The Removal of HCl by CaO in the Presence of Steam

Paper #30

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Abstract

In the off-gas treatment process of incineration for solid waste and other fuels, Ca-based sorbents are used to capture HCl to produce $CaCl_2$. In this paper, the effect of steam to the reaction with Ca^{2+}/Cl^- molar ratio of 1 and 2 has been investigated in the temperature range from 160°C to 750°C in a fluidized-bed reactor. CaO with sands as the bed materials reacts with the input gas, which consists of 4 % O_2, 1000 ppm HCl, 1.5 % - 15 % steam, and the balance gas of N_2. An ion meter is used to measure the Cl^- concentration of the alkali solution in the absorber so as to obtain the removal efficiency (RE) of HCl. The results show that HCl removal by CaO sorbents reveal different trend at different operating temperature in the presence of steam. At 160°C, the effect of steam is not obvious with the RE of approximately 20% to 40%. As the steam concentration increases, the RE decreases at 380°C. At 580°C and 750°C, the RE decrease at the steam concentration of 5% and 10% and then increase at 15%. It reveals that CaO reacts more completely with HCl at 580°C than other temperatures in the steam concentration of 5%, 10% and 15%. It also indicates that the presence of steam prevents the reaction progress and the RE with the steam concentration of 5%, 10% and 15% are much lower than 1.5%. 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

For many years, incineration technology instead of land filling has been used to treat solid wastes from industry, hospital and residential area, which have become a major source of environmental pollutants. However, in a solid waste incinerator, the emission of HCl has many negative impacts on the incinerating process. As a corrosive acid gas, not only does HCl pollute the environment but also results in metals corrosion of heat exchanging surface at high temperature and off-gas channel at 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 the heat exchanger where the flue gas contains chlorinated compounds, unburned organic molecules and catalysts such as fly ash containing heavy metals.[1-4] Accordingly, it is a critical task to remove gaseous HCl in flue gas treatment process.

Three methods for the removal of gaseous HCl are wet, semi-dry and dry process. The characteristics of these three processes are shown in Table 1. In a 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 be as high as 99%, the consumption of a large amount of water and cost of waste water treatment has a negative impact on industrial application, especially in large areas of China, where water resource is scarce. A semi-dry process can achieve as high efficiency as a 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.

Table1 Main processes for Removal of Gaseous HCl [5]

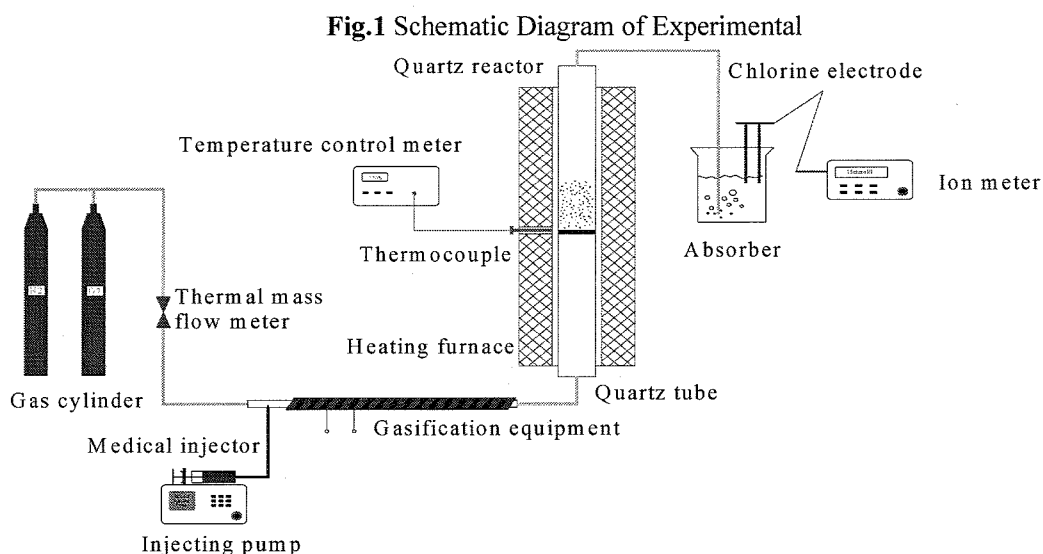| HCl Removal Process	Removal Efficiency		Sorbent Consmption	Power Consmption	Water Consmption	Waste Water Production	Investment Cost	Maintenance Cost
	Single	With Bag Filter						
Dry	50%	95%	120%	80%	100%	Non	90%	80%
Semi-Dry	90%	98%	100%	100%	100%	Non	100%	100%
Wet	99%	—	100%	150%	150%	100%	150%	150%

