causes the environmental concerns due to the high salinity level, the high chloride concentration and the high water hardness.

Two types of FGD wastewater treatment technologies, thermal-based technologies and membrane-based technologies, are developed to meet the desalination requirement of the coal-fired power plants. Thermal-based technologies mainly include multieffect distillation, mechanical vapor recompression, flue duct evaporation and spray dryer [4,5]. Membrane-based technologies mainly include reverse osmosis, forward osmosis and membrane distillation [6–8]. However, as mentioned previously, FGD wastewater is characterized by the high hardness. High concentration of dissolved calcium and magnesium in water may lead to scaling. Boiling promotes precipitation of calcium carbonate, which

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* Corresponding author.

easily adhere to the heat exchanger and reduce the heat transfer efficiency [9–12] and sulfate is more easily precipitated in this atmosphere. If the flue duct evaporation was used, the deliquescence caused by mixture of calcium chloride and fly ash may seriously affect the mobility of residual solids in flue [13], and if the high-Cl and high-Ca coal is utilized, this situation could be worse due to the enrichment of Cl and Ca in particulate matter [14]. Moreover, the scaling will cause the increase of osmotic pressure and the reduction of permeate flux in membrane-based technologies [15,16].

Scaling prevention is of great importance for the industrial FGD wastewater treatment. Many approaches can be employed to remove dissolved calcium and magnesium from wastewater, including ion exchange [17], nanofiltration membrane [18], carbon nanotube sheets [12], natural clinoptilolite [19] and calcite ooids [20]. However, these technologies have limited effects on scale prevention for FGD wastewater. For example, ion exchange resin has been proven to be effective only when the total dissolved solids concentration is less than 500 mg L^{-1} in wastewater due to adsorption capacity of resin [21].

It is generally believed that the softening is indispensable for FGD further wastewater treatment, and the chemical precipitation-based method is favored, especially the two step softening method via NaOH and Na_2CO_3 addition [22,23]. However, large quantities of chemicals are consumed in this process. In this work, the NaOH–CO_2 method is employed to remove dissolved magnesium and calcium from FGD wastewater and thereby help the further wastewater desalination process. The effects of carbon dioxide concentration, wastewater temperature, wastewater initial pH, wastewater initial calcium concentration and gas velocity on softening are investigated in detail.

2. Materials and methods

2.1. FGD wastewater

A model solution was prepared with $CaCl_2$, $MgCl_2$, KCl, NaCl, $NaHCO_3$, $NaNO_3$ and deionized water according to the composition of FGD wastewater from power plants. The composition of the model solution is shown in Table 1. All the reagents in the model solution are analytical reagents, which are purchased from Aladdin (Shanghai, China).

2.2. Experimental device

In order to provide a carrier for the FGD wastewater softening experiments, an internal airlift loop reactor (IALR) was employed in this work. IALR is an important type of modified bubble columns. The gas holdup difference between ascending and descending regions drives the liquid circulation due to the density difference, which has a lot of advantages, for example, lower power consumption, higher gas holdup, higher mass-transfer coefficient, homogeneous shear and rapid mixing [24]. The reactor consisted of a vertical cylindrical external tube and a concentric draft tube, both of them were made with plexiglass, the gas was dispersed by a stainless steel gas distributor which was located at the bottom of the draft tube, the characteristics of the IALR is shown in Table 2 and the schematic of the experimental device is shown in Fig. 1.

Table 1
Composition of the FGD wastewater model solution

Parameter	Concentration (mg l^{-1})
TDS	29,900
Ca^{2+}	1,037, 2,073, 3,100, 4,147, 5,184
Mg^{2+}	3,365
Na^+	4,025
K^+	351
Cl^-	21,424
HCO_3^-	256
NO_3^-	351

Table 2
IALR characteristics

Parameter	Value
IALR height	400 mm
Height diameter ratio of IALR	4
Draft tube stage	1
Draft tube height	200 mm
Height diameter ratio of draft tube	3.125
Sectional area ratio of ascending and descending regions	0.803
Gas–liquid separation zone height	100 mm
Gas distributor	30 holes with 1 mm diameter

2.3. Magnesium removal experiment

NaOH solid (AR) was used to remove magnesium and the experiments were conducted in the IALR with the working volume of 2 L at ambient temperature for 20 min. The molar concentration ratio of NaOH and magnesium was 1.8–2.6. The initial magnesium concentration was 3,365 mg L^{-1}. The N_2 (purity > 99.999%) is used as the lifting gas with aeration rate of 1 L min^{-1}. The solution after magnesium removal experiments was immediately subjected to vacuum filter with 0.45 μm membrane (Minipore, Shanghai). The filtrate was collected for magnesium concentration detection. The main reaction involved in the magnesium removal process is shown in Eq. (1).

