

A study of chlorine behavior in a simulated fluidized bed combustion system

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Abstract

Fluidized bed combustion techniques have been widely used throughout the world in an effort to reduce sulfur oxide emissions, especially from burning high-sulfur coal. However, in the utilization of FBC systems for co-firing high chlorine coals with municipal solid waste (MSW) there are some concerns about the possible emission of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). PCDD/Fs may be produced from the reaction of volatile organic compounds (VOCs) and molecular chlorine under relatively low combustion temperature conditions. In oxygen-rich conditions during combustion molecular chlorine can be formed through the Deacon Reaction when the temperature is around 600°C. It is also likely that chloride might affect the detailed chemistry of desulfurization in FBC processes. In order to better understand the behavior of chlorine in an FBC system during combustion processes, a comprehensive study was carried out in a simulated FBC system with an on-line feeder at Western Kentucky University. Conditions used simulated the flue gas and operating conditions of an FBC system. Optimum operating conditions to suppress HCl, Cl₂ and SO_x emissions from FBC systems were determined. A better understanding of the chlorine behavior during combustion will help in controlling possible PCDD and PCDF formation and reducing corrosion in FBC systems. The test results indicated that the formation of molecular chlorine is favored at temperatures above 600°C, in oxygen-rich atmospheres, and in relatively high HCl concentrations. The reaction temperature plays a key role in the capture of HCl. The optimum combustion conditions for controlling PCDD/Fs formation in FBC systems is to maintain combustion temperature around 850°C in the bed area, 600°C in the freeboard area, low oxygen concentrations in the flue gas and enough residence time for fine particles in the freeboard. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

One of the major issues challenging environmental management and pollution control at present is the disposal of a tremendous amount of municipal solid waste (MSW). According to a forecast of the Environmental Protection Agency (EPA), MSW generation in the USA during the past three decades increased by more than 225% [1–3]. Landfilling, the traditional approach to deal with the waste, is becoming more and more expensive and impractical due to growing societal concern over land use. In the USA, the number of active landfills decreased from 6034 in 1986 (EPA, 1991) to 4482 in 1993 [4]. Moreover, it is anticipated that the number of operating landfills will soon drop below 4000. The rapidly declining availability of sanitary landfills has forced most municipalities to evaluate

alternative waste management technologies for reducing the volume of waste sent to landfills.

Incineration is one of the alternative waste management strategies proposed to replace landfilling. This waste-to-energy technology has already displayed a few advantages over conventional methods of disposal. The energy recovery from these plants is attractive to state and local governments. However, extra care needs to be taken in burning RDF to optimize operating conditions of a combustor so that combustion takes place in an environmentally acceptable manner. The development of such facilities has slowed significantly in recent years, resulting from apprehension over possible emissions of hazardous chlorinated organics, especially the harmful polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The emissions of PCDD/Fs from incineration processes were first reported in 1977 by Olie and coworkers [5].

The majority of mechanisms proposed to explain the PCDD/Fs formation in municipal solid waste combustion processes involved chemically similar precursors, such as

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chlorophenols, which may be formed initially as the products of incomplete combustion [6–15]. Laboratory studies have demonstrated that transition metal ions like Cu and Fe are capable of catalyzing the PCDD/Fs formation reactions, which may take place on fly ash particles. The small organic molecules can be adsorbed onto the fly ash from flue gases and are subsequently converted to PCDD/Fs. Compared with Cl₂, HCl is very unlikely to undergo aromatic substitution reactions to yield PCDD and PCDF precursors [16,17]. Therefore, the formation of molecular chlorine may play a controlling role in the production of PCDD/Fs. In the meantime, PCDDs and PCDFs are chemically stable in general and are usually formed in small amounts. As a consequence, a feasible way to reduce their emissions is to prevent their formation during combustion rather than to capture or destroy them thereafter. Therefore, minimization of such species in the effluents of combustion systems is essential to optimize incineration conditions.

On the laboratory scale, a few practical strategies have been adopted to minimize the emission of PCDD/Fs from the combustion of MSW. One such strategy is the use of sulfur or nitrogen compounds as inhibitors [18,19]. Coal with high sulfur content, 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 incinerator emissions [20]. Similar results can be inferred from Lindbauer's study which showed that co-firing MSW with 60% coal drastically reduced the formation of PCDD/Fs [21,22]. Banaee and co-workers studied the co-combustion of Saran wrap with high-sulfur coals and other polymeric materials, and the results showed the promising ability of coal to inhibit the formation of chlorinated benzenes [23]. Ohlsson observed that despite the enhancing levels of HCl due to the addition of RDF, no PCDD/Fs were detected when co-firing high-sulfur coal and RDF pellets [24]. Frankenhaeuser also addressed the adverse effect of SO₂ on the formation of organic chlorides during the co-combustion of plastics with coal [25]. Gullett and coworkers found that sulfur hindered PCDD/PCDF formation even at a sulfur/chlorine ratio of 0.64 [26].

All the studies referred to in this discussion indicate that the addition of coal, especially high-sulfur coal, to municipal solid wastes results in appreciably lower levels of PCDD/Fs being produced. The following equation represents what is thought to be the key reaction step inhibiting the formation of PCDD/Fs [27,28]:



Published experimental data with respect to the mechanism for the effect of sulfur species on the formation of chlorinated organics during combustion is scarce. Also, most of the experimental data were collected in experiments with a small fixed bed furnace in an air atmosphere without

a catalyst. As indicated in the above equation, molecular chlorine is a key intermediate for the formation of PCDD/Fs. Theoretically, the emission of chlorinated organics can be effectively inhibited if the molecular chlorine yield is reduced as far as possible.

Compared to other combustion technologies, fluidized bed combustion (FBC) systems are particularly suited for waste fuels because of their ability to burn low grade fuels as well as fuels with variable energy contents, and the ability to capture hazardous gases (such as SO_x and HCl) directly in the combustor. Matsukata and coworkers reported that the sulfurization of all size particles was markedly accelerated in the presence of HCl [29]. The level of conversion of CaO to CaSO₄ and CaCl₂ always approached 100% upon the simultaneous absorption of HCl and SO₂. It was proposed that this absorption efficiency was the result of both the formation of a mobile chloride ion-containing phase and the formation of voids playing a role in the diffusion of HCl and SO₂ toward the interior of a limestone particle. Deguchi and coworkers tested HCl retention and simultaneous retention of HCl and SO₂ in a bubbling fluidized bed at 1123 K [30]. The results showed that HCl was effectively retained by limestone and the desulfurization efficiency was increased in the presence of HCl.

