Reaction characteristics of $Ca(OH)_2$, HCl and SO_2 at low temperature in a spray dryer integrated with a fabric filter

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Abstract

The objective of this research was to evaluate the reaction characteristics of $Ca(OH)_2$, HCl and SO_2 in the flue gas emitted by a laboratory incinerator. The amount of sulfur retained in the residues (including the spray dryer ash and baghouse ash) was also evaluated in this study. The experimental parameters included HCl concentration (500–2000 ppm), SO_2 concentration (500–2000 ppm), relative humidity (40–80% RH), and the addition of $CaCl_2$ (30 wt.%).

The results indicated that an HCl concentration of 500–2000 ppm did not affect HCl removal efficiency in the spray dryer at 150 °C and $45 \pm 5\%$ RH. On the other hand, increase in SO_2 concentration from 500 to 2000 ppm enhanced SO_2 removal at 150 °C and $75 \pm 5\%$ RH. Moreover, increase in removal efficiency of SO_2 was more obvious when the relative humidity was greater than 80%. When the flue gas contained both HCl and SO_2 simultaneously, the removal efficiency of SO_2 could increase from 56.7 to 90.33% at HCl concentration of 236 ppm. However, when the concentration of HCl exceeded 535 ppm, the removal efficiency of SO_2 decreased with increasing concentration of HCl. The removal efficiency of SO_2 could be increase to 97.7% with the addition of $CaCl_2$.
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Keywords: HCl; SO_2; $Ca(OH)_2$; $CaCl_2$; Spray dryer; Fabric filter

1. Introduction

Contaminants released from the incineration of hazardous and municipal wastes include acid gases, heavy metals, organic compounds, and fly ash. The amount and the compositions of these pollutants are affected by the incineration conditions, feedstock compositions, and the types of air pollution control devices (APCDs).

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A spray dryer integrated with a fabric filter is commonly used to control the contaminants (such as acid gases and fly ash) emitted by incinerators. A fabric filter can improve the extra removal efficiency of the pollutants since unreacted sorbents deposited upon the fabric filter can further react with the flue gas. The acid gases include HCl, SO_2, NO, NO_2, etc.

Previous researchers [1,2] have investigated the influence of inlet concentration of acid gases, relative humidity (RH), reaction temperature and the addition of various chemistries on the removal efficiency of HCl and SO_2 using a spray dryer. However, the simultaneous removal efficiency of HCl and SO_2 in the flue gas emitted by an incinerator using a spray dryer integrated with a fabric filter at low temperature has hardly been studied.
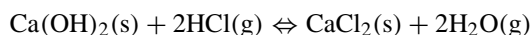
Previous studies have shown that the removal efficiency of HCl by calcium-based sorbents increased with increasing relative humidity and decreasing reaction temperature [3–5]. Weinell et al. [4] have indicated that the HCl-binding capacity for slaked lime ($Ca(OH)_2$) and limestone ($CaCO_3$) reached a maximum in the range of 500–600 °C, but a large binding capacity for slaked lime in the presence of water was also observed below 150 °C. Chisholm and Rochelle [5] have demonstrated that increasing the HCl concentration would decrease the HCl-binding capacity of hydrated lime at HCl concentrations of 2000 and 3500 ppm. However, the absorption capacity of $Ca(OH)_2$ remained unaffected when HCl concentration was below 1000 ppm.
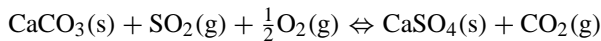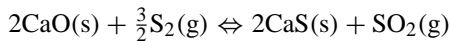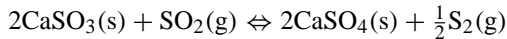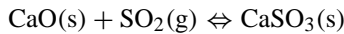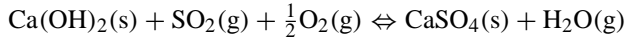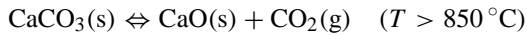
The utilization efficiency of $Ca(OH)_2$ for SO_2 varies with different byproducts in the spray dryer and in the fabric filter. Tsuchiai et al. [6] reported that the main reaction product was $CaSO_4$ when the wet scrubber was used as the control device and $CaSO_3$ was predominantly formed during the spray dry or dry process. A higher reactivity with SO_2 was obtained by using a suitable mixture of $Ca(OH)_2$ and fly ash from coal combustion [7].

Previous studies [8–11] indicated that relative humidity played an important role in SO_2 capture. The results showed that the removal efficiency of SO_2 increased with increasing relative humidity. Other studies have shown that the reaction rate of $Ca(OH)_2$ with SO_2 did not depend on SO_2 concentration when the relative humidity and the concentration of SO_2 were below 70% and 3000 ppm, respectively [9,10,12]. However, the reaction rate between $Ca(OH)_2$ and SO_2 became gradually more dependent on SO_2 concentration when the relative humidity was greater than 70% [10,12].

