Effect of Steam on the Removal of HCl by CaO in a Fluidized-bed Incinerator

Paper #76

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ABSTRACT

In the solid waste incinerator, steam can be found in the flue gas, which has some impact on the HCl removal by Ca-based sorbents. In this paper, the effect of steam on HCl removal has been investigated in the temperature range from 433K to 853K in a fluidized-bed incinerator. An ion meter was used to measure the Cl^- concentration of the alkali solution in the absorber so as to obtain the removal efficiency (RE) of HCl. CaO reacts with the input gas: 4 % O_2, 1000 ppm HCl, 1.5 % - 15 % steam in N_2 balance gas. It shows that the effects of steam on HCl removal by CaO reveal different trend at different operating temperature. At 433K, the effect of steam is not obvious with the RE of approximately 30%. As the steam concentration increases, the RE decreases at 553K and increases at 753K and 853K. It also reveals that at the same steam concentration the RE becomes higher with temperature rise and CaO reacts more completely at 853K than other temperatures with HCl. It explains that the reaction process depends on the exposed surface area of reactant and the diffusion process of gaseous HCl through the product layer.

INTRODUCTION

Along with the industrial development of human beings, a large number of wastes from industry, hospital and residential area have become a major source of environmental pollutants. Instead of land filling, incineration technology as the main technology has been used to treat these wastes for many years. However, in solid waste incinerator, the emission of HCl takes a great deal of negative impacts on the incinerating process. As a corrosive acid gas, not only does HCl pollute environment but also result in metals corrosion of heating surface in high temperature and off-gas channel in low temperature. In addition, during a slow cooling process from 400°C to 250°C, *de novo* reaction (dioxins or furans reformations) will occur in heat exchanger where the flue gas contains chlorinated compounds, unburned organic molecules and catalysts such as fly ash containing heavy metals. Accordingly, the removal of HCl is the core task in flue gas treatment process.

Three methods for the removal of gaseous HCl are wet, semi-dry and dry process, respectively. In wet process, the alkali solutions are injected into flue gas containing HCl through several nozzles. Although it is an efficient method to remove HCl and the RE can attain as high as 98%, the consumption on a large amount of water and additive cost of waste water treatment have negative impact on industrial application, especially in large areas of China, where water resource is scarce. Semi-dry process can achieve as high efficiency as wet process, but it is complex and rather expensive to produce sorbent slurry. Compared with the former two processes, dry process has the advantages of no waste water, simplifying processing, low investment, low operating cost, etc., and

can also get high RE of HCl by selecting operation conditions and methods which accelerate the reaction process. A great number of studies on this process are investigated. In a laboratory investigation of HCl binding on limestone, Ketov *et al.* (1968) found that there was an optimal temperature in the range between 450°C and 550°C, depending on lime type, for which a maximum conversion of $CaCO_3$ to $CaCl_2$ is obtained. Petrini *et al.* (1979) studied HCl binding on porous limestone particles at 350~600°C in a laboratory fixed bed reactor. The product components and a molten phase of $CaCO_3$ to $CaCl_2$ at higher temperature block the pores in the low-porosity solid, which block the progress of the reaction. Weinell *et al.* (1992) found that the presence of water has impact on the capacity of solid slaked lime for binding HCl, a large binding capacity is observed below 150°C [1]. Duo *et al.* proposed a crystallization and fracture model for the formation of the solid product, and the rate limiting step altered with the process of reaction, from chemical reaction control to product layer diffusion control [2,3]. Rushan Bie *et al.* (2005) investigated the mechanism of binding HCl from incineration of organic wastewater. The results showed at higher temperature, the reaction between CaO and HCl is controlled by chemical reaction at first and then by a combination of chemical reaction and product layer diffusion [4].

Little work has been done on the influence of steam to the reaction of HCl with Ca-based sorbents. In waste incinerators, the volume content of steam in flue gas is about 10~30% (the exact value depends on the fuel and amount of excess air used), thus steam will take impact on the removal of HCl in dry process. Moreover, we can learn from steam activation method used for the removal of SO_2 with Ca-based sorbent [5,6] and apply this method to HCl removal. In this paper, the effect of steam to HCl removal has been investigated in the temperature range from 433K to 853K with steam content of 1.5 % to 15 % in a fluidized-bed incinerator.

