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Interaction between emissions of SO_2 and HCl in fluidized bed combustors

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Abstract

The ability to capture SO_2 and halogens is one of the most important advantages of fluidized bed combustion (FBC). In order to clarify the affects of chlorine in the absorption of SO_2 emission, experiments involving the addition of PVC to coals were carried out using the 0.3 m ID bench scale FBC system at Western Kentucky University. During the experiments, PVC was added to three coals in different percentages, and the mixtures fed into the FBC system. The Ca/S ratio was kept constant at 3:1. The experimental results indicate that chloride addition dramatically decreased the SO_2 concentration in flue gases. The sulfur and chlorine contents in both fly ash and bed ash increased. At the same time, the utilization efficiency of calcium increased with an increase in the PVC weight percent. This reduction in SO_2 is attributed to more voids on the sorbent particle surface (limestone and/or ash) through transient formation of a mobile halide ion-containing phase ($CaCl_2$), and to the reactions:

$$4HCl + O_2 \leftrightarrow 2Cl_2 + 2H_2O \tag{1}$$

$$Cl_2 + SO_2 + H_2O \leftrightarrow 2HCl + SO_3. \tag{2}$$

A proposed mechanism involving the interaction between SO_2 and HCl is discussed in detail. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fluidized bed combustion; Municipal solid waste; Dioxins

1. Introduction

It is well know that the emission of SO_x from fossil fuel-fired power plants is one of the causes of acid rain. It is also known that SO_2 together with HCl emitted from fossil fuel combustion may play roles in the corrosion of boiler components and in power plant operational problems [1–6]. In situ sulfur and halogen capture by limestone is the major advantage of fluidized bed combustion (FBC). The use of calcium-based sorbents, such as limestone or dolomite, in fluidized bed combustion of coal to reduce sulfur dioxide (SO_2) emission is a well established technique. Limestone is introduced into the fluidized bed combustor within the temperature range 750–900°C, the limestone is rapidly calcined to the porous calcium oxide, which can subsequently react with SO_2 to form calcium sulfite and calcium sulfate. Also, the addition of limestone can capture hydrogen chloride to form liquid or solid phase calcium chloride under the relatively low combustion temperatures used in an FBC system, which subsequently can suppress the corrosion of heat exchange tubes sometimes caused by chloride compounds, especially when firing municipal solid waste (MSW) or high chlorine fuels.

Experimental work in the retention of sulfur and halogen species has been studied extensively in this decade. It has been found that sulfur and halogen capture by sorbents is interrelated [7,8]. A study by Liang and others [9] showed that chloride capture shows a large variation with temperatures, moving from a low of 18% gaseous HCl at 700°C to 99% HCl at 950°C. The resulting product was almost entirely in the form of liquid $CaCl_2$. Munzner and Schilling [10] reported that a greater recapture of chloride was reached with larger excesses of limestone, or when the Ca/S atomic ratio was greater than 2. However, from pilot plant studies and industrial tests [11] it was reported that using calcium-based sorbent injection in fluidized bed coal combustors demonstrated utilization efficiencies of 30%.

Incineration is an important waste-to-energy technology used for the disposal of municipal solid waste (MSW) or

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Table 1
Analytical values (moisture is as-received, all other values are reported on a dry basis) for the coals and limestone used in the study

	Coal 95010	Coal 95011	Coal 95031	KY Limestone
Proximate analysis (%)				
Moisture	2.32	10.07	8.32	0.19
Ash	7.22	9.37	10.78	57.93
Volatile matter	39.97	43.34	37.21	18.90
Fixed carbon	52.82	47.29	52.02	22.98
Ultimate analysis (%)				
Ash	7.22	9.37	10.78	57.93
Carbon	79.38	74.08	72.16	11.18
Hydrogen	5.31	5.08	4.82	0.16
Nitrogen	1.63	1.54	1.54	0.00
Sulfur	0.67	3.2	2.38	0.00
Oxygen	5.69	6.72	7.57	30.73
Chlorine (ppm)	1039	118	3070	36
BTU/pound	14 077	13 203	12 842	n/a

refuse-derived-fuels (RDF). However, it is necessary that the possibility of the formation of volatile organic compounds (VOCs) during combustion be reduced before incineration can reach its full potential. For instance, polychlorinated organics, including polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDF), have been reported as products of MSW combustion [12,13] in the parts-per-billion to parts-per-trillion range. These materials, which may be formed under conditions similar to those in which molecular chlorine is formed, have been found in the fly ash and flue gases of some incinerator facilities in the US and Europe. This has slowed or even stopped the construction and operation of waste-to-energy plants.

Municipal solid waste varies considerably in composition [14]. Many organic materials present in the MSW possess a chemical structure capable of releasing chlorinated organic compounds under pyrolysis and combustion conditions, especially plastics. Most plastics used for household applications are disposable and nonbiodegradable. Plastics account for 8% (by weight) of the total amount of municipal solid wastes and can make up to 20% of the volume of the wastes [15]. As their usage is anticipated to grow in the future, the amount of plastics discarded will also increase. PVC is one of the leading plastics in total production. The existence of PVC plastic, and other chloride-containing organics such as pesticides, herbicides, flame retardants, etc. in municipal solid wastes, is responsible for the formation of corrosive or toxic substances like HCl, other halogenated acids, chlorinated organic materials, and possibly PCDD/Fs, in the flue gases and particles from waste incinerators. Since MSW in the US generally consists of notable quantities of PVC, Saran and other chlorinated polymers, the yield of HCl from combustion of MSW will be significant.

Chlorine gas is a key intermediate in the formation of chlorinated dioxin compounds. It is generally thought that it is molecular chlorine, and not HCl, that reacts with aromatic compounds such as phenols to produce chlorinated aromatic compounds, including chlorophenols and polychlorophenols, which are precursors of PCDDs and PCDFs. In contrast, it is also possible that chlorine gas instead of HCl will more readily attack metal in combustion systems to cause severe corrosion.

Coal, as a co-firing energy source for municipal solid wastes, is able to suppress the formation of chlorine-containing organic compounds. Scheidle and co-workers demonstrated that adding lignite coal as an auxiliary fuel to paper recycling residues decreased the levels of dioxins in fluidized-bed combustion emissions [16]. Similar results can be inferred from Lindbaurer's study which showed that co-firing MSW with 60% coal drastically reduced the formation of PCDD/Fs [17]. Banaee and co-workers studied the co-combustion of Saran wrap with high-sulfur coals and other polymeric materials, and the results showed the ability of high-sulfur coal to inhibit the formation chlorinated benzenes [18]. Bonfanti and co-workers investigated the environmental aspects relevant to the co-firing of pulverized coal and RDF in a slag forming combustor, and the results show that the micro pollutant emissions were very low [19]. Ohlsson observed that despite the enhanced level of HCl due to the addition of RDF, no PCDD/Fs were detected when co-firing high-sulfur coal and RDF pellets [20]. Frankenhaeuser and coworkers also addressed the adverse effects of SO_2 in the formation of chlorinated organics during the co-combustion of plastics with coal [21].