Only limited studies on the simultaneous absorption of HCl and SO_2 by calcium-based sorbents have been performed at high temperature [13–16]. Matsukata et al. [14] have investigated simultaneous chlorination and sulphation of calcined limestone with HCl and SO_2 in fluidized-bed combustion at 750 °C. Their results indicated that sulphation was accelerated markedly in the presence of HCl. Wang et al. [15] found that spent calcium-based desulfurization sorbents could still react with HCl in the range of 125–225 and 375–475 °C. Lawrence et al. [16,17] demonstrated that sulfur capture by limestone was enhanced significantly by the presence of HCl in a fluidized-bed incinerator at 680–900 °C. The above-mentioned studies have also found that increasing HCl concentration would increase SO_2 absorption rate.

The reactions of HCl and SO_2 with $Ca(OH)_2$ or $CaCO_3$ to form $CaCl_2$ and $CaSO_4$ are potentially important for various removal processes. The binding reactions are described as following [18–21]:

$$Ca(OH)_2(s) + 2HCl(g) \Leftrightarrow CaCl_2(s) + 2H_2O(g)$$

$$CaCO_3(s) + 2HCl(g) \Leftrightarrow CaCl_2(s) + H_2O(g) + CO_2(g)$$

$$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g) \quad (T > 850\,^\circ C)$$

$$CaO(s) + 2HCl(g) \Leftrightarrow CaCl_2(s) + H_2O(g)$$

$$Ca(OH)_2(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \Leftrightarrow CaSO_4(s) + H_2O(g)$$

$$CaO(s) + SO_2(g) \Leftrightarrow CaSO_3(s)$$

$$2CaSO_3(s) + SO_2(g) \Leftrightarrow 2CaSO_4(s) + \tfrac{1}{2}S_2(g)$$

$$2CaO(s) + \tfrac{3}{2}S_2(g) \Leftrightarrow 2CaS(s) + SO_2(g)$$

$$CaCO_3(s) + SO_2(g) + \tfrac{1}{2}O_2(g) \Leftrightarrow CaSO_4(s) + CO_2(g)$$

In a previous paper [22], we showed experimentally that the presence of PVC in the feedstock could increase the removal efficiency of SO_2 in the spray dryer. To realize the extent of the effect of PVC on the removal efficiency of SO_2 emitted by an incinerator, the detailed experimental conditions have been investigated in the present study. The experimental parameters included HCl concentration (500–2000 ppm), SO_2 concentration (500–2000 ppm), relative humidity (40–80%), and the addition of $CaCl_2$ (30 wt.%).

2. Experimental

2.1. Preparation of artificial feedstocks

The artificial incinerator feedstocks for this experiment were composed of sawdust, polyvinyl chloride (PVC) and sulfur. These feed materials were enclosed in a polyethylene (PE) bag. The feedstock compositions and operating parameters of the spray dryer for this experiment are shown in Table 1.

2.2. Apparatus

Fig. 1 illustrates the incineration system which consisted of a laboratory-scale fluidized-bed incinerator equipped with a spray dryer and a fabric filter used as the particulate control devices in this study. The height and inner diameter of the spray dryer were 885 and 165 mm, respectively. A Nomex fabric filter (E.I. Du Pont de Nemous & CO., USA) with a surface area of $3.39\,m^2$ was used. The fluidized-bed material (200 g silica sand) was fed into the combustion chamber. A thermocouple was used to determine the temperature in the sand bed. The combustion gases were treated in the spray dryer integrated with the fabric filter, and then released into atmosphere.

2.3. Experimental procedure

The needed air for an excess air ratio of 50% was input at room temperature. The combustion chamber was heated to a desired temperature (800 °C) by electrical heaters. When

Table 1
Feedstock compositions and operating conditions of the spray dryer for each test

Test	Operating conditions of the spray dryer[a]	Feedstock compositions (g/min)				Relative humidity of the spray dryer (%)
		PE[b] bag	Sawdust	PVC[c]	S	
Run 1	HCl only: different concentration of HCl entering the spray dryer	0.92	4	1.2	0	45 ± 5
Run 2		0.92	4	2.4	0	
Run 3		0.92	4	3.6	0	
Run 4		0.92	4	4.8	0	
Run 5	SO_2 only: different concentration of SO_2 entering the spray dryer	0.92	4	0	0.064	75 ± 5
Run 6		0.92	4	0	0.128	
Run 7		0.92	4	0	0.2	
Run 8	SO_2 only: different relative humidity	0.92	4	0	0.1	40 ± 5
Run 9		0.92	4	0	0.1	60 ± 5
Run 10		0.92	4	0	0.1	80 ± 5
Run 11	Addition of $CaCl_2$ in the spray dryer[d]	0.92	4	0	0.1	75 ± 5
Run 12	HCl and SO_2 coexistence: different concentration of HCl entering the spray dryer	0.92	4	0.6	0.1	75 ± 5
Run 13		0.92	4	1.2	0.1	
Run 14		0.92	4	1.8	0.1	
Run 15		0.92	4	2.4	0.1	

[a] The surface area of $Ca(OH)_2$ and $CaCl_2$ were 12.561 and 1.4976 m^2/g. The spray flow rate of the slurry was 10 ml/min. The mole ratio of $Ca(OH)_2$ to acid gas was 1 (Ca:S = 1:1; Ca:Cl_2 = 1:1).

