The effect of hydrogen peroxide solution on SO_2 removal in the semidry flue gas desulfurization process

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ABSTRACT

The present study attempts to use hydrogen peroxide solution to humidify $Ca(OH)_2$ particles to enhance the absorption of SO_2 to achieve higher removal efficiency and to solve the valuable reuse of the reaction product in the semidry flue gas desulfurization (FGD) process. Experiments were carried out to examine the effect of various operating parameters including hydrogen peroxide solution concentration, Ca/S molar ratio and approach to adiabatic saturation temperature on SO_2 removal efficiency in a laboratory scale spray reactor. The product samples were analyzed to obtain semi-quantitative measures of mineralogical composition by X-ray diffraction (XRD) with reference intensity ratio (*RIR*) method and the morphology of the samples was examined by scanning electron microscope (SEM). Compared with spraying water to humidify $Ca(OH)_2$, SO_2 removal efficiency was improved significantly by spraying hydrogen peroxide solution of 1–3 wt.% to humidify $Ca(OH)_2$ because hydrogen peroxide solution enhanced the dissolution and absorption rate of SO_2. Moreover, XRD and SEM analyses show that the desulfurization products contain less amount of unreacted $Ca(OH)_2$ and more amount of stable calcium sulfate with increasing hydrogen peroxide solution concentration. Thus, the process mechanism of the enhanced absorption of SO_2 by spraying hydrogen peroxide solution to humidify $Ca(OH)_2$ was elucidated on the basis of the experimental results.

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1. Introduction

The semidry flue gas desulfurization (FGD) processes are effective in reducing SO_2 emission from medium- and small-scale coal-fired power stations with the advantages of small space requirement, low water consumption and low investment and operation costs [1–3]. Thus, these processes are very attractive for the desulfurization retrofits in the old units. However, compared with wet FGD processes, SO_2 removal efficiency and sorbent utilization in the semidry FGD processes are relatively low [4,5]. Moreover, a great variety of analytical methods have revealed that the products of the semidry FGD processes primarily contain $Ca(OH)_2$ and $CaSO_3 \cdot 1/2H_2O$ [6–8]. The unstable calcium sulfite could release SO_2 again at high temperature or acid atmosphere, which restricts the reuse of the desulfurization products. Therefore, it is important to add a small amount of chemical oxidants into the semidry FGD processes to enhance SO_2 absorption to improve the removal efficiency and simultaneously to obtain more stable products which are primarily comprised of calcium sulfate.

Hydrogen peroxide (H_2O_2), as a strong oxidant, can react fast with SO_2 and NO_x and enhance the absorption of the gaseous pol-

lutants. Additionally, H_2O_2 can be safe to store and will not cause secondary pollution because it is itself non-toxic and non-polluting and decomposes into water and oxygen [9]. Using aqueous solution of hydrogen peroxide to scrub flue gas containing SO_2 and NO_x will enhance the absorption rate even with a small gas scrubber. Furthermore, it could produce valuable sulfuric acid or nitric acid of high concentration with the recycle of acid solutions containing hydrogen peroxide in wet flue gas cleaning system [10–13]. Wang's investigation showed that adding 1–5 mL/L hydrogen peroxide solution into lime slurry in spray dryer FGD process could increase SO_2 removal efficiency by 20% [14]. Our previous study also showed that SO_2 removal efficiency and sorbent utilization were significantly improved when hydrogen peroxide solution was used to humidify $Ca(OH)_2$ particles for high SO_2 concentration in the simulated flue gas for high sulfur content coal [15]. However, the mechanism of the enhanced absorption of SO_2 with hydrogen peroxide solution in the semidry FGD processes is not clear.

The objective of this paper is to investigate the effect of various operating parameters including hydrogen peroxide solution concentration, Ca/S molar ratio and approach to adiabatic saturation temperature on SO_2 removal efficiency in a laboratory scale spray reactor when using hydrogen peroxide solution to humidify $Ca(OH)_2$ particles. Moreover, the process mechanism on the enhanced absorption of SO_2 with hydrogen peroxide solution was analyzed and elucidated by semi-quantitative analysis
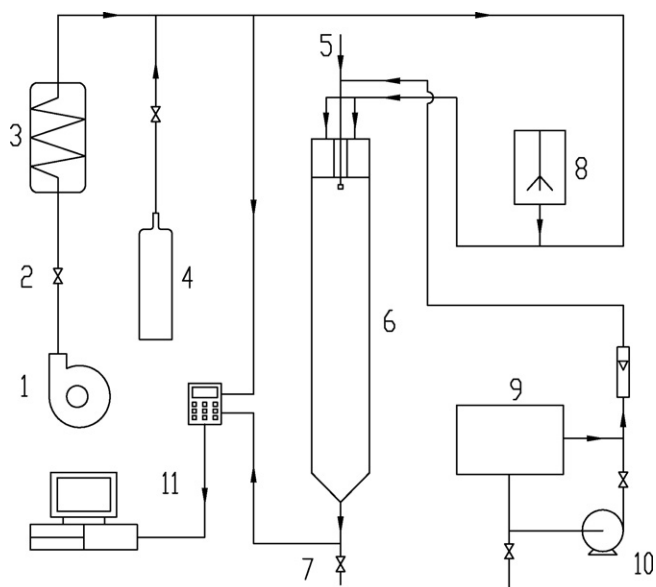
Fig. 1. Schematic experimental setup: (1) blower; (2) control valve; (3) electric heater; (4) SO₂ cylinder; (5) Y-jet nozzle; (6) spray reactor; (7) sample collector; (8) variable speed screw feeder; (9) water tank; (10) pump; (11) flue gas analyzer.