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2 \downarrow \quad (1)$$

2.4. Calcium removal experiment

The solution from magnesium removal experiments was filtered with the 0.45 μm membrane and then simulated flue gas was used to remove calcium from the filtrate. The removal experiments were conducted in the same IALR at 30°C–60°C. The initial calcium concentration was 1,037–5,184 mg L^{-1}. The compressed mixture gas of CO_2 and N_2 was used as the lifting gas and the reactant gas with aeration rate of 0.5–7 L min^{-1}. The volume ratio of CO_2 in the mixture gas was 5%–25%. The initial pH value of wastewater was 10–12.8. The solution after

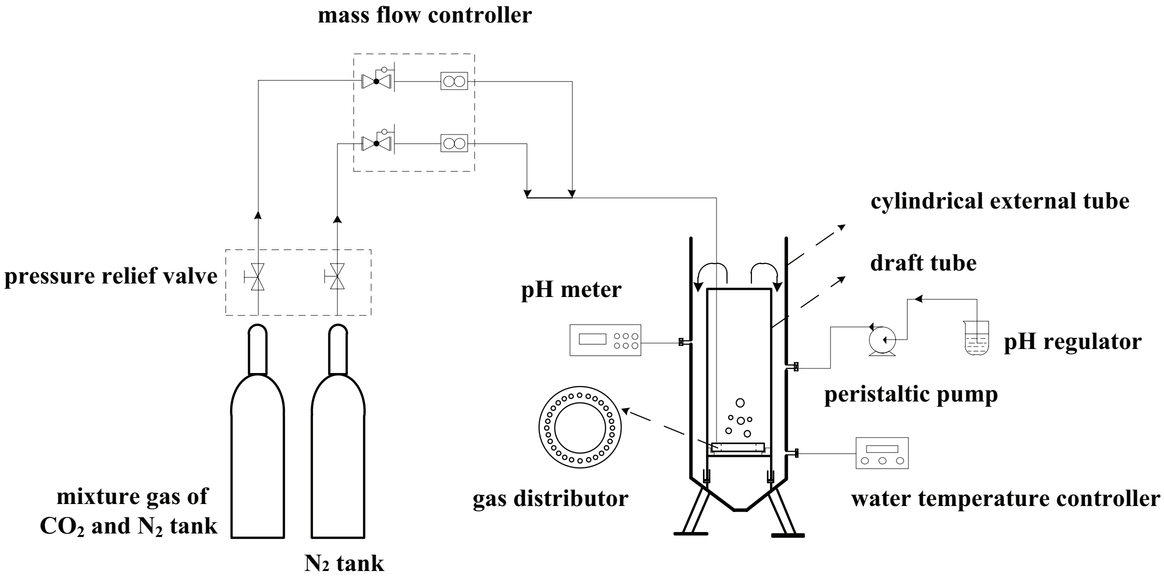

Fig. 1. Schematic of experimental device.

calcium removal experiments was also subjected to filter unit with 0.45 μm membrane. The filtrate was collected for calcium concentration detection. The main reaction involved in the calcium removal process is shown in Eqs. (2)–(6).

$$CO_2(g) \rightarrow CO_2(aq) \tag{2}$$

$$CO_2(aq) + H_2O \rightarrow H_2CO_3 \tag{3}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{4}$$

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{5}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \downarrow \tag{6}$$

2.5. Detection of calcium and magnesium concentration

The collected samples are analyzed to determine the calcium and magnesium concentration with the inductively coupled plasma atomic emission spectrometry (Optima 3000, PerkinElmer, New York, USA). In order to prevent the wavelength shift, the spectrometer was preheated 1 h before the samples were detected. The samples used for the detection were first diluted with deionized water (1:50) and then were introduced into spectrometer.