[b] PE: polyethylene.

[c] PVC: polyvinyl chloride.

[d] The mass ratio of $CaCl_2$ to $Ca(OH)_2$ was 0.3 ($Ca(OH)_2$:$CaCl_2$ = 1:0.3).

the temperature reached steady state, the artificial feedstocks were fed into the incinerator at the rate of one bag per 15 s, and the air pollution control devices turned on. The inlet and outlet temperature of the spray dryer were maintained at 400–450 and 150 °C, respectively. The temperature at the exit of the fabric filter was approximate 45 °C. The pressure drop and filtration velocity of the fabric filter were less than 10 mm H_2O and 0.54 cm/s, respectively. Sampling tasks were performed after 20 min. Total operating time for each test was 60 min.

2.4. Sampling and analytical methods

To estimate the removal efficiency of the spray dryer integrated with the fabric filter, the flue gas was sampled prior to and after the spray dryer and the fabric filter at the same time. The contaminants sampled included SO_2 and HCl. A flue gas analyzer (Bacharach Model 300) was used to measure the concentration of SO_2. The analyzer was calibrated with standard gases prior to the experiments. The range of concentration for SO_2 monitoring was 0–1999 ppm and the accuracy was ±10 ppm.
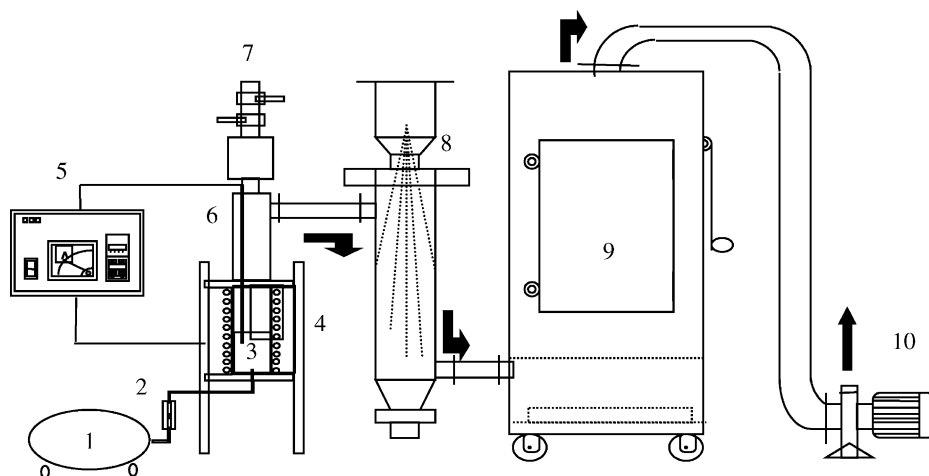
Fig. 1. Schematic of fluidized-bed incinerator and air pollution control devices used in this experiment: (1) air compressor; (2) flowmeter; (3) combustion chamber; (4) electrical heater; (5) thermal feedback controller; (6) thermocouple; (7) feeder; (8) spray dryer; (9) fabric filter; (10) induced fan.
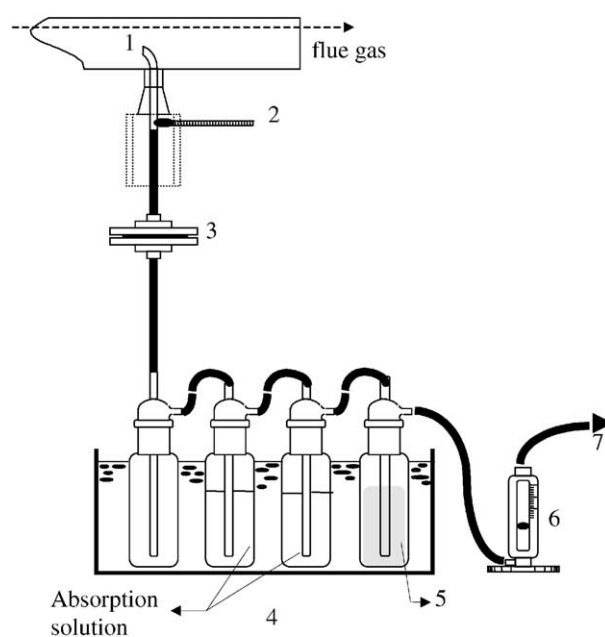

Fig. 2. Sampling train for HCl: (1) sampling probe; (2) thermometer; (3) filter holder; (4) impingers; (5) silica gel; (6) flow meter; (7) connect to vacuum pump.