of mineralogical compositions with X-ray diffraction (XRD) reference intensity ratio (*RIR*) method and microscopic analysis of the semidry FGD products with scanning electrical microscope (SEM).

2. Experimental

2.1. Experimental setup and procedure

The schematic experimental setup, as shown in Fig. 1, was composed of a simulated flue gas system, a laboratory scale spray reactor, a variable speed sorbent feeder, one set of spray water humidification system and a gas sampling and analyzing system. The spray reactor was a stainless steel cylinder with an internal diameter of 0.2 m and a height of 1.0 m. The flue gas flow rate in the reactor was 70 m^3/h (STP) and gas residence time was 1.1 s. The air stream from the blower was measured by a rotameter and heated to 120–140 °C by an electric heater. The SO₂ gas from a SO₂ cylinder (purity >99.9%) measured by a rotameter was mixed into the air stream to produce the simulated flue gas of a desired SO₂ concentration. The chemical grade Ca(OH)₂ particles were fed by a variable speed feeder and the simulated flue gas entrained the given amount of Ca(OH)₂ particles into the spray reactor through the top gas distributor. The Y-jet twin fluid nozzle located at the centerline of the reactor atomized hydrogen peroxide solution to fine droplets, and Ca(OH)₂ particles were humidified by spray droplets to form aqueous lime slurry droplets which reacted with SO₂ in flue gas. The dry FGD product samples at the reactor outlet were colleted for microscopic analysis and then the flue gas containing the reaction products was cleaned by dust filter to discharge into the atmosphere.

The SO₂ concentrations in flue gas were measured online at the inlet and outlet of the spray reactor with Testo 350XL type flue gas analyzer. The analyzer was calibrated with standard gases before the experiments were conducted, and the range of the monitored SO₂ concentration was 0–1000 ppm with the accuracy of ±4 ppm. The inlet SO₂ concentration in the reactor is 1425 mg/m^3 (500 ppm) for low sulfur content coal in the present experiments. SO₂ removal efficiency was calculated from the inlet and outlet SO₂ concentrations in the reactor for each run. The flue gas dew point temperature was measured by Testo 645 type humidiometer. In order to indicate

Table 1
Physical properties of Ca(OH)₂ sorbent.

Surface area (m²/g)	6.664
Pore volume (cm³/g)	0.0449
Mean pore diameter (nm)	25.946

the repeatability of the experimental results, the experiments were carried out repeatedly at the same operating parameters such as Ca/S molar ratio, approach to adiabatic saturation temperature and hydrogen peroxide solution concentration.

2.2. Experimental materials

The chemical grade calcium hydroxide particles (Shanghai Huangdu Lime Company) were used as a sorbent which consisted of 99.7% Ca(OH)₂ to eliminate the effect of impurity in the sorbent on XRD analysis. The particle mean diameter of Ca(OH)₂ was 73 μm measured by laser particle size analyzer. The Brunauer–Emmett–Teller (BET) surface area and the Barrett–Joyner–Halenda (BJH) pore volume of Ca(OH)₂ particles were determined from the N₂ adsorption–desorption isotherms at 77 K using an ASAP 2010 vacuum volumetric sorption instrument. Before N₂ sorption analysis, the samples were preheated at 493 K for degassing and cooled at room temperature under vacuum conditions. The physical properties of Ca(OH)₂ sorbent used in the present study were listed in Table 1.

The 35 wt.% industrial hydrogen peroxide solution was diluted by the given amount of distilled water and well-stirred in the water tank to obtain hydrogen peroxide solution of a low concentration ranging from 1 to 3 wt.% before the experiments were conducted. The heat transfer equation was used to determine spray droplet mean diameter to ensure the complete evaporation of the droplets at the outlet of the reactor, expressed by Eq. (1).

$$\tau = \frac{\gamma \rho d^2}{8\lambda \Delta t_m} \tag{1}$$

where τ is the evaporation time of spray droplets, determined by the flue gas residence time in the reactor, ρ is the droplet density, d is the droplet mean diameter, λ is the thermal conductivity, and Δt_m is the logarithmic mean temperature difference in the reactor, expressed as

$$\Delta t_m = \frac{t_{in} - t_{out}}{\ln[(t_{in} - t_{as})/(t_{out} - t_{as})]} \tag{2}$$

where t_{in} and t_{out} are the flue gas inlet temperature and outlet temperature measured by thermocouples, respectively. t_{as} is the adiabatic saturation temperature in the reactor measured by Testo 645 humidiometer.