3. Results and discussion

3.1. Removal of magnesium

The magnesium removal rate is shown in Fig. 2(a). The removal rate is enhanced with increasing NaOH addition. The removal rate of more than 99% is observed when the molar concentration ratio of NaOH and magnesium amounts up to 2.2. The removal rate decreases to 95% at molar concentration ratio of 2.0. The reason for the removal rate reduction may reside in that the magnesium removal process was accompanied by calcium removal. The average removal rate of calcium ranges from 11% to 38% at different initial calcium concentration conditions during magnesium removal experiment (Fig. 2(b)). The dissolved calcium may be converted into the hydroxyl compound when pH value is more than 9.5 [25]. The change of pH value in the process of magnesium removal is shown in Fig. 2(c). Actually, pH value of wastewater is more than 10 even at the molar concentration ratio of sodium hydroxide and magnesium of 1.8. The detected calcium concentration after the removal of magnesium will be used as the basis for the calculation of calcium removal rate of the subsequent calcium removal experiments.

3.2. Removal of calcium

3.2.1. Effect of carbon dioxide concentration

The removal rate of calcium at different CO_2 concentration levels is shown in Fig. 3. The maximum and minimum calcium removal rate of 96% and 26% are obtained within 60 min, indicating that CO_2 concentration has a significant effect on the removal rate of calcium. The formation of calcium carbonate is influenced by the crystal growth [26]. Higher CO_2 concentration promotes the growth of calcium carbonate crystal and the precipitate of calcium carbonate. The diffusion of CO_2 into bulk liquid is the rate-limiting step of calcium removal reaction. It is enhanced with increasing CO_2 concentration in the simulated flue gas, which subsequently promote the removal of calcium. The typical CO_2 concentration in the flue gas of the coal-fired power plants is about 13%–15% [27]. The simulated flue gas with CO_2 concentration of 15% by volume is used in the following experiments.

3.2.2. Effect of wastewater temperature

The temperature of FGD wastewater ranges 30°C–50°C [28]. The effect of different temperature conditions

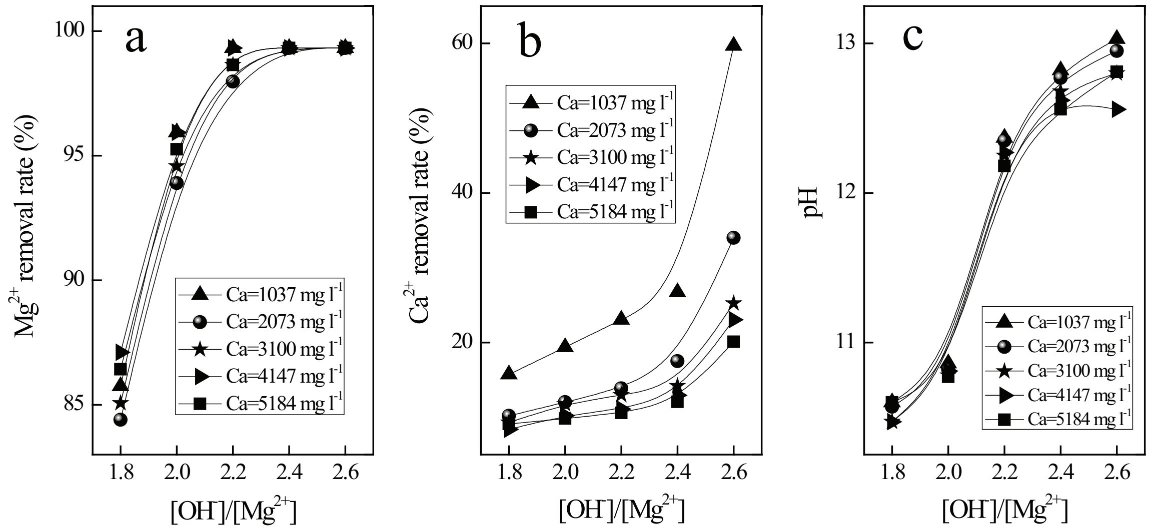

Fig. 2. Effect of the molar concentration ratio of NaOH and magnesium ion on magnesium removal rate (a), calcium removal rate (b), and pH variation (c).