In order to better understand the behavior of chlorine in an FBC system during combustion processes, a comprehensive study was carried out at Western Kentucky University in a simulated FBC system with an on-line feeder. The study concentrated on the reduction of HCl emissions in the flue gases, molecular chlorine formation characteristics, and the interaction between HCl and SO_x. Conditions used simulated the flue gas and operating conditions of an FBC system. A better understanding of the mechanism for the formation of molecular chlorine during combustion will be helpful in controlling PCDD and PCDF formation in FBC systems.

2. Experimental

All experimental investigations were conducted with a simulated fluidized bed combustion system, as illustrated in Fig. 1. It consists of a fluidized bed reactor made of quartz, an electrical furnace, sample line, pump, and flowmeters. The reactor has an inner diameter of 45 mm, and a height of 80 cm. FBC simulated gas (13% CO₂, 5% O₂ and 0.5% CO, and 81.5% N₂) supplied from a cylinder was injected into the reactor from the bottom at a velocity of ~4 cm/s, distributed and mixed by a fritted filter, then reacted using the FBC's bed ash as a catalyst. The powdered lime and limestone with a 0–0.43 mm size range were used as sorbent in the tests. All experiments were carried out in a bubbling fluidizing condition. The concentrations of the reactive compounds (HCl, SO₂, O₂) in the gas mixtures were adjusted using calibrated teflon flowmeters. N₂ and CO₂ were used to give the appropriate concentrations of

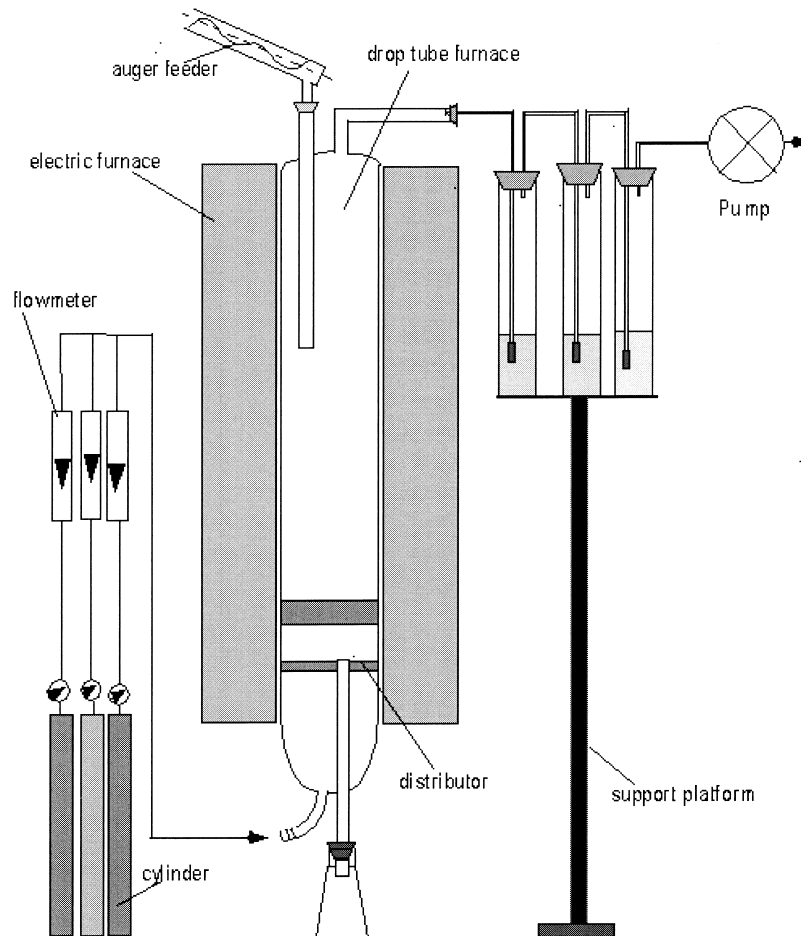


Fig. 1. The schematic diagram of electric tube furnace system.

the reactive gases. The reaction temperature was automatically controlled by an electrically heated furnace. The experimental runs in this study were divided into three steps. The first is the interaction between HCl and SO_x , the second is the formation of molecular chlorine, and the final test is the reduction of HCl emissions in flue gases.

A Dionex Model 120 Ion Chromatograph was used to determine the concentration of anions (Cl^- , SO_4^{2-}) in the solution. The mobile phase was $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ and the flow rate was 1.2 ml/min. The compressed gas pressure was 1500 psi. The chloride content in solid samples was measured by bomb decomposition followed by determination of chloride with the ion chromatograph. The conversion rate of reactants can be calculated using the following equation:

$$R = \frac{(C_{ic}(V_{so}/FW)) \times 22.4}{(273G_s t P_1)/P_0 \times (273 + T)} \times 10^{-3}$$

where V_{so} is the bulk of the solution (ml), G_s the flow rate of SO_2 in the flue gas (ml/min), t the sampling time period, C_{ic} the SO_4^{2-} concentration in the solution as determined by IC (ppm), FW the the molecular weight of SO_4^{2-} , P_1 the pressure at exit of flowmeter (0.995 atm), P_0 the atmospheric pressure (1 atm) and T the temperature (Celsius).

3. Results and discussion

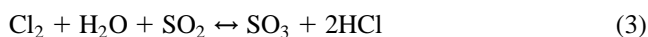
3.1. Interaction between HCl and SO_x

In order to determine the behavior of chloride and its effect on SO_x emissions under FBC conditions, a study was carried out in a quartz tube in an electrically heated tube furnace. In this study, the effects of temperature, and concentration of HCl on SO_x emission in the flue gas was determined. The reaction products were swept into a cooled trap containing a mixture of Na_2CO_3 and NaHCO_3 as absorbents, it was assumed that only SO_3 can produce the SO_4^{2-} ion under the test conditions.