The HCl sampling apparatus was comprised of a probe, a glass fiber filter, and impingers containing solutions (100 ml of 0.1N NaOH) as shown in Fig. 2. The flue gas containing HCl was sampled using a stainless probe and passed through a glass fiber filter and impingers to remove particles and HCl, respectively. Then mercuric thiocyanate ($Hg(SCN)_2$) and ammonium ferric sulfate ($FeNH_4(SO_4)_2 \cdot 12H_2O$) were added into the NaOH solution contained HCl and subsequently reacted with Cl^- to form salmoncolored ferrocyanic acid complex compound ($Fe(SCN)_3$). The solution contained $Fe(SCN)_3$ was analyzed by a spectrophotometer at wavelength of 460 nm [23]. The sampling flow rate for HCl gases was 8 l/min and a 5 min period. An element analyzer (Heraeus CHN-OS Rapid Element Analyzer) was used to analyze the amount of sulfur in the spray dryer ash and baghouse ash.

2.5. XRD and SEM analysis

An X-ray Powder Diffractometer (Japan MAC Science, MXP18) was used to identify the chlorination and sulphation products in the spray dryer ash and baghouse ash. A Cu tube served as the X-ray source, and the working voltage and current were 30 kV and 10 mA, respectively. The scanning range of 2 theta (2θ) was from 5 to 75°, in steps of 0.02°. The scanning speed was 4°/min. Micrograph of the spray dryer ash was carried out by a scanning electron microscopy (SEM, TOPCON ABT-150 S).

3. Results and discussion

3.1. HCl only

Table 2 reports the concentration of HCl and SO_2 in the flue gas emitted from a laboratory incinerator after each test. The concentration of HCl entering the spray dryer in Runs 1–4 was controlled in the range of 500–2000 ppm. Fig. 3 shows the effect of HCl concentration entering the spray dryer on the removal efficiency of HCl. The results indicate that all the removal efficiency of HCl were greater than 98% at 45±5% RH when the HCl concentration was 500–2000 ppm. Different inlet HCl concentrations in the range of 500–2000 ppm did not affect the removal efficiency of HCl in the spray dryer.

Chisholm and Rochelle [5] demonstrated that an increase in the concentration of HCl from 250 to 1000 increased HCl removal and $Ca(OH)_2$ utilization at 19% RH. This finding obviously does not agree with our experimental results. It may be due to the relative humidity in our experiment (45 ± 5% RH) being greater than that in the previous study (19% RH). Weinell et al. [4] have found that the large binding capacity of calcium-based sorbent with HCl below 150 °C required water to be present and was believed to be influenced by the formation of a partially liquid product phase.

3.2. SO_2 only

The concentration of SO_2 entering the spray dryer in Runs 5–7 and 10 was controlled in the range of 500–2000 ppm (Table 2). Fig. 4 illustrates the effect of SO_2 concentration entering the spray dryer on the removal efficiency of SO_2. The results show that the removal efficiency of SO_2 increased with increasing SO_2 concentration in the flue gas at 75 ± 5% RH. The result is similar to that found by other researchers mentioned earlier [10,12].

Table 2

The concentrations of HCl and SO_2 entering the spray dyer and the removal efficiency of HCl and SO_2 for each test

Test	HCl concentration (ppm)	SO_2 concentration (ppm)	Removal efficiency in the spray dryer (%) HCl/SO_2	Total removal efficiency (%) HCl/SO_2
Run 1	505	–	98.08/–	99.14/–
Run 2	1039	–	98.91/–	99.28/–
Run 3	1459	–	99.49/–	99.75/–
Run 4	2105	–	99.76/–	99.88/–
Run 5	–	480	–/54.19	–/94.27
Run 6	–	1220	–/89.97	–/90.61
Run 7	–	1813	–/84.73	–/96.97
Run 8	–	970	–/44.46	–/91.47
Run 9	–	967	–/42.12	–/93.76
Run 10	–	980	–/56.7	–/98.11
Run 11	–	921	–/97.73	–/100
Run 12	236	1073	98.46/90.33	98.46/91.8
Run 13	535	984	98.86/60.8	99.78/90.68
Run 14	792	1095	97.99/42.34	99.94/88.61
Run 15	1018	990	98.95/44.2	99.4/91.98

Comparison of Fig. 4 with Fig. 3 indicates that the relative humidity for removing SO_2 was greater than that for HCl to achieve a similar removal efficiency. This result is because the reactivity of $Ca(OH)_2$ for HCl is greater than that for SO_2.

To understand the amount of sulfur retained in the residues, the mass balance of sulfur is summarized in Table 3. Fig. 5 illustrates the effect of SO_2 concentration entering the spray dryer on the weight percentage of sulfur retained in the residues. The amount of sulfur retained in the spray dryer ash increased as the SO_2 concentration increased. This result also verifies that the removal efficiency of SO_2 increased with increasing SO_2 concentration in the spray dryer.