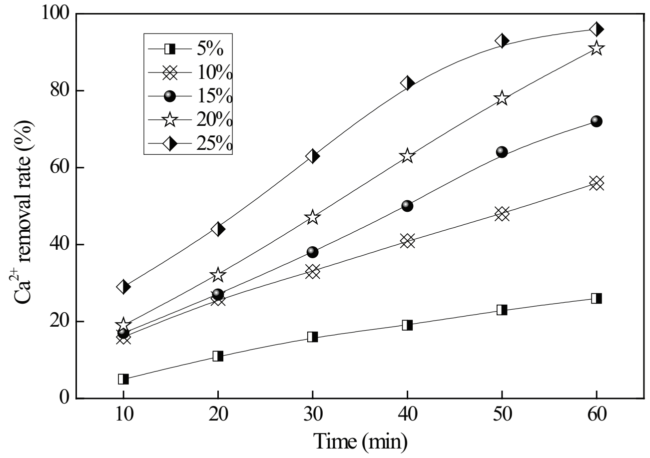

Fig. 3. Effect of carbon dioxide concentration on calcium removal rate with time (experimental conditions: wastewater initial pH of 12.8; ambient temperature; initial calcium concentration of 3,100 mg L^{-1}; calcium concentration after magnesium removal of 2,700 mg L^{-1} and aeration rate of 1 L min^{-1}).

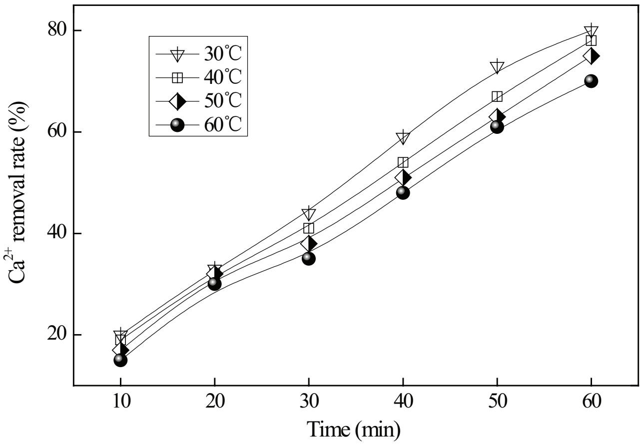

Fig. 4. Effect of wastewater temperature on calcium removal rate with time (experimental conditions: wastewater initial pH of 12.8; carbon dioxide concentration of 15%; initial calcium concentration of 3,100 mg L^{-1}; calcium concentration after magnesium removal of 2,700 mg L^{-1} and aeration rate of 1 L min^{-1}).

on the removal of calcium is investigated at 30°C–60°C (Fig. 4). The linear relationship between the removal rate and the reaction time is observed. The maximum and minimum values of calcium removal rate of 80% and 70% are obtained within 60 min, indicating the temperature effect is not significant. The removal rate of calcium decreases with the increasing temperature. Arrhenius equation and Van't Hoff equation are normally used to explain the variation of reaction and solubility of CO_2 with temperature [29,30]. Arrhenius equation is an empirical formula for the relationship between chemical reaction rate and temperature. Van't Hoff equation is the formula for the solubility of carbon dioxide in high salinity water. The formation rate of calcium carbonate is promoted at higher temperature based on Arrhenius equation whereas the escape of carbon dioxide is dominant based on Van't Hoff equation. With the increasing temperature, the motion transmissibility of gas molecules is enhanced, resulting in the escape of CO_2 from the water.

3.2.3. Effect of wastewater initial pH

The effect of wastewater initial pH change on calcium removal is shown in Fig. 5. The decalcification is promoted at higher pH. The carbonation reaction is the main reaction in the removal of calcium process at high pH value, which is shown in Eq. (7) [31].

$$2OH^- + Ca^{2+} + CO_2 \rightarrow CaCO_3 \downarrow + H_2O \tag{7}$$

In practice, limewater is often utilized to remove the heavy metal and magnesium from FGD wastewater in coal-fired

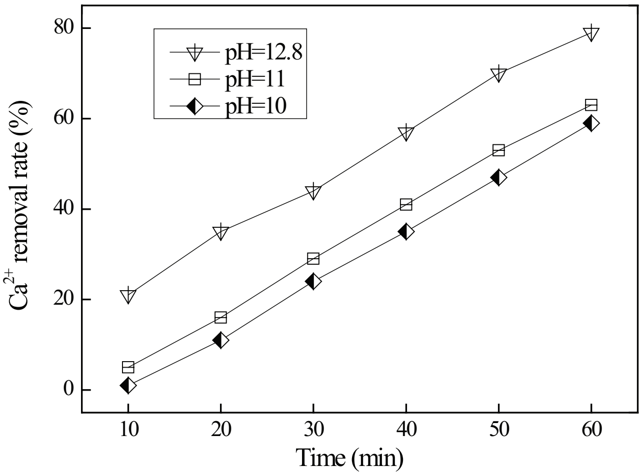

Fig. 5. Effect of wastewater initial pH on calcium removal rate with time (experimental conditions: wastewater temperature of 30°C; carbon dioxide concentration of 15%; initial calcium concentration of 3,100 mg L^{-1}; calcium concentration after magnesium removal of 2,700 mg L^{-1} and aeration rate of 1 L min^{-1}).