The effect of the HCl concentration on the rate of conversion of SO_2 to SO_3 at 600–800°C is illustrated in Fig. 2. These results indicate that the conversion rate was changed by the concentration of HCl. At 600°C, the curve rises slowly when the HCl concentration is increased from 0 to 500 ppm, then increases very fast and reaches a maximum at 1000 ppm. After reaching a maximum at 1000 ppm HCl, the conversion rate decreases very fast as the HCl concentration is increased. The curve's shape for the 700 and 800°C tests are similar to that obtained at 600°C. The maximum peak for the conversion rate (optimum HCl concentration) was

shifted to higher than 1000 ppm. This information can be very helpful for the operation of an AFBC system. At the beginning of the combustion, the concentration of HCl and the bed temperature (above 800°C) are both higher in the bed area than in the freeboard area where the temperature is in the range of 550–700°C. In the bed area, the effect of a high concentration of HCl on the conversion rate is significant. If the temperature decreases from the bed to the freeboard area, as a result of heat exchanges between the flue gas with a high temperature to heat transfer tubes with a low temperature, the reaction between CaO and HCl becomes more significant forming liquid and/or solid phase calcium chloride. Consequently, the HCl concentration in the flue gas is reduced gradually as it rises in the combustor. In the freeboard area, low concentrations of HCl at low temperatures can accelerate the conversion of SO₂ to SO₃, as was found in this study.

Based on the information reported in this paper, the following two-step mechanism is proposed to explain the interactive effect between HCl and SO₃ emission:

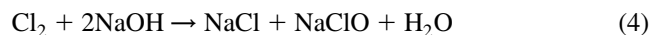


3.2. Formation of molecular chlorine

The oxidation of HCl to Cl₂ in excess oxygen has been

known as a catalyzed reaction for nearly a century. Known as the Deacon Reaction, the oxidation is represented by Eq. (2). CuCl₂, Cu₂Cl₂ and other transition metal salts were utilized as catalysts in most of the earlier studies [31]. Consistent with the JANAF thermochemical tables, most thermodynamic measurements and calculations for the reversible Deacon Reaction show that the forward reaction dominates up to 600°C under standard conditions. The Deacon Reaction has a standard free energy of reaction of -76, -49, -9.2 and +4.4 kJ at 298, 500, 800 and 900 K, respectively [32].

In this part, 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 H₂SO₄ to capture HCl. In these two gas absorption bulbs, Cl⁻ was detected in the first absorption bulb, while no Cl⁻ was found in the second absorption bulb. Molecular chlorine was trapped in the third bulb containing 0.1 M NaOH according to the following reaction:



In this part, the study identified the temperature range, concentrations of components in the flue gas, catalyst, retention time in the furnace, and other operating conditions needed for the formation of molecular chlorine using a simulation of the flue gas and operating conditions in FBC systems.

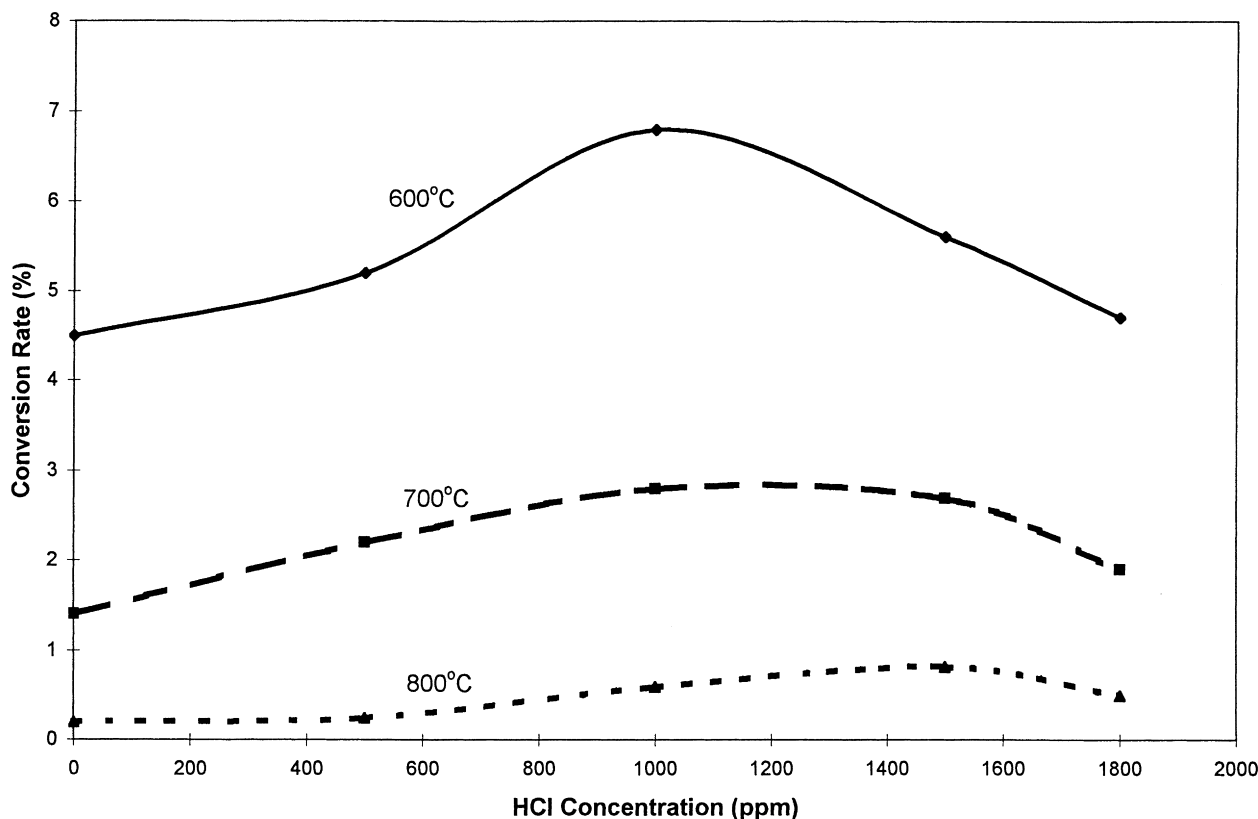


Fig. 2. The effect of HCl concentration on the conversion rate of SO₂ to SO₃.