EXPERIMENTAL SETUP

The experiment in this paper was conducted in a lab-scale fluidized-bed, as shown schematically in Figure 1. The reactor was made of a quartz tube with a quartz sinter board in it. CaO and sands were located on the board where the reaction of HCl and CaO occurred and a thermocouple was mounted. The reactor was placed in an electronically heated furnace with a height of 600mm and the inside

Figure 1: Schematic Diagram of Experimental Apparatus
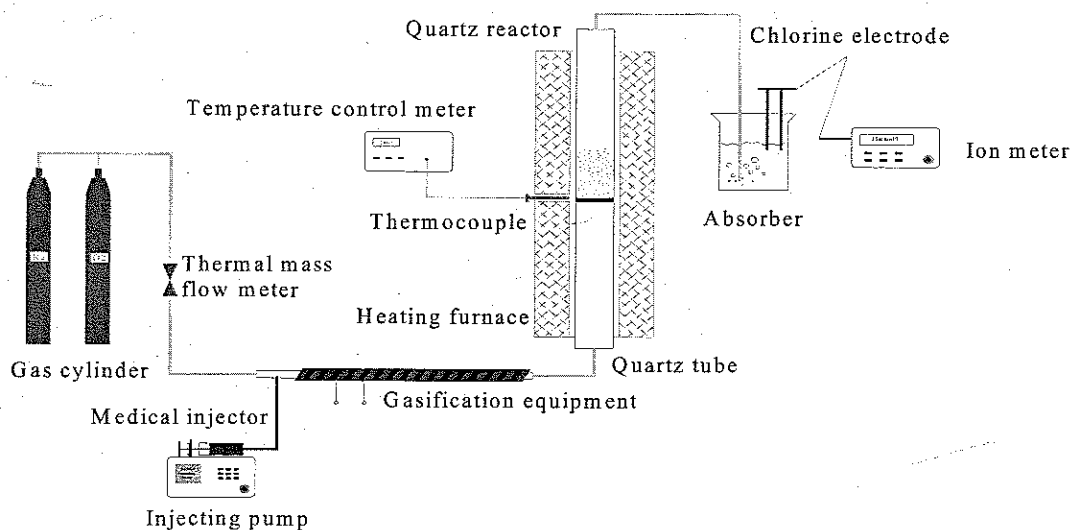
diameter of 40mm, where the temperature of the reactor was controlled precisely in the range from 293K to 1625K. The volume flow of individual gas from gas cylinders was measured by thermal mass flow meter. Hydrochloric acid (37 wt%) and water were mixed according to designed proportion, then the mixed solutions were sucked into the medical injectors, and then injected into the gasification equipment by an injection pump, which can achieve the flow rate of 0.5 ml/hour. The gaseous HCl and steam were carried by N_2 and O_2 into the reactor. After reaction, the flue gas from the reactor was introduced into an absorber with 0.1mol/l alkali solution in it, and the channels from the reactor to the absorber were heated by heating belts in order to avoid the condensation of steam. A Cl^- electrode and an ion meter were used to measure the Cl^- concentration of the alkali solution in the absorber so as to obtain RE of HCl.

The bed materials were quartz sands with diameter of 0.3~0.5mm, CaO was analytical purity (above 98 wt%) with diameter of 0.18~0.355mm, and the mass ratio of sands to CaO was 10:1. The gas in the reactor with total flow rate of 4 l/min consists of 4 % O_2, 1000 ppm HCl, 1.5 % ~15 % steams in N_2 balance gas. The reaction with the Ca^{2+}/Cl^- molar ratio of 2 had been investigated in the temperature range from 433K to 853K. The reaction lasted 1 hour in every experiment.

The RE of HCl is calculated as the following Equation 1 [7]:

$$\eta = (1 - [HCl]_{outlet} / [HCl]_{inlet}) \times 100\% \qquad\qquad \text{Equation 1}$$

Where $[HCl]_{outlet}$ and $[HCl]_{inlet}$ are the molar concentrations of the HCl at the outlet and inlet of the incinerator respectively.