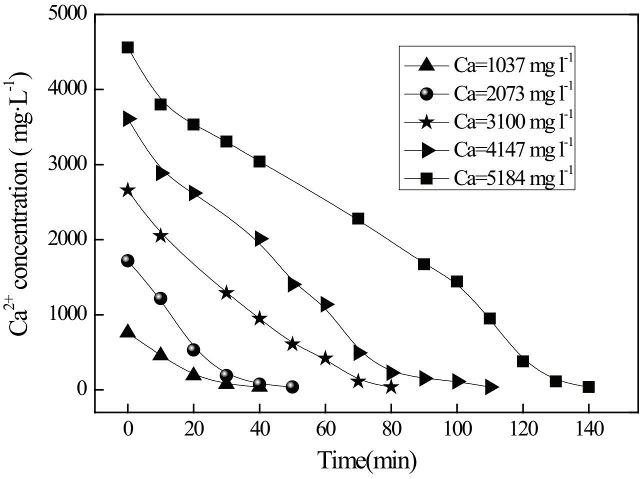

Fig. 6. Effect of wastewater initial calcium concentration on calcium removal with time (experimental conditions: wastewater initial pH of 12.8; wastewater temperature of 30°C; carbon dioxide concentration of 15% and aeration rate of 1 L min^{-1}).

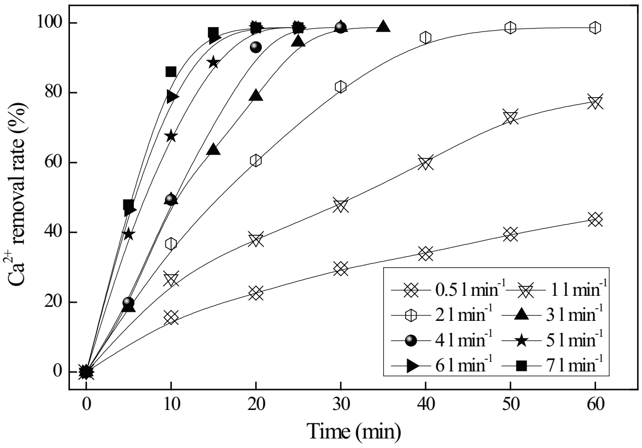

Fig. 7. Effect of aeration rate on calcium removal rate with time (experimental conditions: wastewater initial pH of 12.8; wastewater temperature of 30°C; carbon dioxide concentration of 15%; initial calcium concentration of 3,100 mg L^{-1} and calcium concentration after magnesium removal of 2,700 mg L^{-1}).

power plants. As mentioned above, FGD wastewater is particularly rich in chlorine. The carbonic acid is the weak acid. Theoretically, it is not feasible to completely remove calcium with CO_2 after magnesium removal with limewater. That is why NaOH–CO_2 method is employed to remove magnesium and calcium from FGD wastewater treatment in this work. Along with the reaction, the wastewater is partially neutralized by CO_2 addition.

3.2.4. Effect of wastewater initial calcium concentration

The effect of calcium removal under different initial calcium concentration conditions is shown in Fig. 6. The dissolution of carbon dioxide is promoted at higher pH. The removal rate of calcium of more than 99% is obtained under different calcium concentration conditions. The required reaction time for calcium complete removal increases from 30 to 140 min with the increasing initial calcium concentration, indicating a linear relationship between the initial calcium concentration and the reaction time. The FGD slurry discharge amount is very large. For example, the 2 × 300 MW coal-fired power unit discharges 6.5–15 t h^{-1} every day [32]. Both the removal rate and reaction time are important concerns for the industrial FGD wastewater treatment. In order to improve the efficiency of calcium removal, it is necessary to study continuous FGD wastewater treatment to figure out the influence of the residence time.