Molecular chlorine was clearly found in this experiment while the mixed gas (5% O₂ in N₂) passed through the furnace. Fig. 3 shows the results of the conversion rate (*R*) from HCl to Cl₂ at different temperatures at an HCl concentration of 1500 ppm in air. These results indicate that the higher temperatures favor an increase in the production of molecular chlorine. Thus, it can be said that the Deacon Reaction is favored at higher temperatures.

The effect of the HCl concentration on the formation of Cl₂ at 700°C under FBC conditions is illustrated in Fig. 4. CaO (at a Ca/Cl mole ratio of 3) was fed into this system as an absorbent to capture HCl. Ash was also added into the system to promote the Deacon Reaction. Two different types of results were observed in the studies. The conversion rate decreased dramatically before the concentration reached 1000 ppm. This is due to the reaction between HCl and CaO. More HCl was converted to chlorine for the lower concentration than that for the high concentration. This indicates the reaction between CaO and HCl not only depends on the temperature, but also depends on the concentration of HCl in the flue gas. However, the conversion rate slowly increased after the concentration reached 1100 ppm. This may be due to the reaction between CaO and HCl reaching an equilibrium. Thus, the excess HCl is converted to Cl₂.

The effect of flue gas composition on the conversion rate is shown in Fig. 5. The dashed line indicates the presence of CO₂ and CO in the system (13% CO₂, 0.5% CO, and 5% O₂, in N₂). The solid line represents the gas 5% O₂ in N₂ without CO₂ and CO. These results indicate that carbon monoxide and carbon dioxide retard the Deacon Reaction when the temperature is raised over 700°C. This difference is not significant at lower temperatures, which indicates the Deacon reaction is not favored at the lower temperatures in an FBC system. The normal operating temperature for AFBC systems is around 850°C.

Fig. 6 presents test results with and without ash as a catalyst. The conversion rate of molecular chlorine increases sharply above 700°C with the addition of ash in the system. It indicates that the ash has a significant catalytic effect on the formation of Cl₂. The formation of chlorine could be controlled if the right HCl concentration and temperature is used. The amount of ash and the concentration of HCl will depend on the fuels used.

3.3. Reduction of HCl emissions in the flue gas

According to Pan and coworkers [33], almost all the chlorine in coal or MSW/RDF is volatilized and emitted as gaseous HCl during combustion. Under fluidized bed combustion conditions, the equilibrium partial pressure over calcium oxide is about 2000 ppm. Therefore, significant capture of HCl by limestone at fluidized bed temperatures can only occur in systems with high chlorine concentrations. However, the HCl equilibrium partial pressure is temperature dependent. HCl can react with

CaO downstream from the freeboard where the flue gases are cooled, although chlorine capture does not occur within the fluidized bed section.

As mentioned above, the temperature is a controlling factor in the capture of HCl. Fig. 7 shows that the optimum temperature for the reaction between HCl and CaO in an air atmosphere is around 650°C. With an increase of the reaction temperature, the retention of HCl by CaO decreased as expected. This may be due to the melting point of CaCl₂, which is around 782°C. It can be seen that the capture efficiency decreases dramatically when the temperature reaches the FBC operating temperature around 850°C. It can be predicted that when limestone, instead of CaO, is employed in the FBC system, the capture efficiency should decrease even further due to large particle size and low active surface area for limestone. Table 1 shows the distribution of chlorine in the gas phase and solid phase. At the lower temperature of about 600°C most of the HCl can be captured by CaO.