The main objectives of the study reported in this article were to study the chloride-sulfur interactions during fossil fuel combustion and to investigate new ways for using FBC systems with high sulfur/high chlorine coals/MSW or RDF to minimize SO_x emission and the emission of chlorinated compounds, including PCDDs and PCDFs.

2. Experimental

All experimental work was conducted with the 0.1 MW_{th}

Table 2
The operating parameters

Fuel compositions:	(1) 100% coal (2) 89% coal, 1% PVC and 10% wood pellets (3) 86.7% coal, 3.3% PVC and 10% wood pellets		
	95010	95011	95031
Fuel feed rate (kg/h)	7.95	8.41	8.72
Limestone feed rate (kg/h)	0.52	2.53	1.95
Ca/S molar rate	~ 3.0	~ 3.0	~ 3.0
Air flow rate (kg/h)	89.9	89.9	89.9
Fluidizing velocity (m/s)	1.15	1.15	1.15
Fly ash rate (kg/h)	0.93	2.95	2.59
Bed ash rate (kg/h)	0.47	1.57	1.45
Oxygen concentration in gas		4–5%	

bench scale FBC system at Western Kentucky University. A full description of the FBC system has been presented by Orndorff and others [22], so only a brief description is given here. In this project, an underbed continuous fuel/limestone feeding system was installed at the 0.1 m point above the air distributor in the FBC system. Six moveable heat exchange tubes were added in the bed area of the FBC system. Typical operation of the combustor involves setting the correct fuel/limestone feed and air flows and then use the moveable heat exchange tubes to adjust the bed temperature to the desired setting. Another sixty-six gas heat exchange tubes are in a fixed position located approximately one meter from the top of the combustor. The hot gases from the combustor are allowed to enter the wet cyclone scrubber where they are met with a wall of water (which keeps the cyclone cool), which subsequently takes solids from the cyclone into a holding tank. The operating parameters (air/water flow, coal/lime feed, bunker weight, temperatures, and pressure) are controlled and logged to file with a Zenith 150 MHz computer utilizing the LABTECH software version 3.0. During the combustion runs any needed changes in the parameters could easily be entered into the computer, by accessing the correct control screen and making the necessary corrections on line.

Three coals were used in this study, an Illinois # 6 coal (95031; 0.31% Cl and 2.4% S), an Eastern KY coal (95010; 0.10% Cl and 0.67% S) and a western KY coal (95011; 0.01% Cl and 3.2% S). Analytical data for the three coals and limestone used in this study are presented in Table 1. The limestone came from Kentucky Stone in Princeton, KY. The coal and limestone both were air dried before being crushed to −4 mesh (4.75 mm). The limestone was also used as the bed material in the FBC system. The PVC was mixed with coal in three ratios: 0.5% by weight, 1% by weight, and 3.3% by weight. During combustion runs, limestone was fed into the system at a constant rate, depending upon the fuel used.

The gases eluting from the furnace were swept into three ice-cooled traps with impingers. The first two traps and impingers contained 0.1 M H_2SO_4 to trap HCl and the last

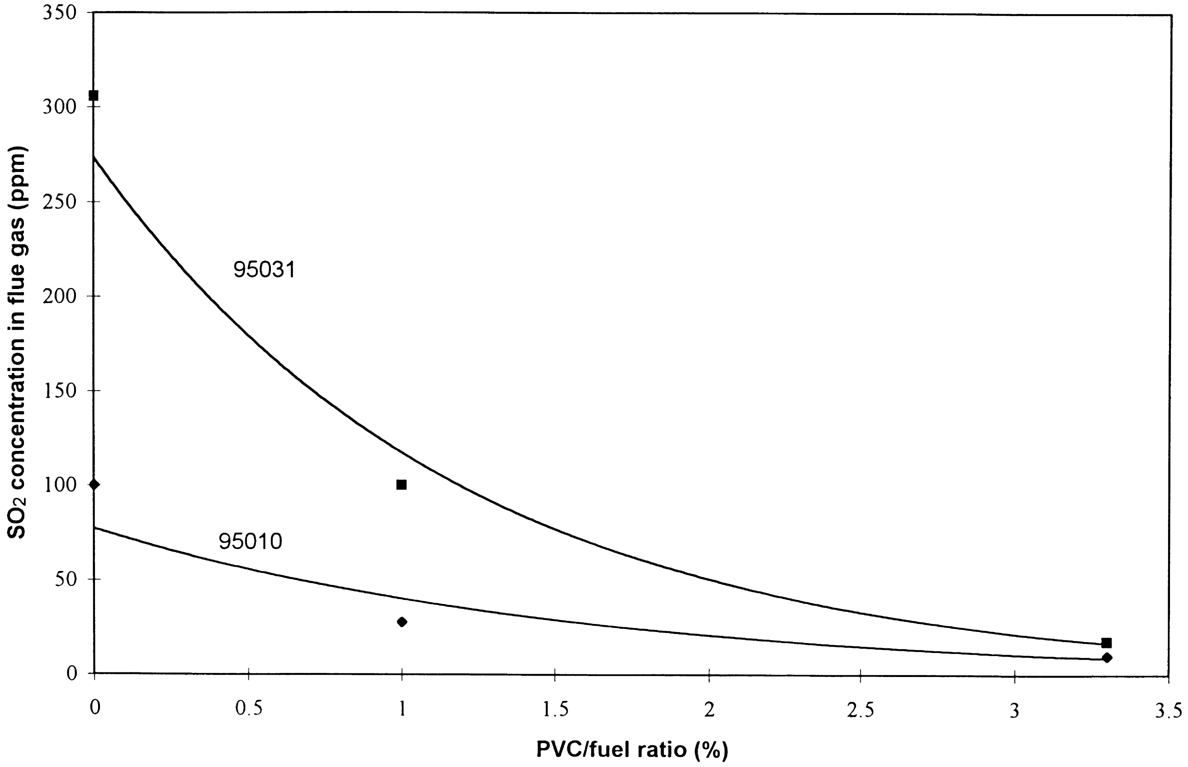

Fig. 1. The effect of the PVC/fuel ratio on SO_2 emission in the flue gas.