Therefore, the droplet mean diameters and size distributions of Y-jet nozzle at different spray water mass flow rates were measured by laser particle size analyzer in advance. The spray cone angle of Y-jet nozzle was 15°, and the droplet mean diameter was controlled to be less than 60 μm to obtain the dry products at the outlet of the reactor by adjusting the operating parameters of Y-jet nozzle.

2.3. Semi-quantitative analysis of desulfurization samples by XRD

The dry FGD product samples for typical runs were collected at the reactor outlet and analyzed to determine the physical and chemical properties of the products. A Bruker-AXS type XRD over the angular range 10–70° (2θ) in 0.010° steps and 8 s per step was used to obtain semi-quantitative measures of mineralogical composition of the desulfurization products. A JSM-6460 type SEM was used to examine the surface morphologies of the samples.

Quantification of samples obtained from XRD was performed by measuring the intensity of the peaks acquired in the scan. In

samples containing a mixture of materials, the intensity of a peak is proportional to the mass fraction and the atomic number of the elements responsible for that reflection. The derivation of the equations relating intensity and mass is described by Nuffield [16].

The basic equation describing the intensity of a peak from a given material, 'a', in a mixture of n materials is given by [16,17]

$$I_a = K_a \frac{W_a/\rho_a}{\sum_1^n W_n \mu_n^*} \qquad (3)$$

where I_a is the intensity of a peak associated with the component 'a', K_a is the constant dependent on the nature of the component 'a' and the instrumental arrangements, W_a is the weight fraction of the component 'a', ρ_a is the density of the component 'a', W_n is the weight fraction of the component 'n', and μ_n^* is the mass absorption coefficient associated with the component 'n'. If Eq. (3) is applied to two components in a heterogeneous mixture of materials, the ratio of the intensities of two components is given by

$$\frac{I_a}{I_b} = \frac{RIR_a W_a}{RIR_b W_b}$$

$$\frac{W_a}{I_a/RIR_a} = \frac{W_b}{I_b/RIR_b} \qquad (4)$$

where I_b is the intensity of a peak associated with the component 'b', RIR_a and RIR_b are the constants representing K_a/ρ_a and K_b/ρ_b, respectively, and W_b is the weight fraction of the component 'b'.

For n phase components in a heterogeneous mixture of materials, Eq. (4) is expressed as

$$\frac{W_1}{I_1/RIR_1} = \frac{W_2}{I_2/RIR_2} = \cdots = \frac{W_i}{I_i/RIR_i} = \cdots = \frac{W_n}{I_n/RIR_n} \qquad (5)$$

and

$$\sum_{i=1}^n W_i = 1 \qquad (6)$$

Therefore, the weight fraction of particular crystal phase i in samples containing a mixture of n materials can be determined by reference intensity ratio (RIR) method [18,19]:

$$W_i = \frac{I_i/RIR_i}{\sum_{k=1}^n I_k/RIR_k} \times 100\% \qquad (7)$$

where I_i is the integrated intensity of diffraction of the ith phase, RIR_i is the reference intensity ratio of the ith phase, W_i is the weight content of the ith phase, and n is the phase number of the multiphase mixture.

With Jade's Easy-Quant package and the ICSD subfile available with ICDD 1998 and later releases of the PDF2 CD, we can perform quantitative analysis on multi-phase mixture easily by means of reference intensity ratio (i.e., RIR, also called I/I_c in the PDF database). The ~40 K patterns calculated from the crystal structures in the ICSD subfile make it possible to look up the RIR values for most of the common phases encountered [19].

3. Results and discussion

3.1. Only spraying water droplets to humidify Ca(OH)₂ particles

The effect of Ca/S molar ratio and approach to adiabatic saturation temperature on SO_2 removal efficiency is shown in Fig. 2 when only spraying water droplets to humidify $Ca(OH)_2$ particles. The repeatability errors of the experiments are also shown in Fig. 2. It can be seen that SO_2 removal efficiency increases significantly when Ca/S molar ratio increases from 1.0 to 2.0 at the same approach to adiabatic saturation temperature, and it increases
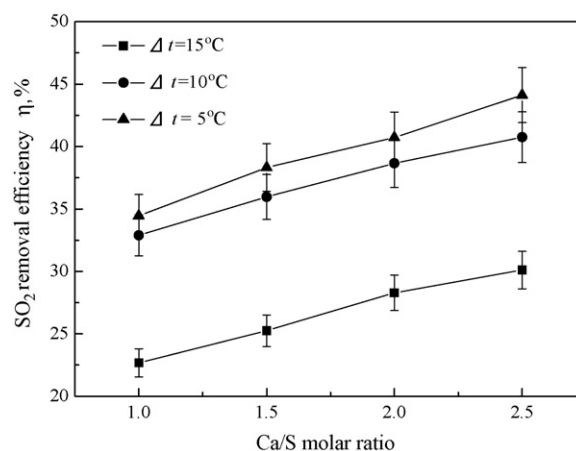

Fig. 2. Effect of Ca/S molar ratio on SO_2 removal efficiency when only spraying water droplets to humidify $Ca(OH)_2$.

relatively slow when Ca/S molar ratio exceeds 2.0. Thus, the suitable Ca/S molar ratio in the semidry FGD process is 2.0 or so when operation costs are taken into account, which agrees well with the results in the typical semidry FGD process of sorbent humidification activation [2]. The approach to adiabatic saturation temperature decreases with the increase of spray water mass flow rate. SO_2 removal efficiency increases sharply when the approach to adiabatic saturation temperature decreases from 15 to 10 °C even 5 °C. However, too small approach to adiabatic saturation temperature may cause the wetting and corrosion of the desulfurization reactor wall. Therefore, it is better to control spray water mass flow rate to ensure that the approach to adiabatic saturation temperature is about 10 °C.