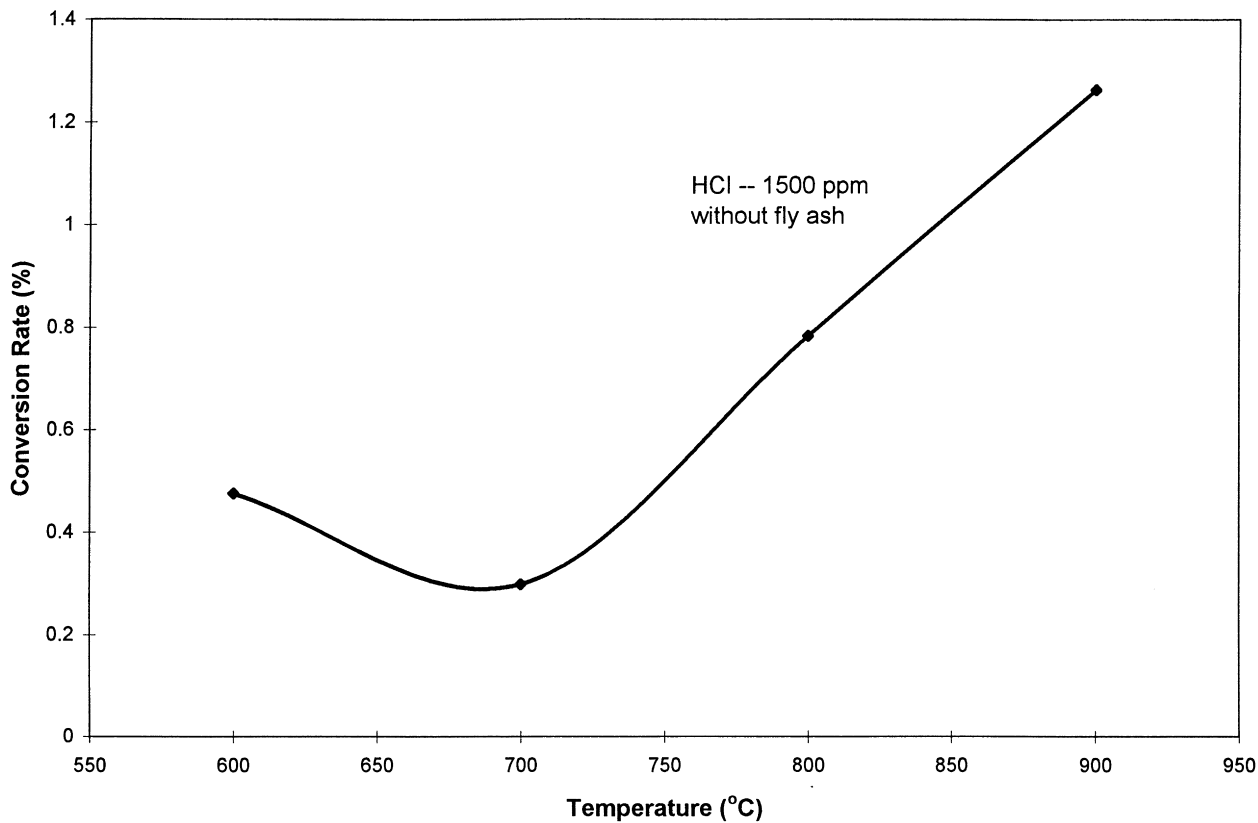
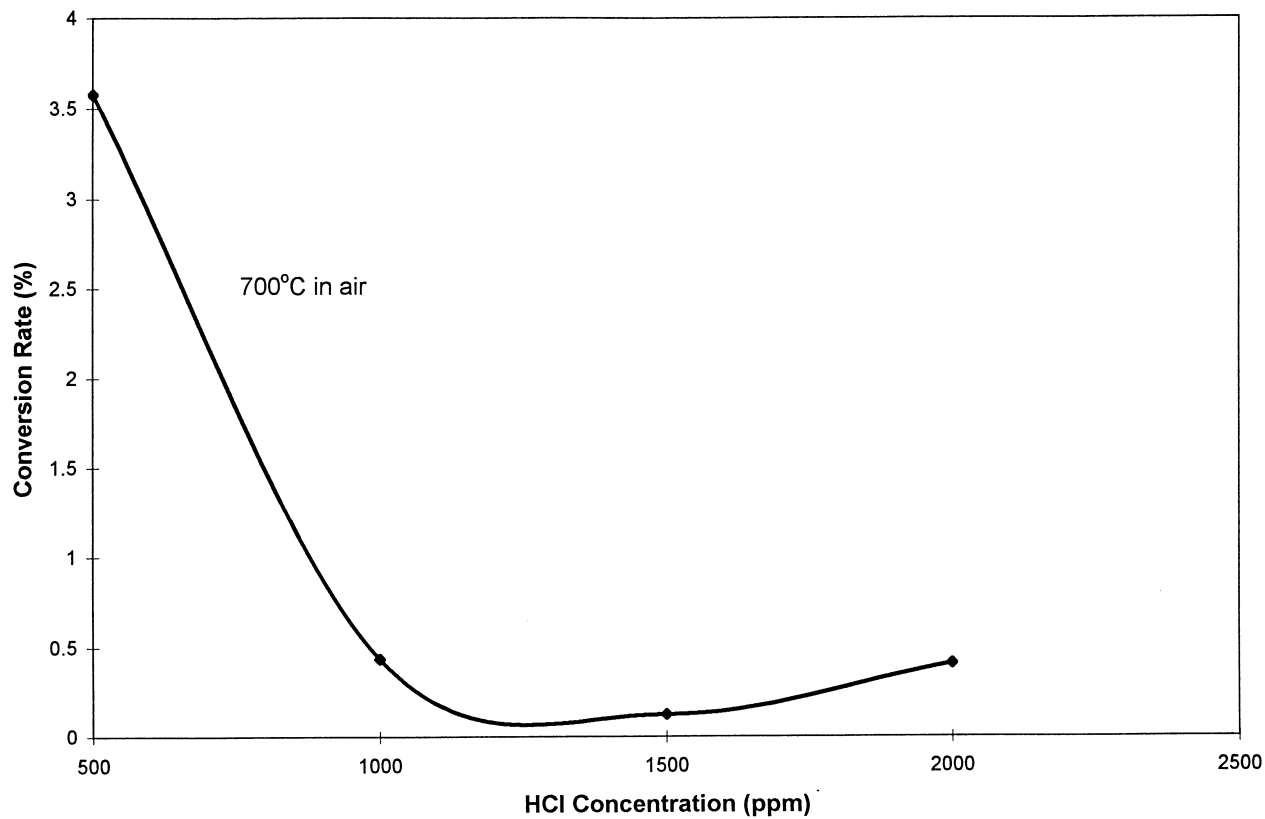
The concentration of HCl is an important factor in its capture by CaO, as shown in Fig. 8. Under 700°C and in an air atmosphere, the HCl retention efficiency increases with the increase in the HCl concentration. The retention efficiency increases when the HCl concentration goes from 500 to 1500 ppm, then it seems to level off in the 1500–2000 ppm range. It is known that the active surface of CaO is the main attribute in the capture of HCl. However, when the HCl concentration reaches a certain point, it does not have enough time to penetrate into the CaO particles to be reacted. This may be the reason that the capture efficiency of HCl levels off.

Fig. 9 illustrates the effect of atmosphere on the capture efficiency of HCl. The results indicate that there is a significant difference when the different reaction atmospheres are used. Compared to the case of an air atmosphere, when the FBC simulated gas was employed, the HCl capture efficiency has a larger decrease with increasing temperature.

4. Conclusions

Based on the studies thus far, the following conclusions can be made:

1. HCl can promote the conversion of SO₂ to SO₃. The conversion rate reached a maximum at temperatures around 600°C.
2. The rate of conversion of SO₂ to SO₃ can be increased either at a high concentration of HCl with a high temperature, or at a low concentration of HCl with a low temperature.
3. The formation of molecular chlorine is favored at temperatures above 600°C, in oxygen-rich atmospheres, and in relatively high HCl concentrations. This is the most important information for avoiding PCDD/F formation. The optimum combustion conditions for controlling molecular chlorine formation in FBC systems is to

Fig. 3. The effect of temperature on the conversion of HCl to Cl₂.Fig. 4. The effect of the HCl concentration on the conversion of HCl to Cl₂.