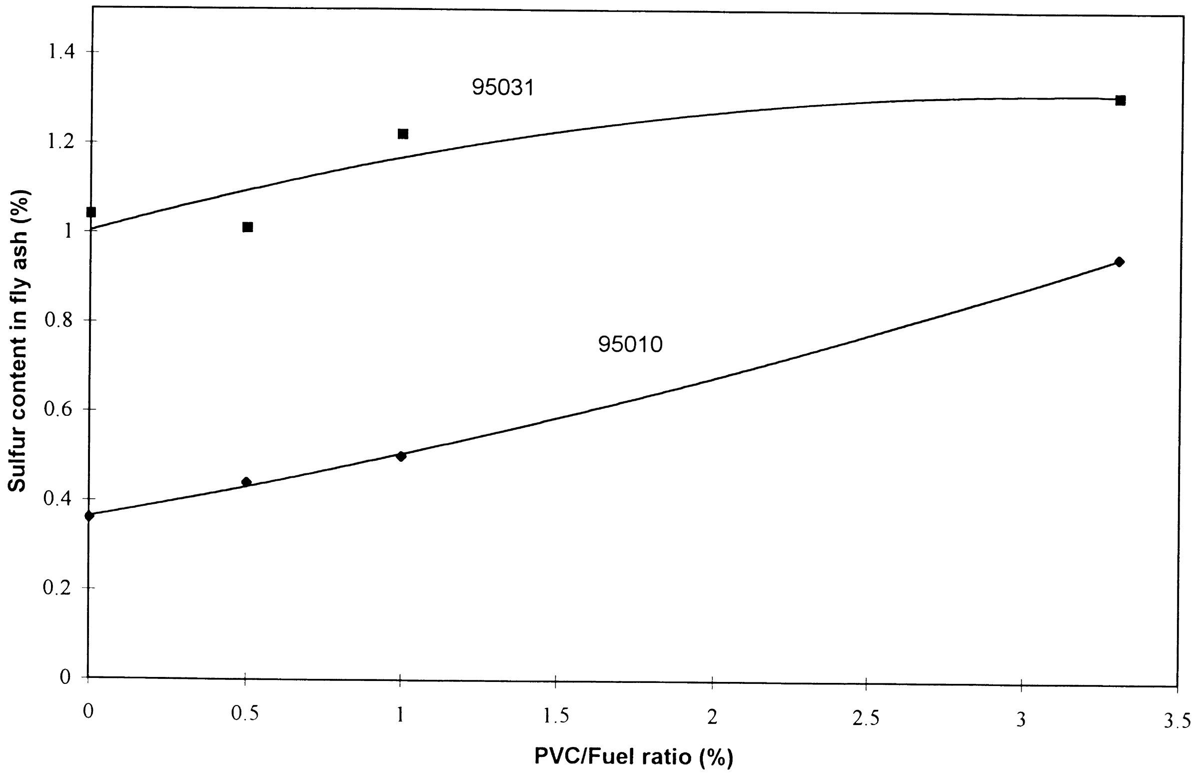

Fig. 2. The effect of the PVC/fuel ratio on the sulfur content in fly gas.

one contained 0.1 M NaOH to trap Cl_2 on the basis of the following reaction:

$$Cl_2 + 2NaOH \leftrightarrow NaCl + NaClO + H_2O \quad (3)$$

A Dionex Model 120 Ion Chromatograph was used to determine the concentration of chloride in both the acidic and basic solutions. The mobile phase was Na_2CO_3/$NaHCO_3$ and the flow rate was 1.2 ml/min. In all tests, no chloride was detected in the second impinger, meaning that all HCl was absorbed in the first bottle. Therefore, all chloride species in the third bottle resulted from the molecular chlorine produced in the combustion process.

The fly ash and bed ash sampling procedures used have been discussed previously [22–24]. A brief description for the mass balance test process is as follows: the first samples of solids (fly ash and bed ash) were collected after an 8 h stable combustion period for each FBC test. Within the following 2–4 h, the second (10 h after the start) and the third samples (12 h after the start) of solids (fly ash and bed ash) and the first (9 h after start) were collected. The first and second flue gas samples were collected 9 and 11 h after the start, respectively. The mass flow rates of fly ash and bed ash were measured in the tests. The concentrations of the compounds in the fly ashes and bed ashes were re-calculated on the basis of the mass flow rates of fly ashes and bed ashes, respectively. The difference in the concentration of each compound in the bed ashes between two adjacent samples was due to the addition of each compound as captured in the combustor. The concentration of each compound in the flue gases was calculated by the average of two sample values. The effects of adding limestone and coal ash during the test period were considered in the content change of each compound in the bed material absorption calculation.

During combustion runs the flue gases at the gas heat exchange region were analyzed continuously using on-line FTIR spectroscopy and gas chromatography. The major operating parameters for the experiments were as follows: excess air level—around 1.3; Ca/S ratio—approximately 3; bed temperature was controlled between 1140 and 1160 K. Other details of the combustion conditions are listed in Table 2 [25].

3. Results and discussion

3.1. SO_x Emission

One of the objectives of this study was to demonstrate that SO_x emissions decrease as the amount of chloride in the flue gas in the FBC system is increased. PVC is the principal source of chloride in the fuels used in the study. Fig. 1 shows that the SO_2 emissions decrease as the amount of PVC in the fuel blend increases. It can be clearly seen that the SO_2 emissions decrease dramatically when a mixture of 1% by weight of PVC is fed into the combustor, and then leveled off when the PVC content in the fuel mixture increased from 1 to 3.3 wt%. The sulfur content in the fly ash and bed ash increased with an increase in the amount of PVC used in the