3.2. Only spraying hydrogen peroxide solution of different flow rates

Fig. 3 shows the effect of different hydrogen peroxide solution flow rates on SO_2 removal efficiency when only hydrogen peroxide solution is sprayed to scrub flue gas. SO_2 removal efficiency increases from 8.1% to 31.6% with the increasing mass flow rate of hydrogen peroxide solution at the same concentration. When hydrogen peroxide solution is sprayed to scrub flue gas containing SO_2, hydrogen peroxide can oxidize the dissolved SO_2 to form soluble sulfuric acid as follows: $SO_2 + H_2O_2 \rightarrow H_2SO_4$. It means that hydrogen peroxide enhances the oxidation-absorption of SO_2 in
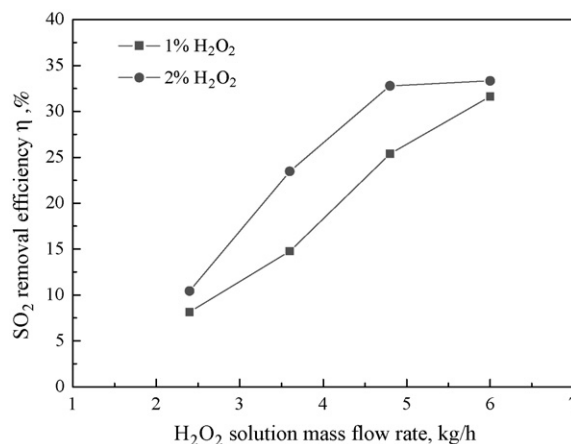

Fig. 3. Effect of different hydrogen peroxide solution flow rates on SO_2 removal efficiency when only spraying hydrogen peroxide solution.
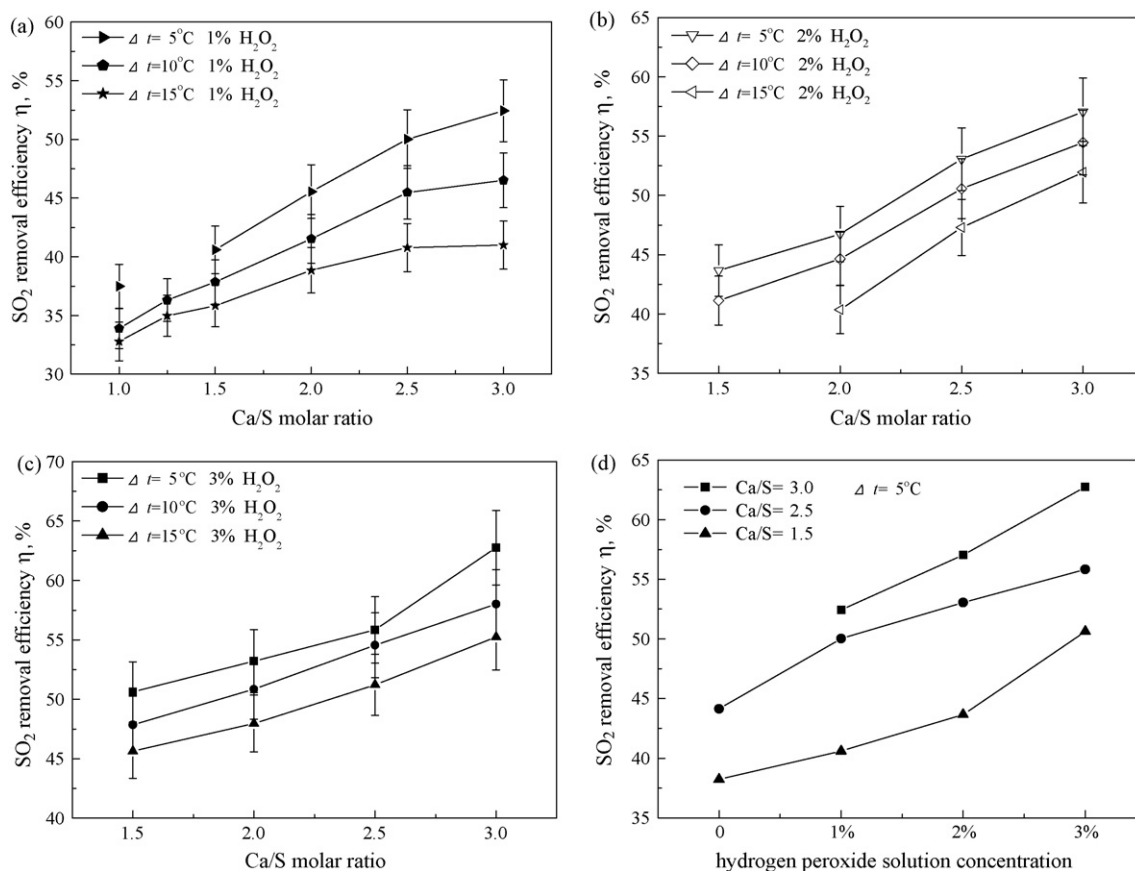
Fig. 4. Effect of different hydrogen peroxide concentrations on SO_2 removal efficiency when spraying hydrogen peroxide solution to humidify $Ca(OH)_2$.