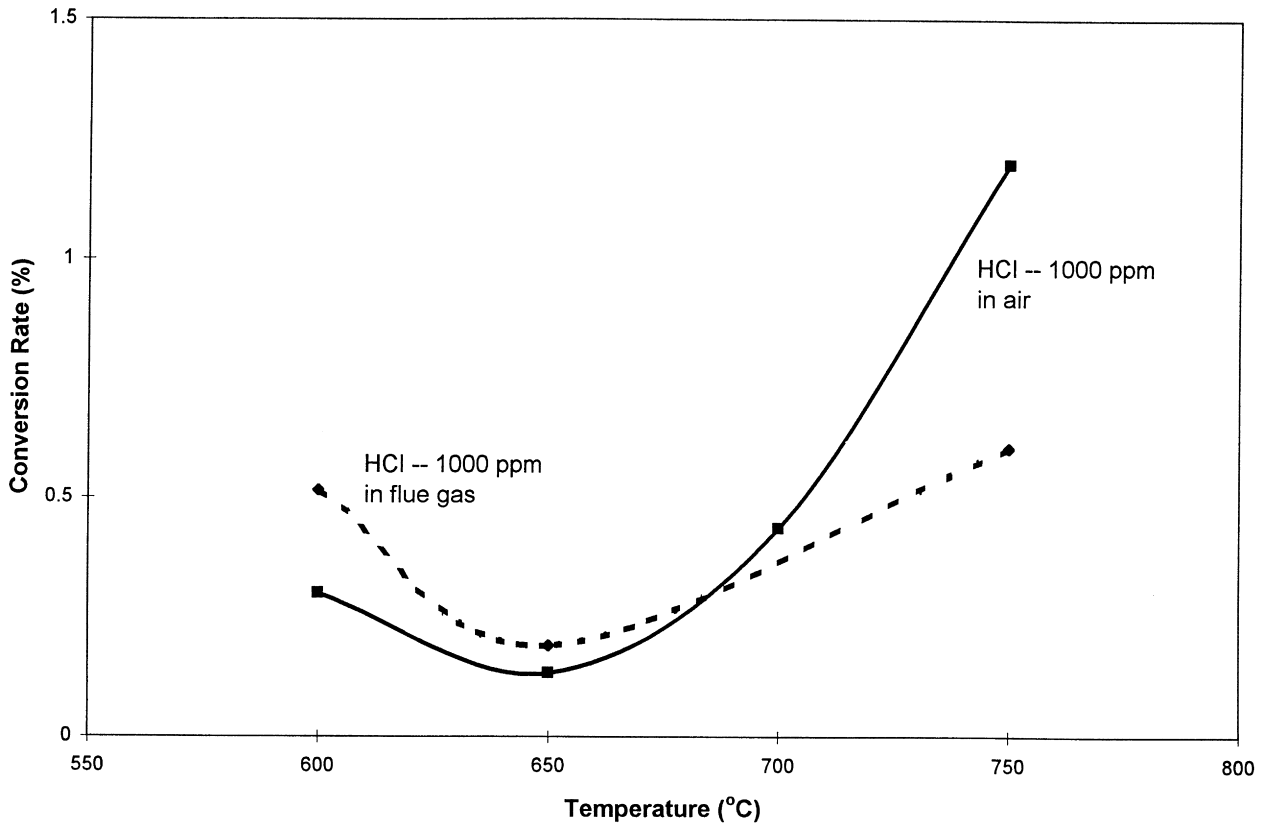


Fig. 5. The effect of reaction atmosphere on the conversion of HCl to Cl₂.

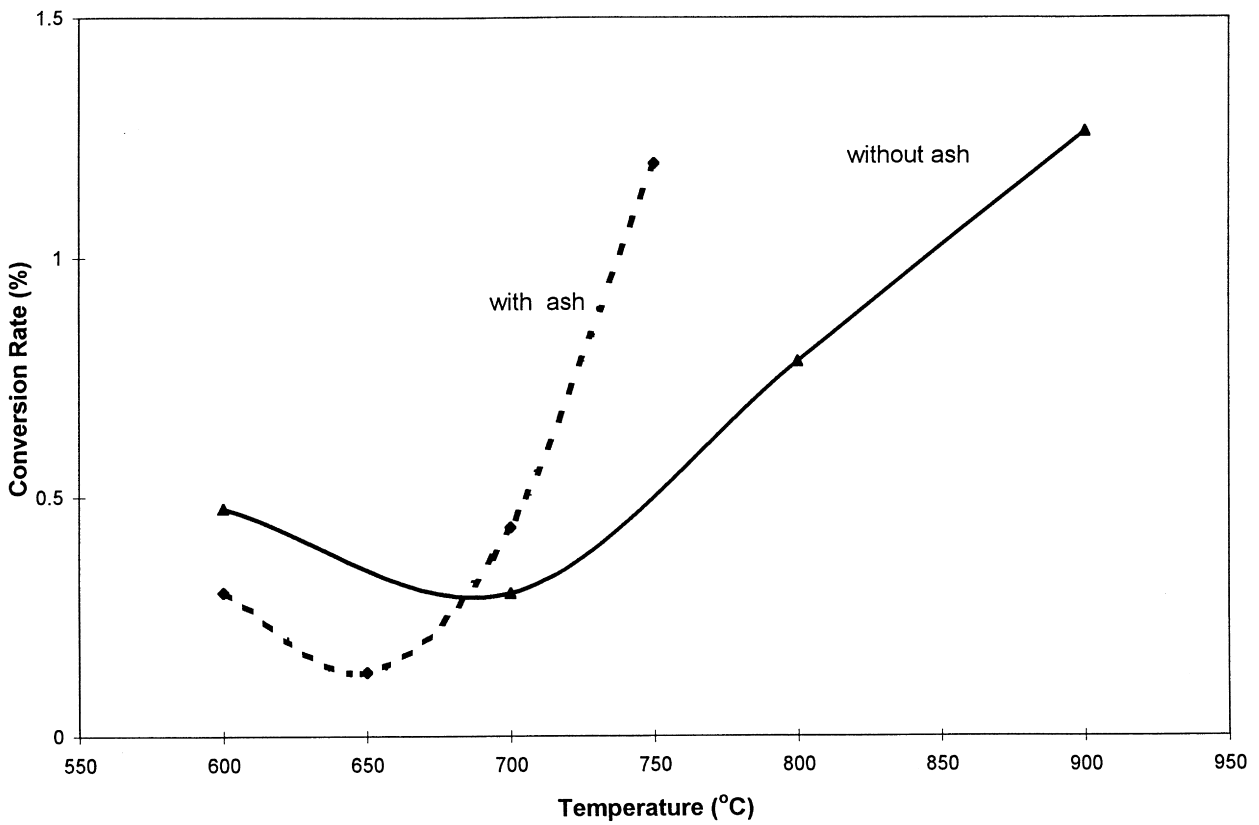


Fig. 6. The change in the conversion rate of HCl to Cl₂ with and without fly ash as a catalyst.