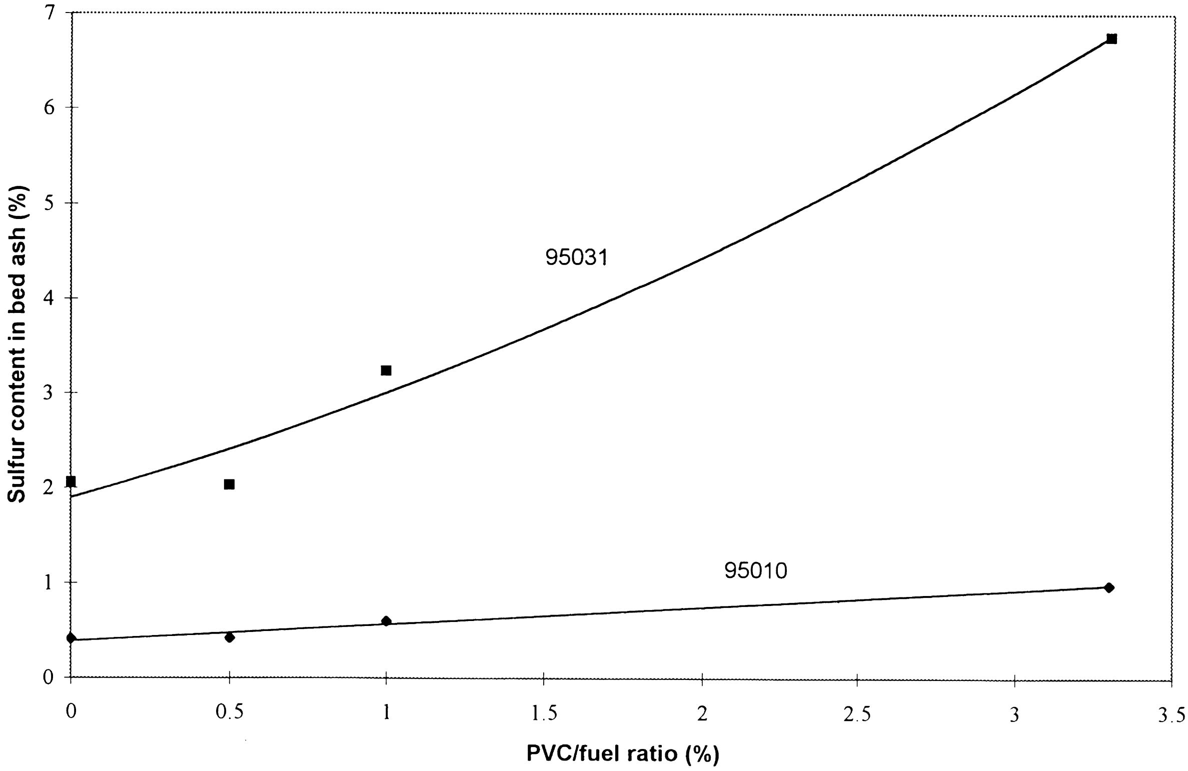

Fig. 3. The effect of the PVC/fuel ratio on the sulfur content in bed ash.

fuel. Fig. 2 illustrates that the sulfur content in the fly ash increases as the PVC/fuel ratio increases. Likewise, Fig. 3 shows that the sulfur content of the bed ash increases with an increase in the PVC/Fuel ratio. One explanation of the increased capture of SO_x by limestone is that the transient formation of a mobile halide ion-containing phases (i.e. $CaCl_2$) can modify the surface of the partially sulfated sorbent particles to form more voids on the surface, which provide diffusion paths for HCl and SO_x toward the interior of a limestone particle, leading to increased SO_2 capture [26]. However, a more complex but possible mechanism involves the interaction of Cl_2 with the SO_2 from the combustion of sulfur in the fuel producing SO_3. Molecular chlorine produced in the combustion process through the Deacon reaction in the presence of excess oxygen is a key organic chlorinating agent is replaced by HCl, which is less likely to cause any chlorination of organic species.

The results of the effects of limestone on the capture SO_2 are shown in Table 3. In this experiment, limestone was used as the bed material, and the change of run conditions was such that no new limestone was added to the combustor with the fuel. The samples of fly ash and bed ash were collected 8 h after the limestone feed to the combustor had stopped. In the presence of limestone, there is a significant improvement in the sulfur capture in the flue gas. Accordingly, the sulfur content in both fly ash and bed ash increases. The material balance data for sulfur are presented in Table 4.

3.2. Chloride emission

For all experimental runs presented in this article, no molecular chlorine was detected in the flue gases, as measured by the ion chromatographic analysis of chloride in the NaOH trapping solutions. In the case of the HCl emissions study, a difference in the behavior of chloride was noted for different amounts of sulfur in the fuels used in the FBC system. Fig. 4 illustrates that a higher concentration of hydrogen chloride occurred in the flue gas from

Table 3
The effect of limestone on the distribution of sulfur

	Coal 95010 with 3.3 wt% PVC		Coal 95031 with 3.3 wt% PVC	
	With limestone	No limestone[a]	With limestone	No limestone[a]
SO_2 emissions in the flue gas (ppm)	9.91	136.86	17.62	1240.29
Sulfur content in fly ash (%)	0.95	0.32	1.30	1.37
Sulfur content in bed ash (%)	0.98	1.53	5.16	4.96

[a] No new limestone was fed with fuel, bed material, and limestone.

Table 4
The percent distribution of sulfur in the different phases

Coal 95010 +	0% PVC	1% PVC	3.3% PVC
Before burning			
Feed rate (kg/h):	7.95	7.95	7.95
Sulfur content in fuel (wt%):	0.67	0.60	0.58
Feed amount of sulfur (kg/h):	5.33×10^{-2}	4.77×10^{-2}	4.61×10^{-2}
After burning			
Solid phase			
Bed ash			
Content (wt%)	0.41	0.60	0.98
Flow rate (kg/h)	0.47	0.47	0.47
Amount (kg/h)	1.93×10^{-3}	2.82×10^{-3}	4.61×10^{-3}
Bed material			
Content change (wt%):	0.076	0.059	0.057
Material inventory (kg):	50	60	60
Amount (kg/h):	0.038	0.0354	0.0342
Fly ash:			
Content (wt%):	0.36	0.50	0.95
Flow rate (kg/h):	0.93	0.93	0.93
Amount (kg/h):	3.35×10^{-3}	4.65×10^{-3}	8.84×10^{-3}
Subtotal	0.043278	0.04287	0.04765
Wt % in total sulfur:	81.20	89.87	103.36
Gas phase			
Concentration in flue gas (ppm):	100.05	27.64	9.91
Temperature of flue gas (°C):	150	150	150
Flow rate of flue gas (kg/h):	89.9	89.9	89.9
Flue gas volume (m^3/h):	113.12	113.12	113.12
SO_2 volume in gas (m^3/h):	0.0113	3.13×10^{-3}	1.12×10^{-3}
Sulfur amount (kg/h):	9.93×10^{-3}	2.88×10^{-3}	1.03×10^{-3}
Wt % in total sulfur:	18.63	6.04	2.23
Total	99.83	95.91	105.59
Coal 95031 +	0% PVC	1% PVC	3.3% PVC
Before burning			
Feed rate (kg/h):	8.72	8.72	8.72
Sulfur content in fuel (wt%):	2.38	2.12	2.06
Feed amount of sulfur (kg/h):	0.208	0.185	0.180
After burning			
Solid phase			
Bed ash			
Content (wt%)	2.06	3.24	6.76
Flow rate (kg/h):	1.45	1.45	1.45
Amount (kg/h)	0.0299	0.0470	0.0980
Bed material			
Content change (wt%)	0.22	0.16	0.07
Material inventory (kg)	60	60	60
Amount (kg/h):	0.133	0.0954	0.042
Fly ash			
Content (wt%)	1.04	1.22	1.31
Flow rate (kg/h)	2.59	2.59	2.59
Amount (kg/h)	0.0269	0.0316	0.0339
Subtotal	0.1898	0.1740	0.1739
Wt.% in total sulfur:	91.25	94.05	96.61
Gas phase			
Concentration in flue gas (ppm)	305.65	100.04	17.62
Temperature of flue gas (°C)	150	150	150
Flow rate of flue gas (kg/h)	89.9	89.9	89.9
Flue gas volume (m^3/h)	113.12	113.12	113.12
SO_2 volume in gas (m^3/h)	0.0346	0.0113	1.99×10^{-3}
Sulfur amount (kg/h)	0.0303	9.93×10^{-3}	1.75×10^{-3}
Wt % in total sulfur	14.57	5.37	0.97
Total	105.83	99.41	97.58