Table 2 shows that the concentration of SO_2 entering the spray dryer in Runs 8–10 was 950 ± 50 ppm. Fig. 6 shows the effect of relative humidity used in the spray dryer on

Run1: 505 ppm   Run2: 1039 ppm
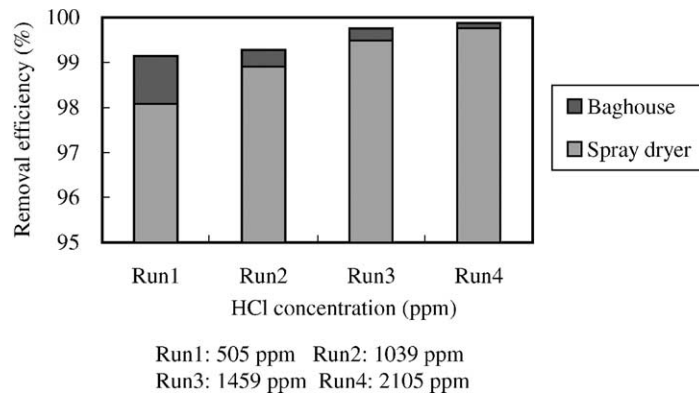Run3: 1459 ppm Run4: 2105 ppm

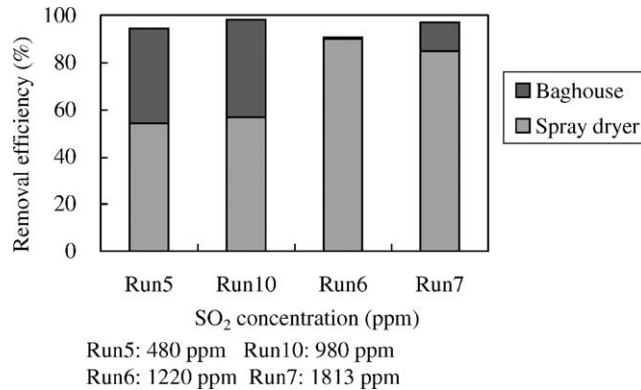Fig. 3. The removal efficiency of HCl with different HCl concentration entering the spray dryer (Runs 1–4).

Fig. 4. The removal efficiency of SO_2 with different SO_2 concentration entering the spray dryer (Runs 5–7 and 10).

Table 3
The weight percentage of sulfur retained in the spray dryer ash, baghouse ash, and flue gas for each test

Test	Spray dryer ash[a] (wt.%)	Baghouse ash[b] (wt.%)	Flue gas[c] (wt.%)	Loss[d] (wt.%)
Run 1	–	–	–	–
Run 2	–	–	–	–
Run 3	–	–	–	–
Run 4	–	–	–	–
Run 5	34.8	40.43	11.45	13.32
Run 6	47.4	23.91	18.78	9.91
Run 7	48.41	22.80	13.65	15.15
Run 8	36.66	35.66	11.33	16.36
Run 9	35.83	39.21	17.06	7.90
Run 10	42.51	34.54	12.48	10.47
Run 11	61.29	28.11	0	10.60
Run 12	53.10	5.54	8.2	33.16
Run 13	43.7	5.41	13.98	36.91
Run 14	22.34	12.85	22.77	42.05
Run 15	28.94	10.30	20.05	40.71

$SO = S1 \times Q1 \times t$; $ST = SO/2$; S1, S2: the concentration of SO_2 entering the spray dryer and exhausting the baghouse (mg/m^3); Q1, Q2: the flow rate of flue gas entering the spray dryer and exhausting the baghouse (m^3/h); t: total experimental time (h); x, y: the amount of spray dryer ash and baghouse ash for each test (mg); A1, A2: the weight percentage of sulfur retained in the spray dryer ash and in the baghouse ash was analyzed by an element analyzer (%); SO: the amount of SO_2 entering the spray dryer for each test (mg); ST: the amount of sulfur entering the spray dryer for each test (mg); SA: the weight percentage of sulfur retained in the spray dryer ash (wt.%); BA: the weight percentage of sulfur retained in the baghouse ash (wt.%); FG: the weight percentage of sulfur retained in the flue gas (wt.%); LOSS: the weight percentage of loss (wt.%).

[a] $SA = A1 \times x/ST \times 100\%$.
[b] $BA = A2 \times y/ST \times 100\%$.
[c] $FG = (S2 \times Q2 \times t/2)/ST \times 100\%$.
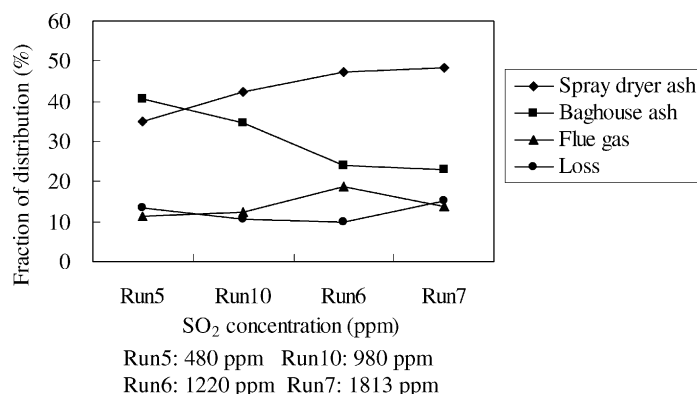[d] $LOSS = (ST - ((SA + BA + FG) \times 100))/ST \times 100\%$.