After the incinerator was heated up to the designed operating temperature, the mixed gas entered into the incinerator and CaO with the bed materials were put into it. Meanwhile, the solution in the absorber was sampled in every twelve minutes, so as to obtain the Cl^- concentration at the outlet.

RESULTS AND DISCUSSIONS

The reaction of HCl and CaO is shown in Equation 2:

$$CaO(s) + 2HCl(g) = CaCl_2(s) + H_2O(g) \qquad\qquad \text{Equation 2}$$

Equation 2 indicates that the appearance of steam accelerates the reversible reaction and releasing gaseous HCl, which takes negative impact on the HCl removal by CaO sorbent. In contrast, steam reacts with CaO (16.9 cm³/mol)[8] to form Ca(OH)₂ (33.1 cm³/mol)[9] and the change of molar volume results in the broken-up of sorbent surface, and then a large number of cracks are formed and more chemical interface between gaseous HCl and CaO sorbent emerged, thus the reaction of consuming HCl is promoted. Accordingly, the effect of steam on the reaction acts as both-sides function: promoting and inhibiting. The reaction process depends on the different operating conditions.

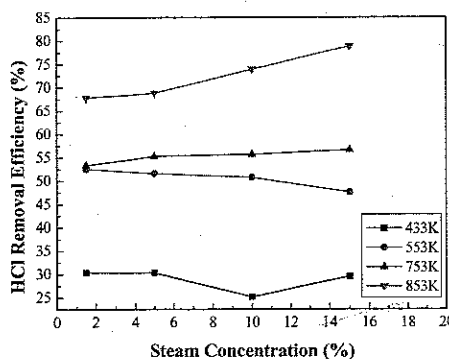Figure 2: HCl Removal Efficiency at Different Temperatures

Figure 2 shows the influence of steam on HCl removal from 433K to 853K, with steam volume content of 1.5~15%. It is shown that the effects of steam behave different trends at different operating temperatures. At 433K, the effect of steam is not obvious; the efficiency is around 30%. As the steam concentration increases, the RE decreases at 553K and increases at 753K and 853K. It indicates that the higher steam content promotes HCl removal more obviously at 853K than 753K. It also reveals that at the same steam concentration, the higher temperature is, the greater RE achieves.

The variations of HCl removal rate with the steam content from 1.5% to 15% at 553K, 753K, or 853K are shown in Figure 3 to 5. At the temperature of 553K or 753K, the removal rate is very fast at

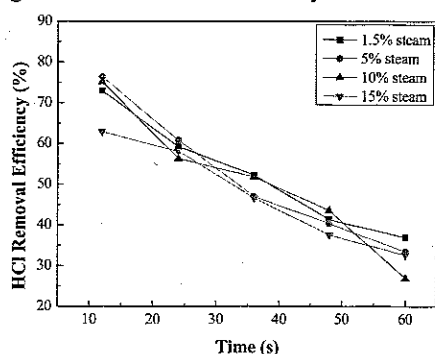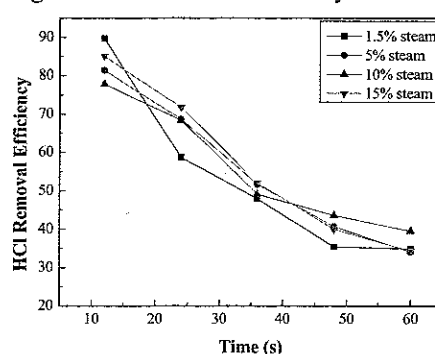Figure 3: HCl Removal Efficiency vs Time at 553K

Figure 4: HCl Removal Efficiency vs Time at 753K

the beginning of the reaction and decreases rapidly as time goes on, however, the effect of steam on the removal rate is not particularly large. At 853K, it is obviously that the removal rate of 1.5% steam gradually decreases with time increasing as the former two cases, however, the rate of 5~15% steam increases in the beginning and reaches a maximum at the 24th minute and then gradually decreases later. Compared with Figure 3 and 4, Figure 5 shows that the influence of various steam contents on HCl removal rate is much greater, the REs at