A great number of works 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.[6] Duo et al. (1995) 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.[7,8] 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. [9]

Little work has been done on the reaction of HCl with Ca-based sorbents in the presence of steam. In waste incinerators, the volumetric content of steam in flue gas is about 10~30% (the exact value depends on the fuel and amount of excess air used), thus it is necessary to investigate the influence of steam on the removal of HCl in a dry process. In this paper, the effect of steam on HCl removal with Ca^{2+}/Cl^- molar ratio of 1 and 2 has been investigated in the temperature range from 160°C to 750°C with steam content of 1.5 % to 15 % in a fluidized-bed reactor.

EXPERIMENTAL METHODS

Apparatus

The experiment in this paper was conducted in a lab-scale fluidized-bed, as shown schematically in Fig.1. The reactor was made of a quartz tube with a quartz sinter distribution 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 an inside diameter of 40 mm, where the temperature of the reactor was controlled precisely in the range from 20°C to 1352°C. The volumetric flow of individual gas from gas cylinders was measured by a 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 a 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 alkali solution in it. The channels from the reactor to the absorber were heated by heating belts in order to avoid the condensation of steam and the loss of HCl before introducing into the absorber.

Fig.1 Schematic Diagram of Experimental

Quartz reactor

Chlorine electrode

Temperature control meter

Ion meter

Thermocouple

Absorber

Thermal mass flow meter

Heating furnace

Gas cylinder

Quartz tube

Medical injector

Gasification equipment

Injecting pump

Measurement Method

A Cl^- electrode and an ion meter were used to measure the Cl^- concentration of the sample solutions in the absorber so as to obtain RE of HCl. The former experiments show that temperature variation and *pH* value are very important factors among several factors which affect the measurement accuracy. In order to obtain the effects on measurable value, a series of experiments are investigated. The temperature of KCl solution is adjusted by heating and cooling instruments, and the *pH* value of KCl solution with the concentration of 1, 5, 8 mmol/L are changed by NaOH or HNO_3 solution. The effects of temperature and *pH* value on Cl^- concentration are shown in Fig.2 and 3. The fitting linear relation of Cl^- concentration with temperature is very specific, and the measurable Cl^- concentration is relative exact in the range of *pH* value with 6.5, which is the calibrating *pH* value of Cl^- electrode. Thus, the concentration of alkali solution is changed by the different amount of HCl absorbing on different operating condition, so as to ensure that the *pH* value of the solution after absorbing is appropriately 6.5, which can not affect the accuracy of the Cl^- electrode.

Fig.2 The effect of temperature on Cl^- concentration in measurement process
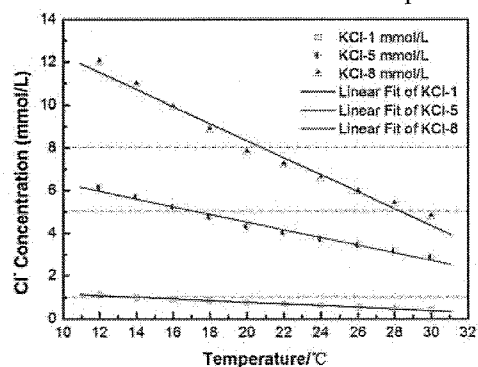
Fig.3 The effect of *pH* value on Cl^- concentration in measurement process
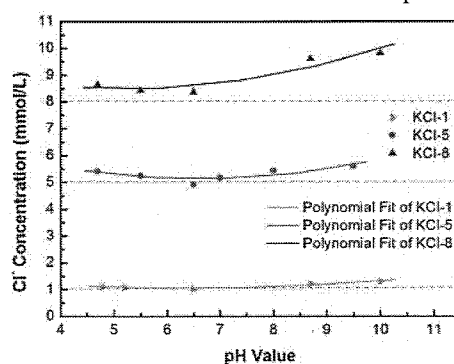
Materials

The reaction materials are shown in Tables 2 and 3.