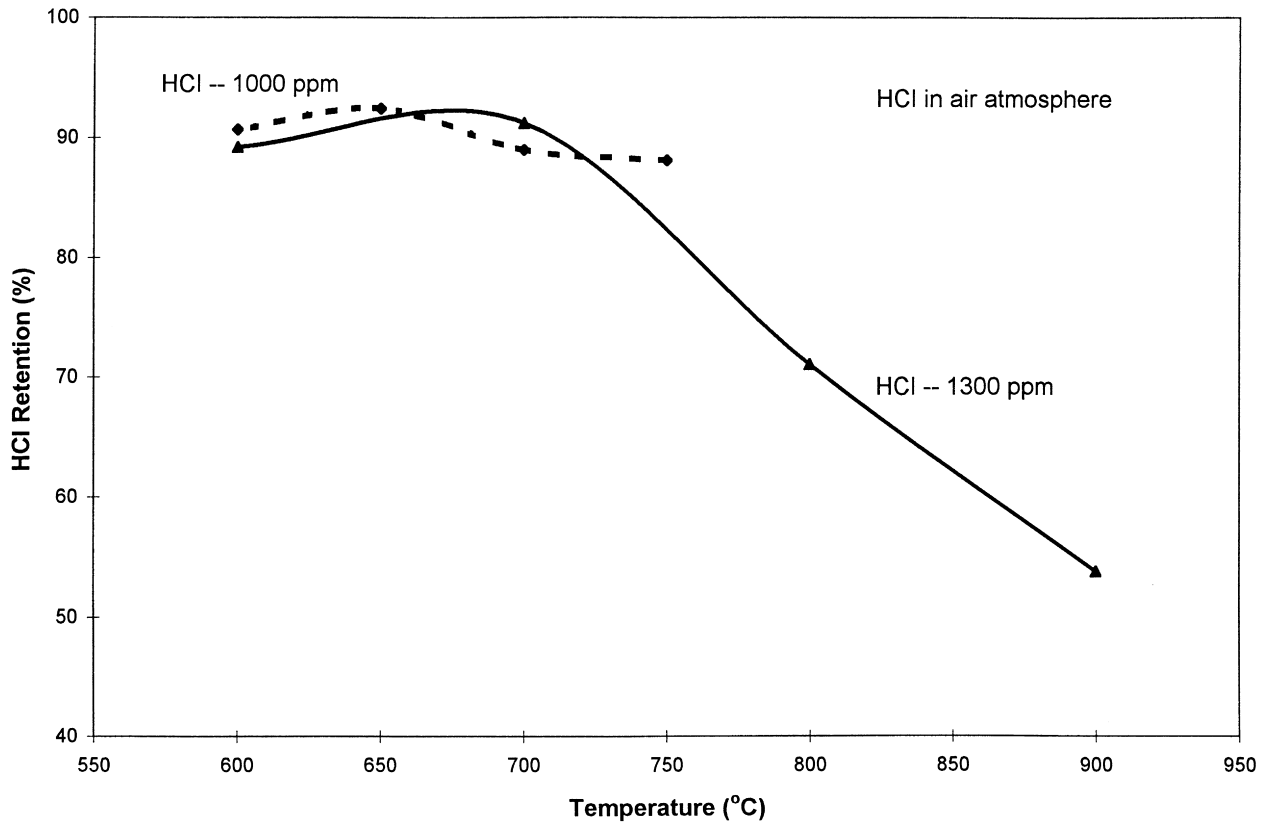


Fig. 7. The effect of temperature on HCl retention by limestone.