3.2.5. Effect of aeration rate

The effect of different aeration rate on calcium removal was studied (Fig. 7). It is found that the aeration rate has a significant effect. The maximum and minimum removal rate of calcium is 99% and 23%, respectively, within 20 min at different aeration rate. With the increasing aeration rate, the efficiency of calcium removal increases gradually and levels off when aeration rate amounts to 6–7 L min^{-1}. The removal efficiency reaches 99% at the aeration rate of over 3 L min^{-1} in 30 min. The change of pH value at different aeration rate is monitored, which was shown in Fig. 8. pH value decreases to around 9 when the removal rate reaches the maximum value. The final pH value of calcium removal process is independent on the aeration rate. Therefore, pH value could be used as an important index to determine the completion of the calcium removal.

3.2.6. Softening of FGD wastewater

The FGD wastewater sample obtained from a power plant in China is subjected to magnesium removal experiment at molar concentration ratio of NaOH and magnesium of up to 2.2. The subsequent calcium removal experiment is conducted at CO_2 concentration of 15% by volume, temperature of 30°C,

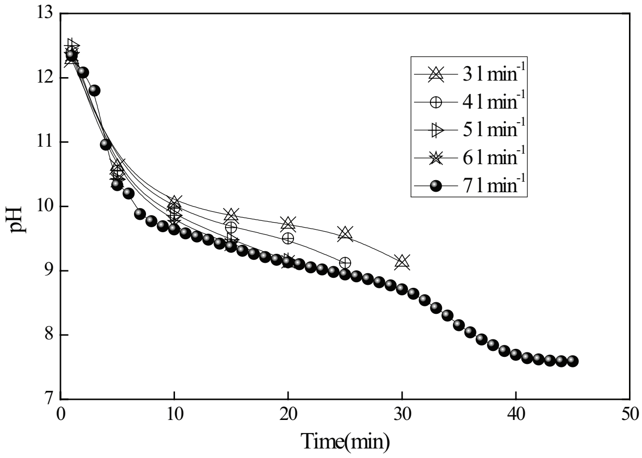

Fig. 8. Change of pH value of calcium removal at different aeration rate with time (experimental conditions: wastewater temperature of 30°C; carbon dioxide concentration of 15%; initial calcium concentration of 3,100 mg L^{-1} and calcium concentration after magnesium removal of 2,700 mg L^{-1}).

Table 3
FGD wastewater characteristics

Parameter	FGD wastewater	After removal of Mg	After removal of Ca
pH	6.7	12.5	8.9
Mg^{2+} (mg L^{-1})	2,180	4.7	4.6
Ca^{2+} (mg L^{-1})	581	292.9	43.8
Na^+ (mg L^{-1})	328	NA	NA
Cl^- (mg L^{-1})	2,850	NA	NA
F^- (mg L^{-1})	29.4	NA	NA
SO_4^{2-} (mg L^{-1})	7,420	NA	NA
TDS (mg L^{-1})	1,930	NA	NA
SS (mg L$^{-1)}$	43	NA	NA

initial pH of 12.8, reaction time of 20 min and aeration rate of 7 L min^{-1}, respectively. Concentration of magnesium and calcium in the wastewater before and after softening is shown in Table 3. The results indicated that NaOH–CO_2 method was effective to remove the dissolved magnesium and calcium from FGD wastewater. After softening, the residual magnesium and calcium concentration were 4.6 and 43.8 mg L^{-1}, respectively. The sediments obtained from magnesium removal and calcium removal experiments were characterized by the scanning electron microscope (SU8010, Hitachi, Tokyo, Japan) and X-ray diffraction (D8 ADVANCE, Bruker, Berlin, Germany), which are shown in Figs. 9 and 10. The sediment formed in the process of magnesium removal is flaky brucite ($Mg(OH)_2$). The crystal type is dense and irregular. The trace calcite was also detected. This may be caused by the dissolution of CO_2 in the aeration. The sediment after calcium removal is calcium carbonate with the crystal type of calcite, which is a pure and regular flaky block and can be used as desulfurizer for wet desulfurization.