Fig. 5. The weight percentage of sulfur retained in the spray dryer ash, baghouse ash, and flue gas with different SO_2 concentration entering the spray dryer (Runs 5–7 and 10).

the removal efficiency of SO_2. There was an increase in SO_2 removal efficiency when the relative humidity was greater than 80%. These data agree with those of Izquierdo et al. [9] who found that the reaction rate of $Ca(OH)_2$ and SO_2 increased exponentially with relative humidity. Therefore, we conclude that an increase in relative humidity (over 40% RH) increases the removal efficiency of SO_2 in the flue gas. Fig. 7 illustrates the effect of relative humidity used in the spray dryer on the weight percentage of sulfur retained in the residues. The trend of sulfur retained in the spray dryer ash and in the baghouse ash corresponds to the result displayed in Fig. 6.

3.3. HCl and SO_2 coexistence

Table 2 shows that the concentrations of HCl and SO_2 entering the spray dryer in Run 10 and 12–15 were 200–1000 ppm and 1000 ± 100 ppm, respectively. Fig. 8 shows the effect
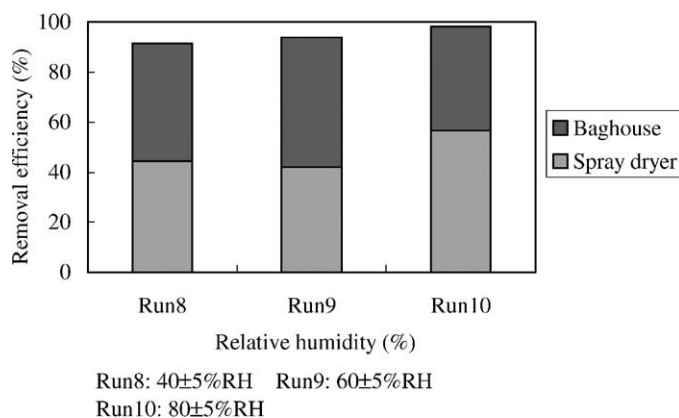

Fig. 6. The removal efficiency of SO_2 with different relative humidity used in the spray dryer (Runs 8–10).
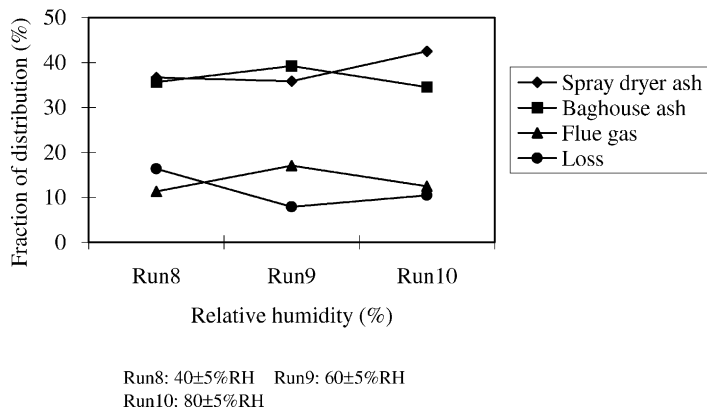
Run8: 40±5%RH   Run9: 60±5%RH
Run10: 80±5%RH

Fig. 7. The weight percentage of sulfur retained in the spray dryer ash, baghouse ash, and flue gas with different relative humidity used in the spray dryer (Runs 8–10).

of HCl concentration entering the spray dryer on the removal efficiency of SO_2. The data indicate that the SO_2 removal efficiency increased when the inlet concentration of HCl was 236 ppm because $Ca(OH)_2$ can react with HCl to form $CaCl_2$ [18]. Moreover, $CaCl_2$ can retain a large amount of water on its surface and thus increase the reactivity of $Ca(OH)_2$ for SO_2 [8,9,12]. Therefore, the presence of HCl can increase the removal efficiency of SO_2. However, when the concentration of HCl exceeded 535 ppm, the removal efficiency of SO_2 decreased with increasing HCl concentration. Two possible reasons are proposed to explain the above-mentioned result. One is that the superabundant HCl may react with the product of $CaSO_3 \cdot (1/2)H_2O$ to form $CaCl_2 \cdot 2H_2O$ and SO_2 is released. This reaction is expressed as follows [5]:

$$CaSO_3 \cdot \tfrac{1}{2}H_2O + 2HCl + \tfrac{1}{2}H_2O \rightarrow CaCl_2 \cdot 2H_2O + SO_2$$