flue gas. Moreover, SO_2 removal efficiency also increases with the increasing hydrogen peroxide concentration at the same hydrogen peroxide solution flow rate.

3.3. Spraying hydrogen peroxide solution of different concentrations to humidify $Ca(OH)_2$

Fig. 4 shows the effect of different hydrogen peroxide solution concentrations on SO_2 removal efficiency when spraying hydrogen peroxide solution to humidify $Ca(OH)_2$ particles in the reactor. The effect of Ca/S molar ratio and approach to adiabatic saturation temperature on SO_2 removal efficiency when spraying hydrogen peroxide solution of 1% to 3% to humidify $Ca(OH)_2$ in Fig. 4a–c is the same as that when only spraying water to humidify $Ca(OH)_2$ in Fig. 2. The data were rearranged in Fig. 4d to indicate the effect of hydrogen peroxide solution concentration on SO_2 removal efficiency. It can be seen that SO_2 removal efficiency increases significantly with increasing hydrogen peroxide concentration from 0% to 3% at the same Ca/S molar ratio and approach to adiabatic saturation temperature.

Fig. 5 shows comparison of SO_2 removal efficiency between the humidification of $Ca(OH)_2$ by spraying hydrogen peroxide solution
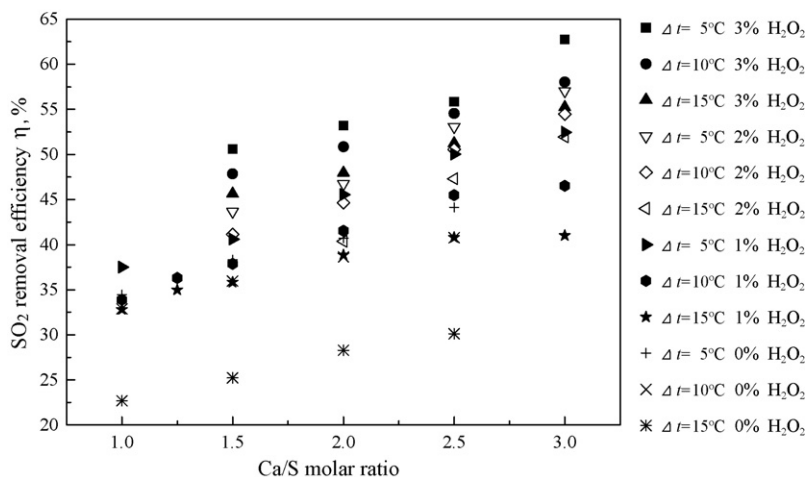

Fig. 5. Comparison of SO_2 removal efficiency between the humidification of $Ca(OH)_2$ by spraying hydrogen peroxide solution and water.

of different concentrations and by only spraying water. As can be seen, SO_2 removal efficiency ranged from 25% to 40% when spraying water to humidify $Ca(OH)_2$, and it increased from 45% to 56% when spraying hydrogen peroxide solution of 3% to humidify $Ca(OH)_2$. Compared with spraying water to humidify $Ca(OH)_2$, SO_2 removal efficiency increased by 15–20% when spraying hydrogen peroxide solution of 1–3%. The calcium-based sorbent utilization is usually defined as the ratio of SO_2 removal efficiency to Ca/S molar ratio. The sorbent utilization was 32.0% and 24.0% at 3% H_2O_2 solution and 0% H_2O_2 solution, respectively, which showed that the sorbent utilization increased by 33.3% at Ca/S molar ratio of 1.5 and approach to adiabatic saturation of 5 °C. Therefore, SO_2 removal efficiency and sorbent utilization were significantly improved with the addition of hydrogen peroxide to humidify $Ca(OH)_2$.