Table 2 The Characteristics of Bed Materials and Sorbents

Bed Materials	Quartz Sand	0.3~0.5 mm
Sorbent	CaO (analytical purity of above 98 wt%)	0.18~0.355 mm
Mass Ratio	Quartz Sands : CaO	10:1

Table 3 Gas Flow Rate

Total flow rate	4 L/min
O_2	4%
HCl	1000ppm
Steam	1.5%~15%
N_2	Balance Gas

Conditions

Several sets of experiments with the Ca^{2+}/Cl^- molar ratio of 1 and 2 were made to investigate the effects of steam to the HCl removal in four temperature levels, 160°C, 380 °C, 580 °C and 750°C. The reaction lasts 1 hour in each experiment.

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

The RE of HCl is calculated as the following equation 1: [10]

$$\eta = (1-[HCl]_{outlet}/[HCl]_{inlet})\times100\% \quad (1)$$
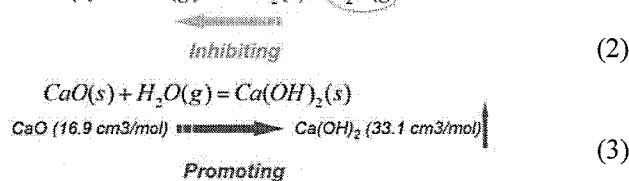
Where $[HCl]_{outlet}$ and $[HCl]_{inlet}$ are the molar concentrations of the HCl at the outlet and inlet of the reactor respectively.

RESULTS AND DISCUSSION

Effects of Steam

The reaction of HCl w $CaO(s) + 2HCl(g) = CaCl_2(s) + H_2O(g)$ tion can be described by equation 2 and 3.

Inhibiting

$$(2)$$

$$CaO(s) + H_2O(g) = Ca(OH)_2(s)$$

CaO (16.9 cm3/mol) ➤ Ca(OH)₂ (33.1 cm3/mol)

Promoting

$$(3)$$

The absorption of HCl with CaO produces solid $CaCl_2$ and releases gaseous H_2O simultaneously; however, the appearance of abundant H_2O accelerates the reversible reaction and releases gaseous HCl, which has a negative impact on the HCl removal by CaO sorbent. In contrast, steam reacts with CaO (16.9 cm^3/mol) to form $Ca(OH)_2$ (33.1 cm^3/mol) and the change of molar volume results in the break-up of sorbent surface, and then a large number of cracks are formed and results in more chemical interface between gaseous HCl and CaO sorbent, 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 and the RE of HCl with CaO depend on the different operating conditions.
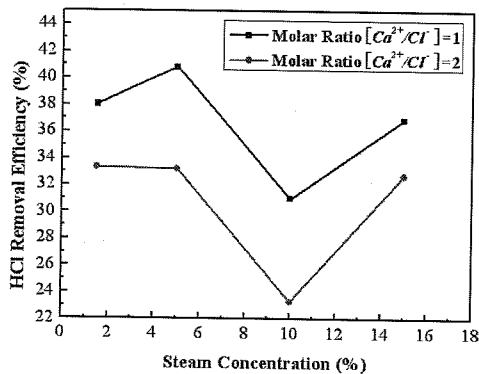
Removal of HCl with CaO in the Presence of Steam