Run10: 0 ppm   Run12: 236 ppm
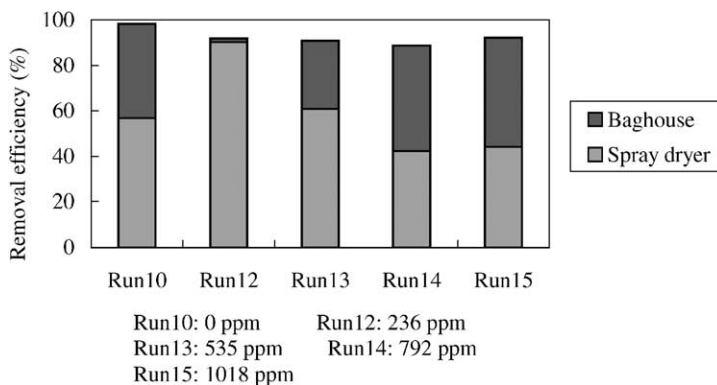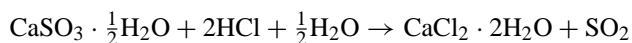Run13: 535 ppm   Run14: 792 ppm
Run15: 1018 ppm

Fig. 8. The removal efficiency of SO_2 with different HCl concentration entering the spray dryer (Runs 10 and 12–15).
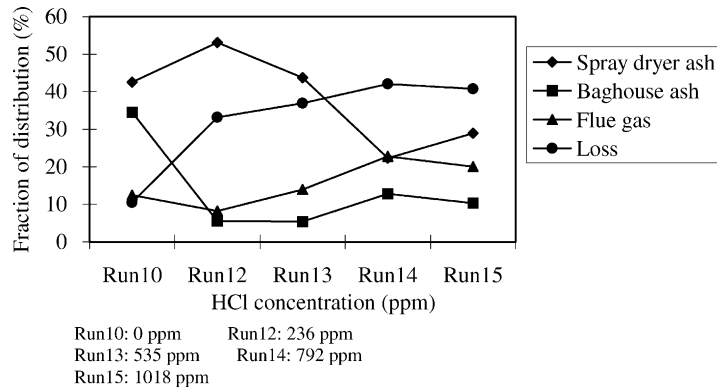
Fig. 9. The weight percentage of sulfur retained in the spray dryer ash, baghouse ash, and flue gas with different HCl concentration entering the spray dryer (Runs 10 and 12–15).

The other reason is that the highly soluble product of $CaCl_2$ will change to a solid product and thus inhibit the gaseous reactant from diffusing through the product layer when the inlet concentration of HCl exceeds a certain value [24]. As a result, an adequate concentration of HCl will increase the reaction of SO_2 with $Ca(OH)_2$. However, a superabundant concentration of HCl will decrease the removal efficiency of SO_2.

Fig. 9 illustrates the effect of HCl concentration entering the spray dryer on the weight percentage of sulfur retained in the residues. It shows that the loss in Runs 12–15 (the simultaneous presence of HCl and SO_2) is greater than that in Run 10 (SO_2 only). Fig. 9 also indicates that the amount of sulfur retained in the spray dryer ash at the HCl concentration of 236 ppm was the highest among the HCl concentration of 200–1000 ppm.

3.4. Effect of addition of $CaCl_2$ on removal efficiency of SO_2

To determine the impact of the presence of HCl on removal efficiency of SO_2, 30 wt.% of $CaCl_2$ was added in the spray dryer (Run 11). The result indicates that the removal

Table 4
The reaction compositions in the spray dryer ash and baghouse ash for each test

Test	Location	Reaction compositions
Run 2	Spray dryer	$CaCO_3$, $CaCl_2 \cdot H_2O$, $CaCl_2$
	Baghouse	$CaCO_3$, $CaCl_2 \cdot H_2O$, $CaCl_2$
Run 10	Spray dryer	CaO, $CaCO_3$, $CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$
	Baghouse	CaO, $CaSO_4$, $CaSO_3 \cdot (1/2)H_2O$
Run 11	Spray dryer	$CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$, $CaSO_4 \cdot 2H_2O$, $CaCl_2$, $CaCl_2 \cdot H_2O$
	Baghouse	$CaSO_4$, $CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$, $CaCl_2$, $CaCl_2 \cdot H_2O$
Run 15	Spray dryer	$CaSO_4$, $CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$, $CaCl_2$, $CaCl_2 \cdot H_2O$
	Baghouse	$CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$, $Ca(SO_3Cl)_2$