3.4. Semi-quantitative XRD analysis and discussion

XRD was used to analyze and identify the mineralogical composition of the FGD products. The XRD patterns of the desulfurization products are shown in Fig. 6 when hydrogen peroxide solution of different concentrations is sprayed to humidify $Ca(OH)_2$. Letters A–E in Fig. 6 denote different crystalline phases: $Ca(OH)_2$, $CaSO_4·1/2H_2O$, $CaSO_4$, $CaSO_3$ and $Ca(SO_4)$, respectively. The characteristic peaks of the XRD spectrum for each particular crystalline phase are based on the International Center for Diffraction Data (ICDD) file. The main peak of the XRD spectrum for $Ca(OH)_2$ appears at $2\theta = 34.169°$ and the minor peaks appear at $2\theta = 18.107°$, $28.728°$, $47.249°$ and $50.896°$. The main peak of the XRD spectrum for $CaSO_4·1/2H_2O$ appears at 2θ $14.739°$ and the minor peaks appear at $2\theta = 25.648°$, $29.729°$, $31.893°$ and $49.321°$. The main peak of the XRD spectrum for $CaSO_4$ appears at $2\theta = 23.143°$ and the minor peaks appear at $2\theta = 20.258°$, $30.283°$, $35.466°$ and $47.279°$. The main peak of the XRD spectrum for $CaSO_3$ appears at $2\theta = 29.050°$ and the minor peaks appear at $2\theta = 27.430°$, $29.880°$, $32.610°$, $35.330°$, $45.180°$ and $49.870°$. The main peak of the XRD spectrum for $Ca(SO_4)$ appears at $2\theta = 14.664°$ and the minor peaks appear at $2\theta = 25.541°$, $29.576°$, $32.010°$, $49.269°$ and $54.030°$.

XRD pattern in Fig. 6a reveals that the desulfurization product when only spraying water to humidify $Ca(OH)_2$ is primarily composed of $Ca(OH)_2$ and $CaSO_3$. The relative peak intensity indicates that there is a significant amount of unreacted $Ca(OH)_2$ and $CaSO_3$, and a small amount of $CaSO_4$, which is the same as XRD analysis of the semidry FGD products such as in spray dryer and in-duct sorbent injection processes [7]. Fig. 6b shows that the desulfurization product when spraying hydrogen peroxide solution of 1% to humidify $Ca(OH)_2$ is primarily composed of $Ca(OH)_2$ and $CaSO_4$, especially no $CaSO_3$ is found in the product. The relative peak intensity indicates that there is a significant amount of unreacted $Ca(OH)_2$ and more amount of two kinds of calcium sulfate crystals $CaSO_4$ and $Ca(SO_4)$ with different unit cell sizes in the desulfurization product. This is because hydrogen peroxide oxidizes the dissolved SO_2 to form sulfuric acid and it reacts fast with the dissolved $Ca(OH)_2$ to produce $CaSO_4$. Fig. 6c shows that the desulfurization product when spraying hydrogen peroxide solution of 2% to humidify $Ca(OH)_2$ primarily contains $Ca(OH)_2$, $CaSO_4·1/2H_2O$ and $CaSO_4$, and no $CaSO_3$ is also found in the product, which is similar to Fig. 6b. However, Fig. 6d shows that the desulfurization product when spraying hydrogen peroxide solution of 3% to humidify $Ca(OH)_2$ primarily contains $Ca(OH)_2$, $CaSO_4$, $CaSO_3$ and $Ca(SO_4)$. This might be because too much hydrogen peroxide significantly enhances the dissolution of SO_2 into the liquid film at sorbent particle surface, and the dissolved SO_2 is partially oxidized by added hydrogen peroxide to sulfuric acid and it reacts with the dissolved $Ca(OH)_2$ to form $CaSO_4$. Additionally, some dissolved SO_2 may directly react with excessive $Ca(OH)_2$ to form $CaSO_3$.

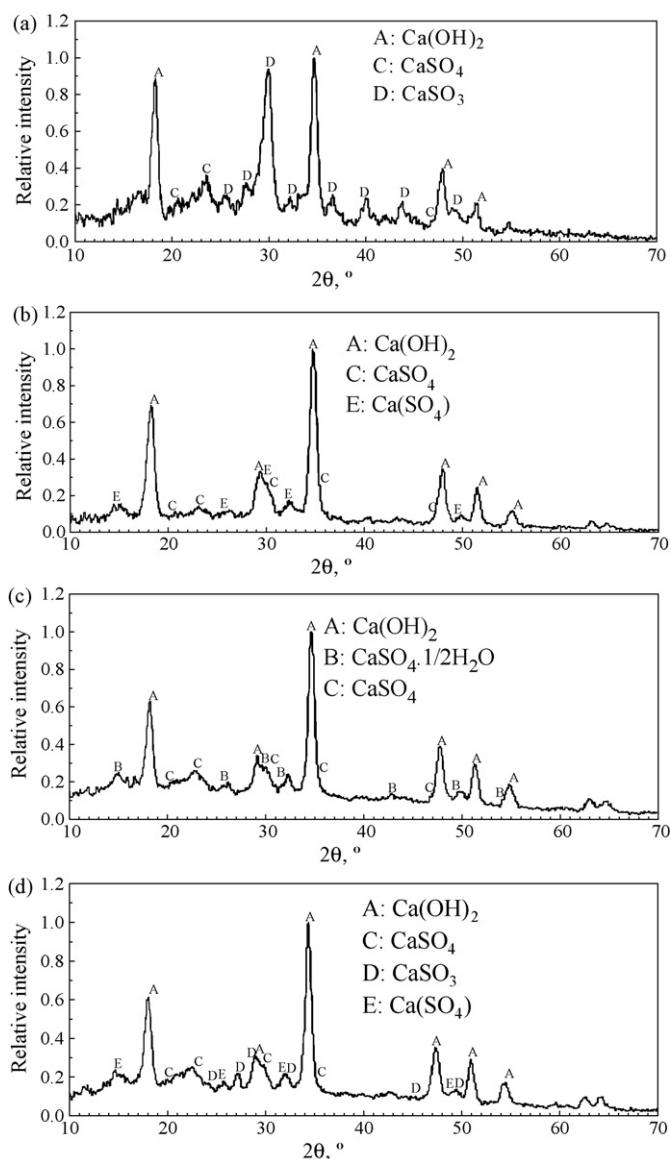**Fig. 6.** XRD patterns of the desulfurization products when spraying hydrogen peroxide solution of different concentrations to humidify $Ca(OH)_2$: (a) hydrogen peroxide solution of 0%; (b) hydrogen peroxide solution of 1%; (c) hydrogen peroxide solution of 2%; (d) hydrogen peroxide solution of 3%.