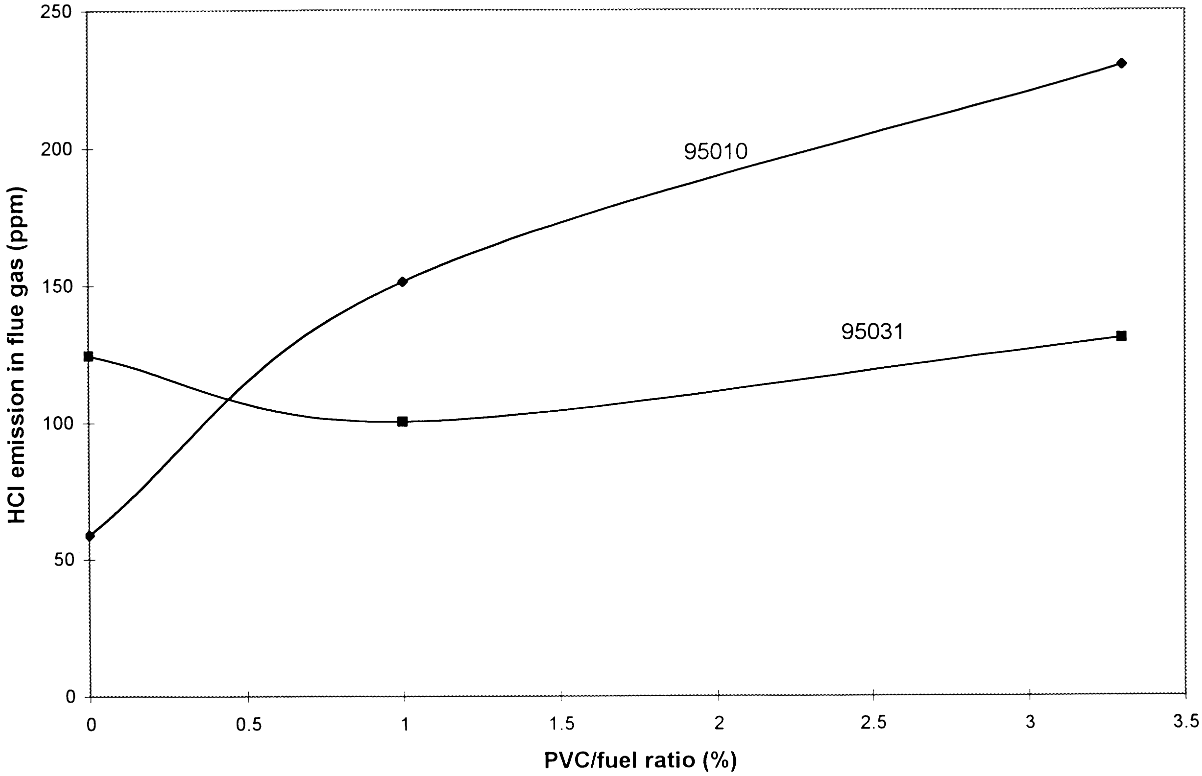

Fig. 4. The effect of the PVC/fuel ratio on HCl emission in the flue gas.

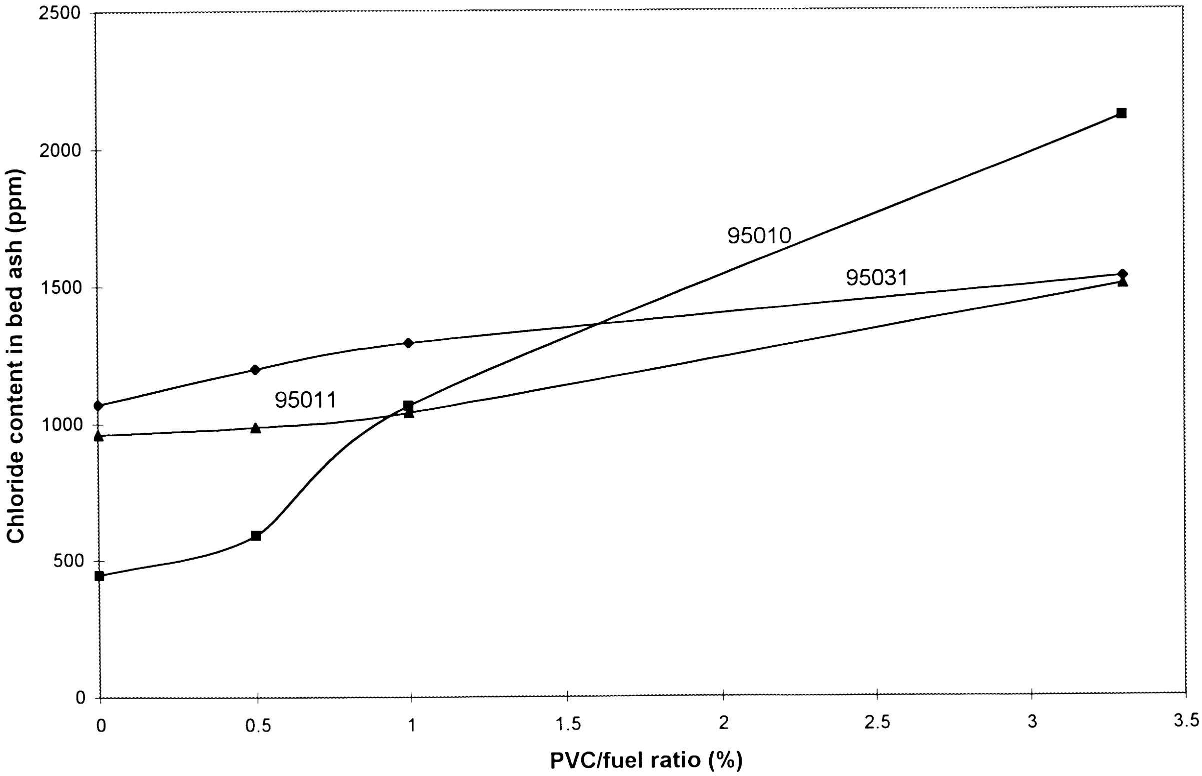

Fig. 5. The effect of the PVC/fuel ratio on the content of chloride in the bed ash.