efficiency of SO_2 can be increase to 97.7% after addition of $CaCl_2$, because inorganic hygroscopic salts can retain a greater amount of water on the absorbent surface and thus increase the reactivity of $Ca(OH)_2$ with SO_2. This conclusion is similar to that found by other researchers mentioned in the introduction [8,9,12]. The influence of the addition of $CaCl_2$ on the removal efficiency of SO_2 is obviously greater than that of the presence of HCl.
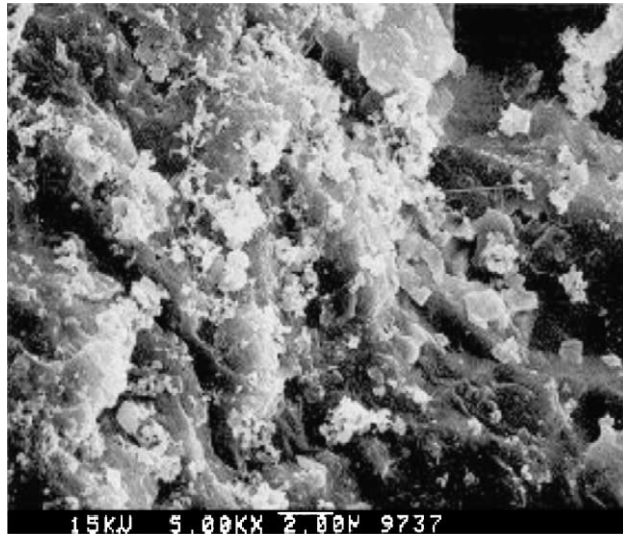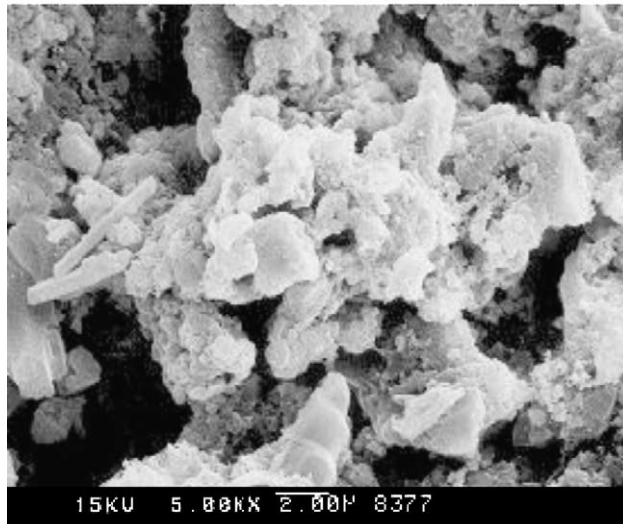
Fig. 10. The micrograph of fly ash: (a) spray dryer ash of Run 6 and (b) spray dryer ash of Run 13.

3.5. Identification and micrograph of fly ash

X-ray diffraction measurements of $Ca(OH)_2$ samples that already reacted with HCl and SO_2 gave information about the chemical structure of the crystals (Table 4). According to this qualitative, the species of $CaCO_3$, $CaCl_2$, and $CaCl_2 \cdot H_2O$ were determined when only HCl existed in flue gas. The species of CaO, $CaCO_3$, $CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$, and $CaSO_4$ were found when only SO_2 existed in flue gas. The reaction products of $CaSO_3$, $CaSO_3 \cdot (1/2)H_2O$, $CaSO_4$, $CaCl_2$, $CaCl_2 \cdot H_2O$ were observed when there simultaneous were HCl and SO_2 in flue gas and the addition of $CaCl_2$. This can further demonstrate the experimental results that mentioned earlier.

Micrograph can enable observation of the aggregation phenomena and surface structure of fly ash. Fig. 10 illustrates the surface micrograph of fly ash collected by the spray dryer. Fig. 10a indicates that the surface of spray dryer ash was smooth compared with the result seen in Fig. 10b. This result suggested that no aggregation phenomena occurred when only SO_2 existed in flue gas (Run 6). Fig. 10b observed that the aggregation and crystalline phases were formed when there were HCl and SO_2 in flue gas (Run 13). These results could also confirm that the highly soluble product of $CaCl_2$ will change to a solid product when it exceeded the solubility. Therefore, a superabundant concentration of HCl will decrease the removal efficiency of SO_2.

4. Conclusion

The experimental results indicated that different HCl concentrations from 500–2000 ppm did not affect the removal efficiency of HCl in the spray dryer and all the removal efficiency of HCl were greater than 98% at 150 °C and $45 \pm 5\%$ RH. An increase in SO_2 concentration from 500 to 2000 ppm increased SO_2 removal at 150 °C and $75 \pm 5\%$ RH. Moreover, the removal efficiency of SO_2 increased clearly until the relative humidity was greater than 80%. When the flue gas contained both HCl and SO_2 simultaneously, the removal efficiency of SO_2 could increase from 56.7 to 90.33% at HCl concentration of 236 ppm. However, when the concentration of HCl exceeded 535 ppm, the removal efficiency of SO_2 decreased with increasing HCl concentration. This result could also confirm by the micrograph of the spray dryer ash. The removal efficiency of SO_2 could be increase to 97.7% when $CaCl_2$ was added in the spray dryer. The influence of the addition of $CaCl_2$ on the removal efficiency of SO_2 was obviously greater than that of the presence of HCl. The amount of sulfur retained in the spray dryer ash and in the baghouse ash also demonstrated the above-mentioned results in this study.

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