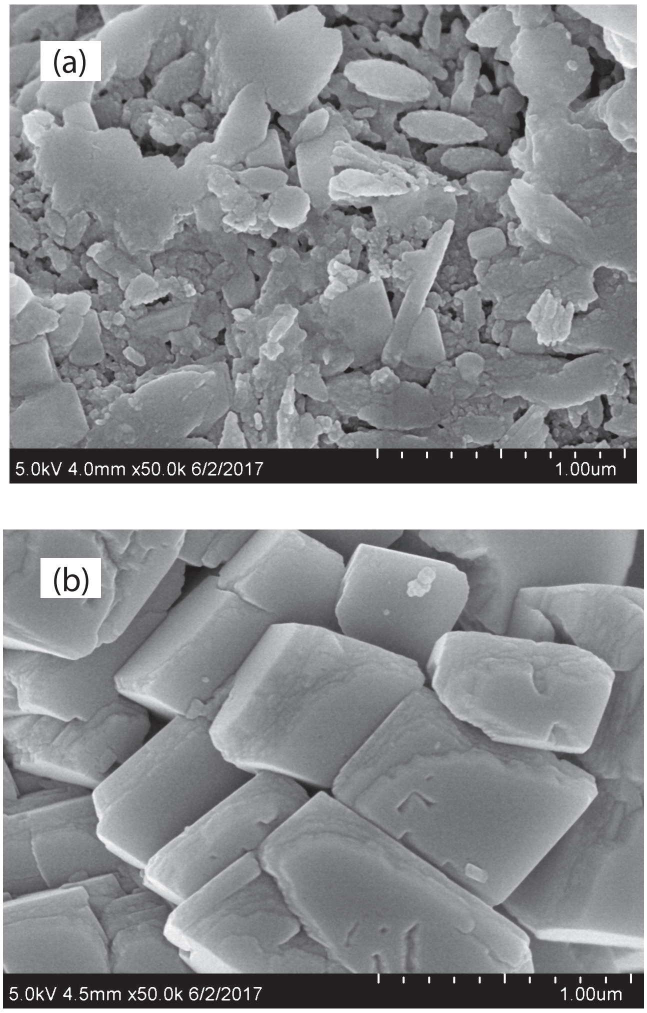

Fig. 9. SEM characteristics of sediments obtained from: (a) magnesium removal and (b) calcium removal.

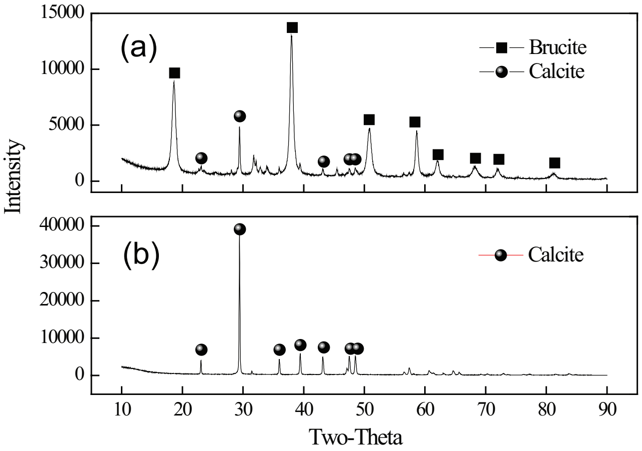

Fig. 10. X-ray diffraction analysis of sediments obtained from: (a) magnesium removal and (b) calcium removal.

4. Conclusion

NaOH and CO_2 two-step method is employed to remove dissolved magnesium and calcium from FGD wastewater. Sodium hydroxide was used for magnesium removal, and CO_2 is used for calcium removal. The main conclusions are as follows:

- The NaOH consumption has a significant effect on magnesium removal, the removal rate could not reach the maximum until the molar concentration ratio of NaOH and magnesium was 2.2, at which the maximum removal rate was more than 99% and the residual magnesium concentration was 4.6 mg L^{-1} when the value is carried out on the sample FGD wastewater with magnesium concentration of 2,180 mg L^{-1}.
- CO_2 concentration, initial pH and aeration rate are significant variables for calcium removal. The optimized calcium removal condition is CO_2 concentration of 15% by volume, initial pH of 12.8, aeration rate of 7 L min^{-1} and reaction time of 20 min. The residual calcium concentration was 43.8 mg L^{-1} when the conditions were carried out on the sample FGD wastewater with initial calcium concentration of 581 mg L^{-1}.
- The main component in the sediment of calcium removal was pure calcite, which could be used as the desulfurizer applying to wet FGD of coal-fired power plant.

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