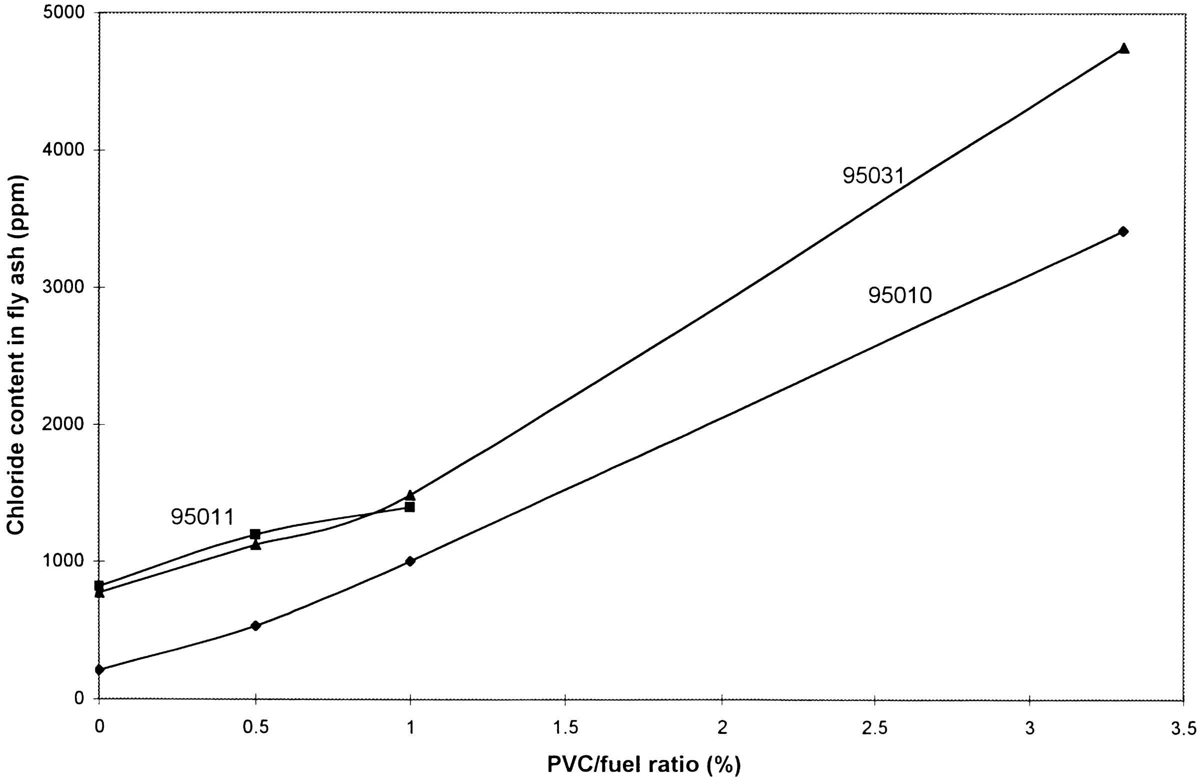

Fig. 6. The effect of the PVC/fuel ratio on the content of chloride in the fly ash.

the combustion of the low sulfur fuel (95010), as compared to the HCl in the flue gas from the combustion of the high sulfur fuel (95031) when PVC was added to the coals. However, the HCl contents in the flue gases are reversed for these two coals when no PVC is added, even though the high sulfur coal (95031) also has about 30 times more chlorine compared to the low sulfur coal. As expected, HCl emission in the flue gases increased with an increase in the amount of PVC added to the fuel. It is known that absorption of SO_2 by calcium oxide causes pore closure of limestone, resulting in the reduction of sulfation, because the molar volume of the final product, $CaSO_4$, is much greater than that of CaO. This is one of the reasons that the utilization of calcium in limestone is only 30–40%. However, the sulfation behavior may help reduce HCl emissions. In contrast to the case of sulfation, it is assumed that chloride trapped on the surface of limestone is transported from the surface into the bulk of the absorbing particle by diffusion or by the migration of $CaCl_2$ to other parts of the particle. With an increase of sulfur content in the coal and progression of sulfation, the $CaSO_4$ layer on the surface of the limestone particle becomes thicker, and diffusion into the particle becomes more difficult, eventually stopping the reaction. So this layer can suppress the escape of chloride in the vapor at a combustion temperature of 850°C, which is higher than the melting point of $CaCl_2$. This suggested behavior is also supported by the chloride contents in the bed ashes from the three coals, as shown in Fig. 5.

The effects of the PVC/fuel ratio on the chloride contents in the fly ashes is presented in Fig. 6. The chloride contents in fly ashes increase dramatically with an increase of the PVC/fuel ratio from zero to 3.3% by weight. Compared to the results shown in Fig. 5, it is obvious that the change of chloride contents in fly ashes is more than that in bed ashes. It is known that the optimum temperature for SO_2 capture by limestone in an FBC system is around 850°C in the fluidized bed itself. However, the favored temperature for HCl retention is relatively lower, and normally less then 650°C. HCl retention by calcium oxide also depends on the concentration of HCl in the flue gases [31]. Compared with bed ash, fly ash has a greater chance to absorb chloride since the temperature of the flue gas decreases along the height of the combustor, resulting in greater absorption of chloride. The material balance data for chloride are presented in Table 5.

The relationship between the chloride and sulfur contents in the combined ashes is shown in Fig. 7. A high sulfur content is always accompanied by a high chloride content in these ashes. The different sulfur contents in the fuels, and the different retention characteristics of sulfur are also expressed in the figure. For instance, fuel 95011 has the highest sulfur content, leading to the sharpest curve among the three fuels. In contrast, only a slight change occurred for fuel 95010, which has the lowest sulfur content. Consequently, it can be said that the SO_x capturing efficiency is sensitive to the chloride content in fuels.