Semi-quantitative XRD analysis with reference intensity ratio (RIR) method was used to obtain the quantitative measures of mineralogical composition of the desulfurization products (see Table 2). Combined with XRD patterns in Fig. 6, it can be quantitatively seen that the amount of $Ca(OH)_2$ in the desulfurization products decreases significantly from 70.9% to 40.8% when hydrogen peroxide solution of 1–3% is sprayed to humidify $Ca(OH)_2$, which means that SO_2 removal efficiency is improved as mentioned above. Moreover, the desulfurization products contain a significant amount of different calcium sulfate crystals when hydrogen peroxide solution of 1% and 2% is sprayed to humidify $Ca(OH)_2$. There also contains some amount of $CaSO_3$ when hydrogen peroxide solution of 3% is sprayed to humidify $Ca(OH)_2$. A great variety of analysis showed that the ratio of the amount of $CaSO_3$ to that of $CaSO_4$ in the conventional semidry FGD products such as in spray dryer process ranged from 2:1 to 3:1 [7,20]. On the basis of the conducted experiments in this paper, it can be concluded that adding a small amount of hydrogen peroxide solution to humidify $Ca(OH)_2$ in the semidry FGD process will not only significantly improve SO_2 removal effi-

Table 2
Semi-quantitative measures of mineralogical composition of the desulfurization products.

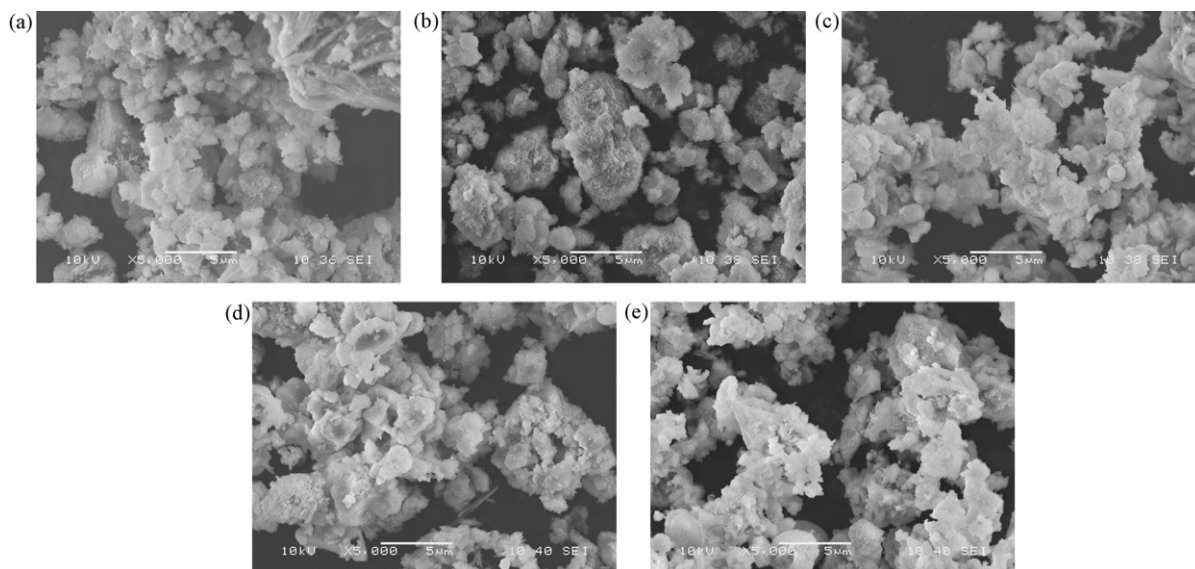| Case condition		Composition (%)					
H_2O_2 concentration	Ca/S	$Ca(OH)_2$	$CaSO_3$	$CaSO_4$	$Ca(SO_4)$	$CaSO_4 \cdot 1/2H_2O$	$\sum$
1%	1.5	70.9	–	20.4	8.7	–	100
2%	1.5	49.0	–	28.9	–	22.1	100
3%	1.5	40.8	36.0	18.4	4.8	–	100

Fig. 7. SEM micrographs of sorbent particle and desulfurization products at different concentrations of hydrogen peroxide solutions: (a) original $Ca(OH)_2$; (b) sample at 0% H_2O_2; (c) sample at 1% H_2O_2; (d) sample at 2% H_2O_2; (e) sample at 3% H_2O_2.

ciency but also produce more amount of stable calcium sulfate in the desulfurization products. Therefore, this method is beneficial to improving the quality and reuse of the semidry FGD products.