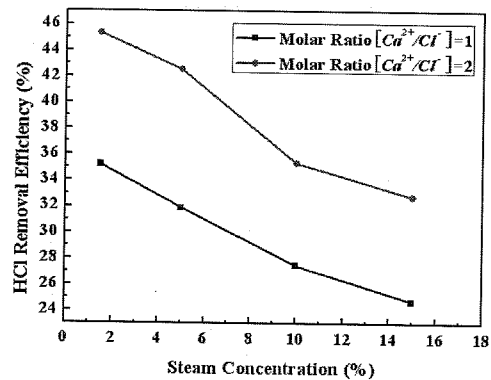**Fig.4** HCl removal efficiency at 160°C, 380°C, 580°C and 750°C with molar ratio $[Ca^{2+}/Cl^-]=1$
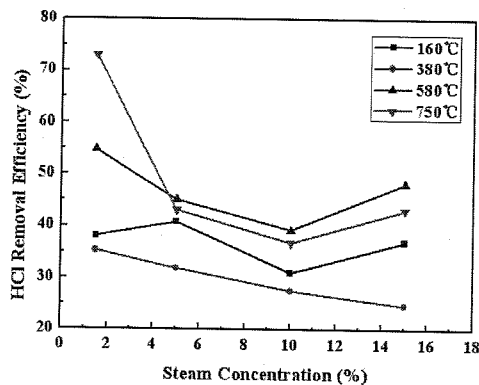
Fig.5 HCl removal efficiency at 160°C, 380°C, 580°C and 750°C with molar ratio $[Ca^{2+}/Cl^-]=2$
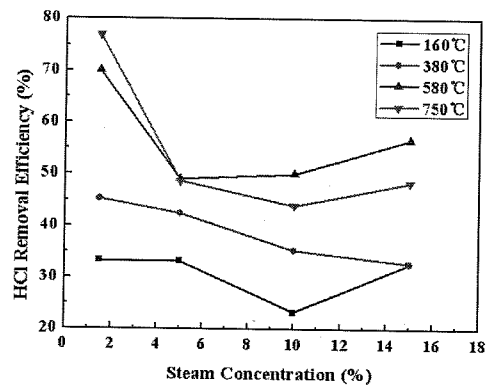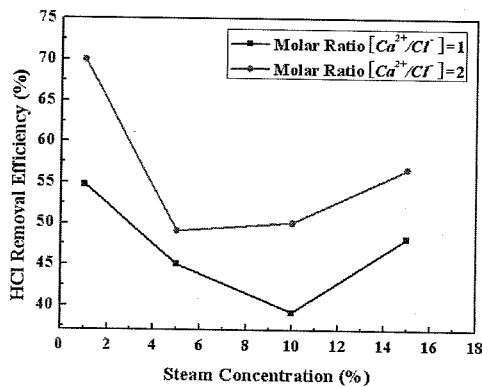

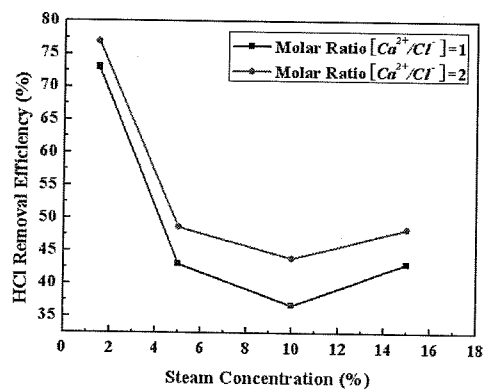**Fig.6** HCl removal efficiency at 160°C with molar ratio $[Ca^{2+}/Cl^-]=1$ and 2

Fig.7 HCl removal efficiency at 380°C with molar ratio $[Ca^{2+}/Cl^-]=1$ and 2

Fig.8 HCl removal efficiency at 580°C with molar ratio $[Ca^{2+}/Cl^-]=1$ and 2

Fig.9 HCl removal efficiency at 750°C with molar ratio $[Ca^{2+}/Cl^-]=1$ and 2


In Fig.4 and 5, the removal efficiency of HCl with CaO in the presence of steam is given for several experiments performed at 160°C, 380°C, 580°C and 750°C, one with the molar ratio $[Ca^{2+}/Cl^-]$ of 1 and the other with 2. The figures indicate that as steam concentration rise, the value of RE reveal

different trends at different temperatures. At 160℃, the effect of steam is not obvious with the RE of approximately 20% to 40%. As the steam concentration increases, the RE decreases at 380℃. At 580℃ and 750℃, the RE decreases at the steam concentration of 5% and 10% and then increases at 15%. As the figures shown, the RE attain maximum values at 580℃ with 5%, 10% and 15% steam concentration, however, when steam concentration is 1.5%, it is more efficient at 750℃ than at 580℃, which is different from other studies mentioned above.