Table 5
The percent distribution of chloride in the different phases

Coal 95010 +	0% PVC	1% PVC	3.3% PVC
Before Burning			
Feed rate (kg/h)	7.95	7.95	7.95
Chloride content in fuel (wt%)	0.104	0.671	1.97
Feed amount of chloride (kg/h)	8.27×10^{-3}	0.0533	0.157
After Burning			
Solid phase			
Bed ash			
Content (wt%)	0.045	0.106	0.211
Flow rate (kg/h)	0.47	0.47	0.47
Amount (kg/h)	2.12×10^{-4}	4.98×10^{-4}	9.92×10^{-4}
Bed material			
Content change (wt%)	0.045	0.0517	0.155
Material inventory (kg)	50	60	60
Amount (kg/h)	2.25×10^{-3}	0.0310	0.0929
Fly ash			
Content (wt%)	0.021	0.100	0.342
Flow rate (kg/h)	0.93	0.93	0.93
Amount (kg/h)	1.95×10^{-4}	9.33×10^{-4}	3.18×10^{-3}
Subtotal	2.66×10^{-3}	0.0324	0.0971
Wt.% in total chloride:	32.16	60.79	61.85
Gas phase			
Concentration in flue gas (ppm)	50.83	151.14	249.86
Temperature of flue gas (°C)	150	150	150
Flow rate of flue gas (kg/h)	89.9	89.9	89.9
Flue gas volume (m^3/h)	113.12	113.12	113.12
Chloride volume in gas (m^3/h)	6.66×10^{-3}	0.0171	0.0260
Amount (kg/h)	6.21×10^{-3}	0.0185	0.0473
Wt % in total chloride	75.09	34.71	30.13
Total	107.25	95.5	91.98
Coal 95031 +	0% PVC	0.5% PVC	1% PVC
Before burning			
Feed rate (kg/h)	8.72	8.72	8.72
Chloride content in fuel (wt%)	0.307	0.591	0.874
Feed amount of chloride (kg/h)	0.0268	0.0515	0.0762
After burning			
Solid phase			
Bed ash			
Content (wt%)	0.107	0.120	0.129
Flow rate (kg/h)	1.45	1.45	1.45
Amount (kg/h)	1.55×10^{-3}	1.74×10^{-3}	1.87×10^{-3}
Bed material			
Content change (wt%)	0.0134	0.0461	0.0761
Material inventory (kg)	60	60	68.5
Amount (kg/h)	8.04×10^{-3}	0.0277	0.0521
Fly ash			
Content (wt%)	0.0773	0.122	0.159
Flow rate (kg/h)	2.59	2.59	2.59
Amount (kg/h)	2.00×10^{-3}	3.16×10^{-3}	4.12×10^{-3}
Subtotal	0.0116	0.0326	0.0581
Wt % in total chloride:	43.28	63.30	76.25
Gas phase			
Concentration in flue gas (ppm)	124.49	131.14	115.52
Temperature of flue gas (°C)	150	150	150
Flow rate of flue gas (kg/h)	89.9	89.9	89.9
Flue gas volume (m^3/h)	113.12	113.12	113.12
Chloride volume in gas (m^3/h)	0.0141	0.0148	0.0131
Amount (kg/h)	0.0152	0.0160	0.0141
Wt % in total chloride	56.72	31.07	18.50
Total	100	94.37	94.75

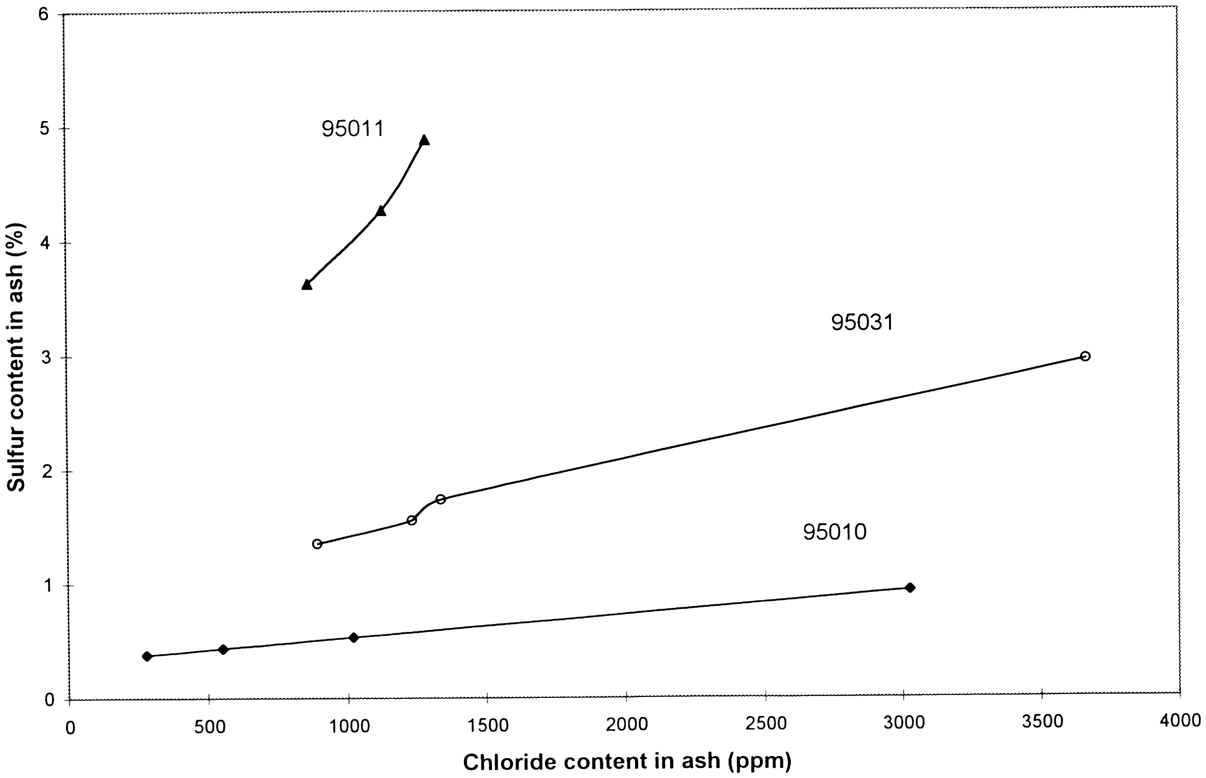

Fig. 7. The relationship between the sulfur and chloride contents in ash (combination of fly ash and bed ash).