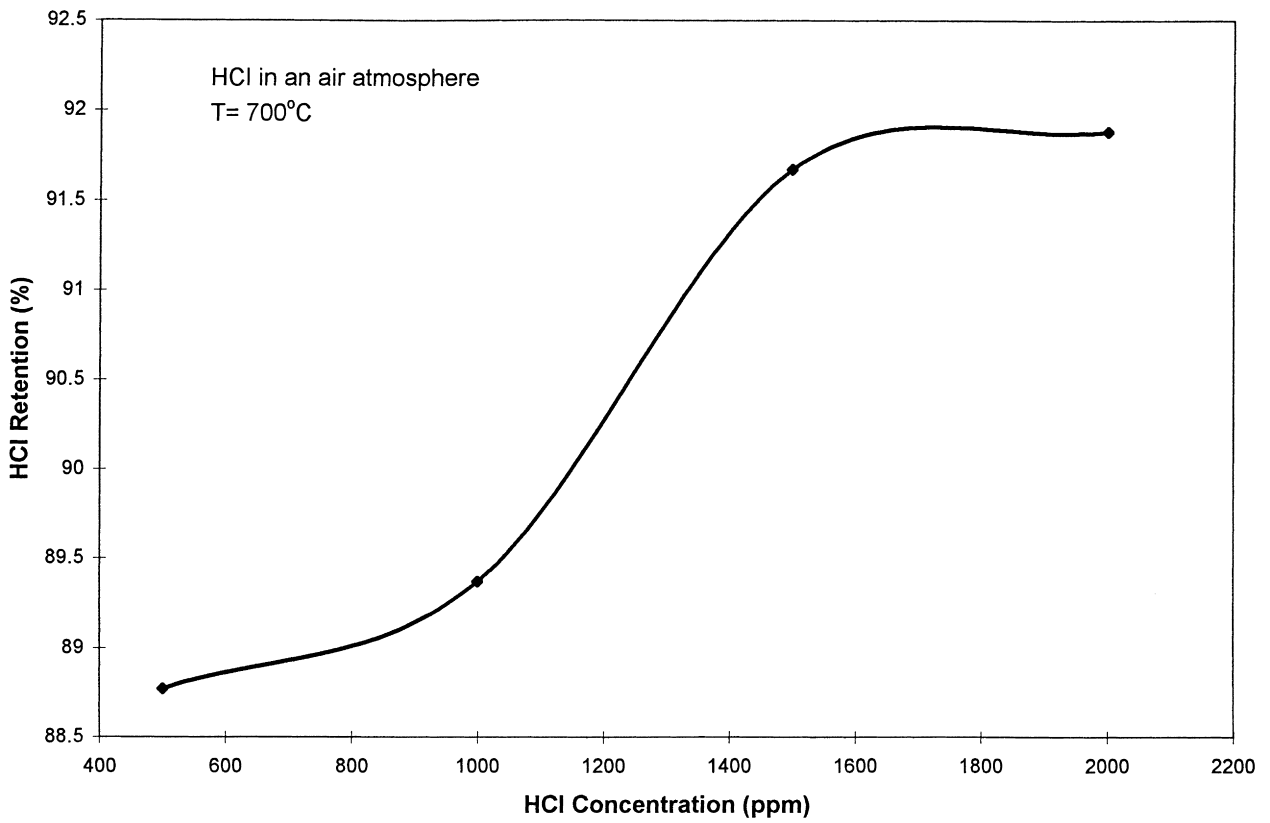


Fig. 8. The effect of HCl concentration on HCl retention.

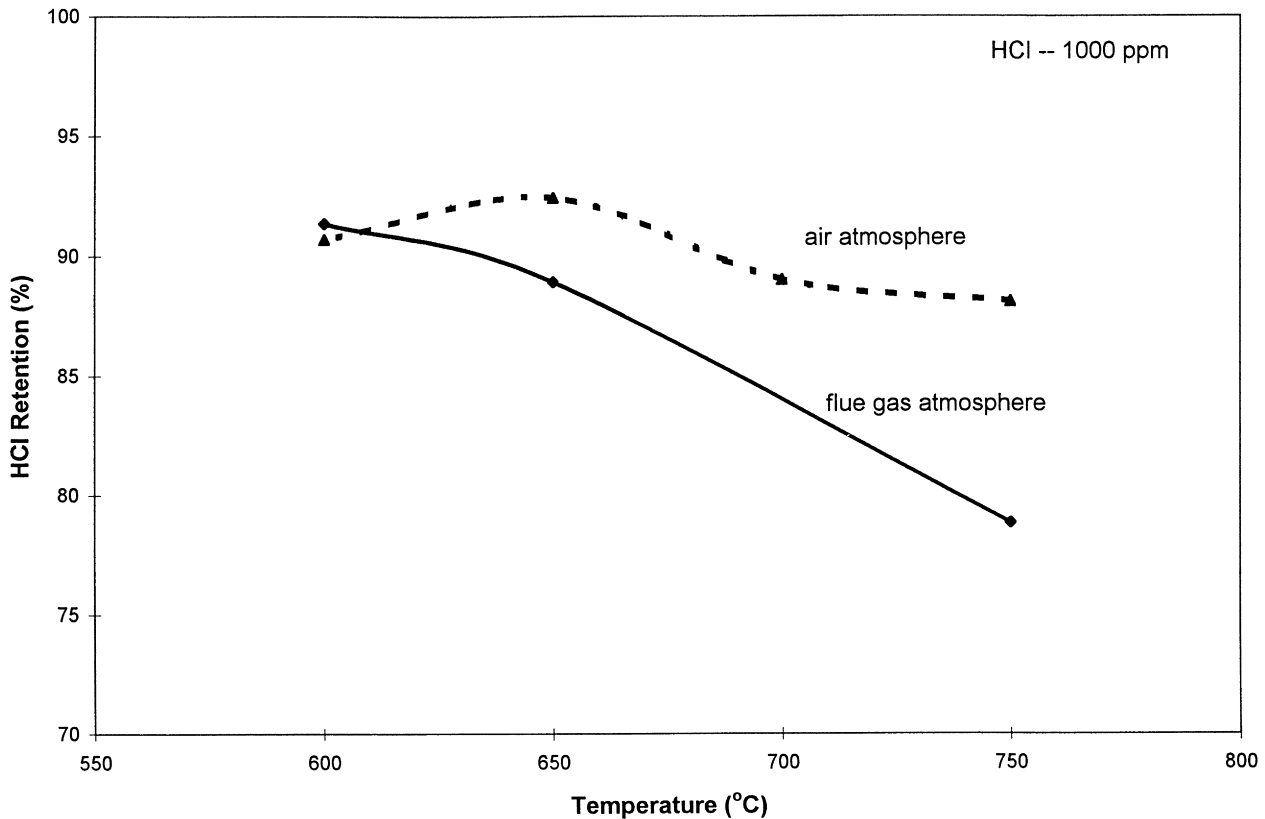


Fig. 9. The effect of atmosphere on HCl retention by limestone.

Table 1
The percent distribution of HCl in different phases

Temperature (°C)	600	650	700	750	800	900
<i>Gas phase:</i>						
HCl	7.6	10.7	10.1	19.9	27.4	43.7
Cl ₂	0.5	0.2	0.4	0.6	0.8	1.3
<i>Solid phase:</i>						
Fly ash	50.9	47.5	56.3	53.2	62.4	51.9
Bed ash	40.5	41.3	32.8	25.6	8.5	1.2
<i>Total</i>	99.5	99.7	99.6	99.3	99.1	98.1

maintain combustion temperatures around 850°C in the bed area, 600°C in the freeboard, low oxygen concentration in the flue gas and sufficient residence time of fine particles in the freeboard.

- The reaction temperature plays a key role in the capture of HCl. The capture efficiency decreases rapidly with an increase in the temperature from 650 to 850°C.
- The capture of HCl by CaO is more difficult in the flue gas atmosphere than in air.

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