The process mechanism of the enhanced absorption of SO_2 by using hydrogen peroxide solution to humidify $Ca(OH)_2$ can be analyzed and discussed as follows on the basis of the experimental results.

(1) In the conventional semidry FGD processes such as spray dryer and in-duct sorbent injection, SO_2 in bulk flue gas diffuses and dissolves into the droplet surface and $SO_2(aq)$ ionizes into ion forms: $SO_2(aq) + H_2O \Leftrightarrow H^+ + HSO_3^-$ and $HSO_3^- \Leftrightarrow H^+ + SO_3^{2-}$. $Ca(OH)_2$ in the slurry droplets also dissolves into ion form: $Ca(OH)_2 \Leftrightarrow Ca^{2+} + 2OH^-$. Thus, calcium species reacts with SO_3^{2-} to form calcium sulfite in the liquid film. Therefore, the product in the conventional semidry FGD processes is primarily consisted of unreacted $Ca(OH)_2$ and unstable $CaSO_3$.

(2) When hydrogen peroxide solution of a low concentration is sprayed to humidify $Ca(OH)_2$, hydrogen peroxide as a strong oxidant can oxidize the $SO_2(aq)$, HSO_3^- and SO_3^{2-} (known as S(IV) forms) into $SO_3(aq)$, HSO_4^- and SO_4^{2-} (known as S(VI) forms), respectively: $SO_2(aq) + H_2O_2 \rightarrow H_2SO_4$, $HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O$, and $SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O$. Thus, the SO_2 dissolution into liquid film will almost not be affected by the liquid side equilibrium. Therefore, adding hydrogen peroxide significantly enhances the SO_2 dissolution and absorption in the liquid film and the S(VI) species reacts with the dissolved $Ca(OH)_2$ to produce more stable calcium sulfate.

(3) The research has shown that $CaSO_3$ solids have lower solubility and could crystallize easily than $CaSO_4$ solids in the semidry FGD pH operating range [14]. Thus, crystals of the formed $CaSO_3$ can deposit on the surface of the sorbent particles and block the

pore to halt SO_2 diffuse and dissolute into the liquid phase in the conventional semidry FGD processes. If S(IV) forms can be oxidized to S(VI) forms by hydrogen peroxide, the product $CaSO_4$ has less crystallization and there is more available sorbent surface area for the dissolution and diffusion of reactants SO_2 and $Ca(OH)_2$ in the reaction process. It was confirmed by the SEM micrographs of the desulfurization products in this paper. Fig. 7 shows the SEM micrographs of the desulfurization products when hydrogen peroxide solution of different concentrations is used to humidify $Ca(OH)_2$. When only water is sprayed to humidify $Ca(OH)_2$, SEM micrograph in Fig. 7b shows that there are fine crystals which deposit on the sorbent surface and block the surface pores, and the produced crystal is determined as $CaSO_3$ by XRD patterns. When hydrogen peroxide solution of different concentrations is sprayed to humidify $Ca(OH)_2$, SEM micrographs in Fig. 7c–e show that there are large crystals on the sorbent surface and more sorbent surface areas are available for the dissolution and diffusion of SO_2 and $Ca(OH)_2$.

4. Conclusions

SO_2 removal efficiency increases by 15–20% when spraying hydrogen peroxide solution of 1–3% to humidify $Ca(OH)_2$ particles at the same Ca/S molar ratio and approach to adiabatic saturation temperature compared with only spraying water to humidify $Ca(OH)_2$. Moreover, semi-quantitative XRD analysis of mineralogical composition of the desulfurization products shows that spraying hydrogen peroxide solution of 1–3% to humidify $Ca(OH)_2$ in the semidry FGD process will not only significantly decrease the amount of unreacted $Ca(OH)_2$ (i.e., improve SO_2 removal efficiency) but also produce more amount of stable $CaSO_4$. Additionally, SEM analysis confirms that the desulfurization product $CaSO_4$ when spraying hydrogen peroxide solution to humidify $Ca(OH)_2$ has less

crystallization and more sorbent surface areas are available for the dissolution and diffusion of SO_2 and $Ca(OH)_2$, which is helpful to improving the removal efficiency and the reuse of the semidry FGD products. Thus, the process mechanism of the enhanced absorption of SO_2 when spraying hydrogen peroxide solution to humidify $Ca(OH)_2$ was elucidated on the basis of the experimental results and microscopic analysis of the desulfurization products.

Acknowledgments

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