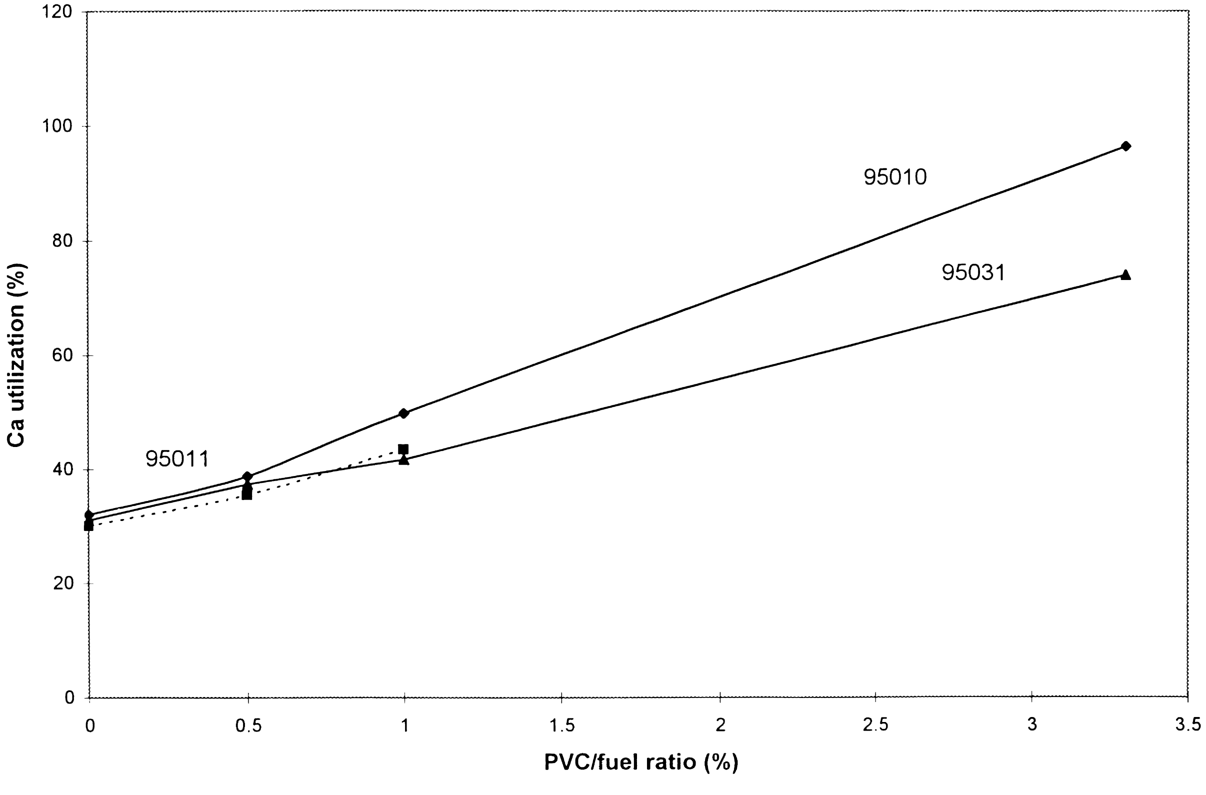

Fig. 8. The effect of the PVC/fuel ratio on a Ca utilization.

3.3. Calcium utilization

To reduce SO_x emission, the Ca/S mole ratio is normally chosen to be 2.5–3, both in lab studies and in conventional power or industrial FBC systems. That means that the conversion rate from porous calcium oxide to calcium sulfate ($CaSO_4$) is only about 30 ∽ 40%. However, in the presence of HCl in the combustor, the utilization of calcium is improved to higher levels, as much as 100% more than when only SO_x exists in system. This improvement is illustrated in Fig. 8. In the reaction with chlorine a number of spherical aggregates and large voids are formed on the absorbing particles, and consequently more SO_x and HCl can easily penetrate into the limestone particle, to react with new calcium oxide. This increases the absorption rate of HCl and SO_x sulfation, and increases the level of conversion of CaO to $CaSO_4$ and $CaCl_2$.

Interaction between SO_2 and HCl. A possible mechanism for the interaction between SO_2 and HCl can be proposed from the combination of the results from previous reports [27] and those given in this paper. Thermodynamic data shows the Deacon reaction

$$4HCl + O_2 \leftrightarrow 2H_2O + 2Cl_2 \tag{4}$$

is favored over the range of temperatures from 300 to 1500 K and is exothermic at 25°C ($H = -114$ KJ/mol, $\Delta G = -76$ KJ/mol). An increase in temperature will cause the equilibrium to move toward the reactants, which will lower the conversion of HCl to Cl_2. Before the equilibrium is reached, however, the reaction is predominantly kinetically-controlled. A rise in temperature will lead to more products. The equilibrium constant for reaction (4) at 1120 K is about 1097 [8]. Typically, the oxygen and water concentrations in the flue gas in an FBC are around 5%. Therefore, when 1000 ppm HCl is present in the flue gas, the equilibrium value for Cl_2 would be 1.48%, which is very much higher than the actual concentration of Cl_2 present in the flue gas. Yang [28] reported that in the case where the reaction takes place in a steady moving flow and no catalysts are present, the reaction is far from equilibrium. Consequently, a higher temperature will lead to a higher reaction rate, meaning more Cl_2 will be produced. Also it should be noted that Le Chatelier's Principle indicates that the addition of oxygen to the system to enhance the combustion process would tend to form more Cl_2.

When SO_2 is present from the combustion of sulfur in coal, a most interesting and important reaction is that SO_2 may be attacked by Cl_2 to form SO_3 and HCl:

$$Cl_2 + SO_2 + H_2O \leftrightarrow 2HCl + SO_3 \tag{5}$$

During fluidized combustion, SO_3 will be absorbed more easily by limestone than SO_2, according to the reactions represented by the following equations:

$$CaO + SO_3 \rightarrow CaSO_4 \tag{6}$$

Compared to

$$CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4 \tag{7}$$

The use of limestone as the bed material and continuous feeding of limestone with the fuel in fluidized bed combustion will keep excess CaO in the combustor. Subsequently, the concentration of molecular chlorine in the flue gas is minimized on the basis of reaction (6) at temperatures below 1000°C.

It has been well established that halogenated species are good flame inhibitors [29]. According to Bulewicz [30] there is a phenomenon of halogen inhibition of oxidation of CO and other species in an FBC system. Thus it might be expected that the concentration of SO_2 may increase due to its incomplete combustion to SO_3 in the presence of chloride. Reaction (7), however, can promote the oxidation of SO_2–SO_3 in different ways through the Deacon reaction in the presence of chloride and oxygen-rich conditions. These two effects probably compete with each other during coal combustion.

4. Conclusions

From experimental investigations in a fluidized bed combustor on the influence of chlorine on sulfur capture, it was shown that the presence of HCl will promote SO_2 capture by the bed material and fly ash particles. However, the presence of sulfur leads to an apparent reduction in the formation of molecule chlorine. As a result, minimization of the formation of the PCDDs and PCDFs during the combustion of high sulfur and high chlorine fuels occurs.

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