The effects of molar ratio $[Ca^{2+}/Cl^-]$ on HCl removal reaction are shown in Fig.6 to 9. To the absorption of HCl by CaO, it is obvious that the more CaO added, the higher HCl RE is achieved, just at the temperature of 380℃, 580℃ and 750℃, the RE is much higher at molar ratio $[Ca^{2+}/Cl^-]$ of 2 rather than $[Ca^{2+}/Cl^-]$ of 1. However, at 160℃, abundant amount of CaO results in much lower RE, compared with molar ratio $[Ca^{2+}/Cl^-]$ of 1.

Analysis on Morphological Change of Reactant Surface and Diffusion Process of HCl through Product Layer

Fig.10 Two factors effect on the reaction process of HCl with CaO
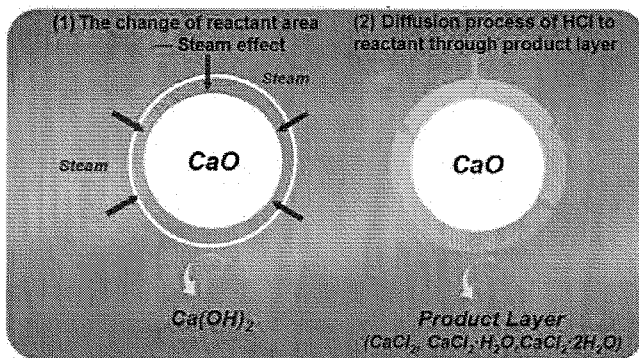
There are two factors that effect the reaction process of CaO with HCl. As shown in Fig.10 and equation (3), CaO and steam produce Ca(OH)$_2$, which makes the reactant area expand, thus, a larger fraction of fresh reactant surface are exposed. As a result, the reaction of HCl with Ca-sorbent will be enhanced. Moreover, as the reaction progresses, the product layer, which inhibits HCl reacting with inner reactants, will get thicker and thicker gradually. Accordingly, the diffusion process of gaseous HCl through the product layer can also have effects on the reaction.

At 160 ℃, the state of H$_2$O in flue gases may be greatly instable. When low operating temperature is close to the saturated temperature of steam, steam easily condenses on the surface of the reactant.[11] In Fig.4, the amount of reactant CaO is much less at molar ratio $[Ca^{2+}/Cl^-]$ of 1 than 2, thus, at the same steam concentration, the surface of reactant CaO with $[Ca^{2+}/Cl^-]=1$ will obtain twice as much steam as $[Ca^{2+}/Cl^-]=2$ and the reactivity of the reactants will be enhanced by the excessive steam. Consequently, the figure shows that the HCl removal process can not be improved by adding more reactants at 160 ℃. On the other hand, the product of CaCl$_2$ will form with steam into CaCl$_2$•2H$_2$O at this low temperature (45 ℃ to 175 ℃), and these compact product layer will resist the HCl approaching the surface of reactant and the reaction process taking place. The effect of promoting or inhibiting in the presence of steam, takes action on the reaction process at the same time, which leads to an uncertain result, as shown as in Fig. 6.

When the operating temperature is up to 380 ℃, 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 form with steam into CaCl$_2$•H$_2$O which exists above 200 ℃.

Therefore, the product layer volume becomes much larger with steam increasing and the product

layer is compacted further. Accordingly, the formation of $CaCl_2 \cdot H_2O$ exerts a strong resistance to HCl diffusivity through the product layer, and the reaction ceases fairly early.