Figure 5: HCl Removal Efficiency vs Time at 853 K

different time keep higher (above 50% in the beginning of 48 minutes) and decrease more slowly as time goes on at 853K than in lower temperatures. Thus, it indicates that CaO reacts more completely at 853K than other temperatures with HCl.
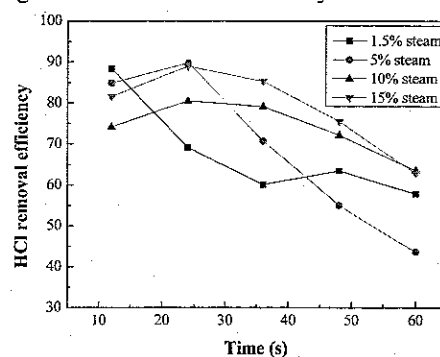
In the reaction of CaO and HCl with steam, CaO and steam can also produce $Ca(OH)_2$, which makes the reactant area expand and even break up the outer layer of the particles, thereby a larger fraction of reactant surface are exposed. As a result, the reaction of HCl with Ca-sorbent will be enhanced. The area change of reactant surface is just one of the factors which affect the reaction process. Moreover, the diffusion process of gaseous HCl through the product layer can also have effects on the reaction. As shown in Figure 2, at 433K, the effect of steam is not obvious due to the co-impacts of these two factors. When low operating temperature is close to saturated temperature of steam, steam is easy to condense at the surface of reactant [10], which makes CaO broken up and then promote the removal of HCl. On the other hand, the product of $CaCl_2$ will compound with steam into $CaCl_2 \cdot 2H_2O$ at this low

temperature (318K to 448K), and these compact product layer will resist the HCl approaching to the surface of reactant and the reaction process going on. Two sides of effects take action on the process at the same time, which leads to an uncertain result. When the operating temperature is up to 553K, the RE decreases with the increase of steam concentration as time goes on, which may attribute to the densification of product layer of $CaCl_2$. In the presence of steam, $CaCl_2$ will compound with steam into $CaCl_2 \cdot H_2O$ which exists above 473K. Therefore, the product layer volume becomes much larger with steam increasing and the product layer is compacted furthermore. Accordingly, the compound of $CaCl_2 \cdot H_2O$ exerts a strong resistance to HCl diffusivity through the product layer, and the reaction virtually ceases fairly early. As shown in Figure 3, the slope of curve changes greatly in the beginning of 36 minutes. At higher temperatures, as mentioned above 753K and 853K, a relatively porous product layer exerts a moderate resistance to the diffusion of HCl and steam through the layer[2]. As the steam concentration increasing, the amount of resulting $Ca(OH)_2$ inside the product layer becomes greater, which leads to the expanding of the cavity in the reactant surface and bulging the product layer with more fresh reactants. Especially at 853K, the decomposition reaction of $Ca(OH)_2$ to CaO takes place, thus the reducing of molar volume and the releasing of steam will increase the amount of cavities in the particles, which will increase the contact area between HCl and the reactant and promote the HCl removal[8]. As a result, higher HCl RE occurs at higher temperature (as shown in Figure 4 and 5, the slope of curve changes more smoothly than Figure 3), longer reaction time and higher steam concentration.

CONCLUSIONS

The experimental results in this paper show that the effects of steam to HCl removal by CaO reveal different trends at different operating temperatures. It has explained that the reaction process depends on the exposed area of reactant and the diffusion process of gaseous HCl through the product layer. At 433K, the effect of steam is not obvious due to the impacts of the two factors together. At 553K, the densification of product layer of $CaCl_2$ is formed and plays an important role in the reaction process, and the reaction process ceases earlier. Therefore, the RE decreases as the steam concentration increasing. Furthermore, The RE increased at 753K and 853K, which attributes to a relatively porous product layer and the expanding of the cavity in the reactant surface. Overall, it is unlikely that the effect of steam on HCl removal is not particularly large, especially at low temperature.

ACKNOWLEDGMENT

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KEYWORDS

HCl removal; Fluidized-bed incinerator; Steam; Ca-based sorbents.