At higher temperatures of 580 °C and 750°C, as mentioned above, a relatively loose and porous product layer exerts a moderate resistance to the diffusion of HCl and steam through the layer. [7] Compared with lower temperatures, the RE is more efficient. It also indicates that the presence of steam prevents the reaction progress and the RE with the steam concentration of 5%, 10% and 15% is much lower than 1.5%. In these cases, the inhibiting factor of H_2O plays a dominate role in the reaction, which accelerates the reversible reaction and release of HCl. However, at 580 °C, the RE dramatically increases with the steam concentration of 15% rather than 5% and 10%. It can be explained by the expanding of cavities in the reactant surface shown in Fig.11. When the steam concentration reaches a relatively sufficient amount such as 15%, 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. In addition, 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]

Fig.11 Morphological change on the reaction process at high temperature
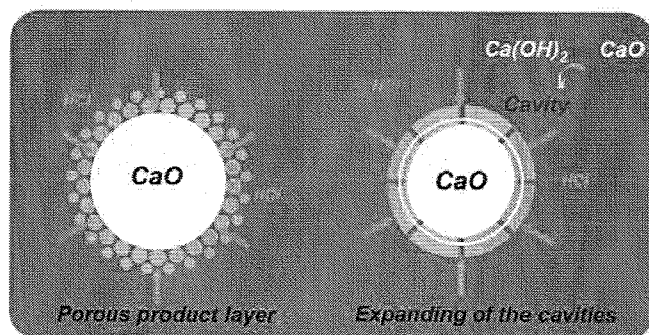
It is known that the melting point of $CaCl_2$ is at 772 °C, and the lowest liquid temperature of the $CaCl_2$-CaO system is 750 °C with a eutectic composition of about 6 mol% CaO (Neumann et al., 1935). Therefore a liquid phase of $CaCl_2$ saturated with CaO is formed at the temperature above 750 °C and the partial melting makes the absorbent particles sticky.[9, 12] In this work, the agglomeration of the bed material was not found in the steam concentration of 1.5%, so the HCl removal is not caused by the negative influence of the melting phase of reactants but rather by the promoting effect of the loose and porous product layer which can be formed at higher temperature. On the other hand, as the steam concentration increases, the abundant steam causes the formation of molten phase, which will result in the acceleration of reversible reaction and releasing of HCl.

SUMMARY

The experimental results in this paper show that HCl removal by CaO sorbents reveals different trends at different operating temperatures in the presence of steam. 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 160°C, the effect of promoting or inhibiting in the presence of steam takes action on the process at the same time, which leads to an uncertain result and the effect of steam is not obvious with the RE of approximately 20% to 40%. The condense of steam to the surface of reactant result in the higher

RE with molar ratio $[Ca^{2+}/Cl^-]$ of 1 than 2, consequently, the results show that HCl removal process can not be improved by adding more reactants at 160 °C.

·As the steam concentration increases, the RE decreases at 380°C, which may attribute to the densification of product layer of $CaCl_2$.

·At 580°C, the RE decrease at the steam concentration of 5% and 10% and then increase at 15%. It reveals that CaO reacts more completely at 580°C than other temperatures with HCl in the steam concentration of 5%, 10% and 15%. It also indicates that the presence of steam prevents the reaction progress and the RE with the steam concentration of 5%, 10% and 15% are much lower than 1.5%. In these cases, the inhibiting factor of H_2O plays a dominate role in the reaction, which accelerates the reversible reaction and release HCl.

·At 750°C, the reaction trend is the same as 580 °C, however, when steam concentration is 1.5%, it is more efficient than 580°C, which represents different from other studies. In this work, the agglomeration of the bed material was not found in the steam concentration of 1.5%, so the HCl removal is not caused by the negative influence of the melting phase of reactants but rather by the promoting effect of the loose and porous product layer which can be formed at higher temperature.

ACKNOWLEDGEMETS

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KEY WORDS

HCl Removal, Steam, Ca-based Sorbents, Fluidized-bed Reactor, Product Layer