

Single and Combined Removal of HCl and Alkali Metal Vapor from High-temperature Gas by Solid Sorbents

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The amounts of HCl and alkali metal vapor in hot gas are generally small, compared to those of sulfur compounds, nitrogen compounds, and particulates. Nevertheless, the removal of these contaminants is very beneficial in any power plant because of corrosion when they contact metal components. In this paper, the experiments by single and combined methods were carried out to remove HCl and alkali metal vapor in hot gas cleaning. The results indicated that all sorbents for the removal of HCl vapor can reduce HCl to less than 1 mg/m³ at 550 °C; sorbent E1 self-prepared by montmorillonite and Mg(OH)₂ presents the highest chlorine content and the longest breakthrough time. It is found that the activated Al₂O₃ having a specific surface area of 258.3 m²/g displays the highest efficiency for the removal of alkali metal vapor at 840 °C. The tests indicate that the removal of alkali metal vapor with activated Al₂O₃ is not a physical adsorption process in the presence of moisture. A multifunctional four-zone reactor system was developed for the combined removal of HCl and alkali metal vapor, and the results show that the removal of HCl and alkali metal vapor with high efficiency is feasible by solid sorbents in a reactor.

1. Introduction

The integrated coal gasification combined cycle (IGCC) and second-generation pressurized fluidized-bed combustion combined cycle (PFBC) power systems using coal-derived gas result in significantly higher efficiency and greater environmental friendliness than conventional combustion technologies. The overall efficiency of IGCC and PFBC systems can be further improved with “hot gas cleaning”. The main contaminants produced in hot gas are particulate, sulfur, and nitrogen compounds. However, the HCl and alkali metal vapor can cause a variety of problems including severe damage of gas turbine blades because of hot corrosion.^{1–3} In recent years, a number of processes have been available for removing HCl and alkali metal vapor from industrial and incinerator waste gases. But using solid sorbents is the most direct and inexpensive method of producing the highest-quality gas.

Despite the fact that the removal of HCl from the gas by means of solid CaO or Ca(OH)₂ is a well-known process, the removal efficiency is not high enough at high temperatures.^{4–6} Previous studies have indicated that solid sorbents are capable of reducing HCl level to less than 1 mg/m³ in a fixed-bed

reactor; however, the sorbents based on multioxides are relatively expensive.^{7–10} Most of the past investigations on the removal of alkali metal vapor were concerned with cleaning high-temperature flue gases from ordinary PFBC under oxidizing conditions. The removal mechanism of alkali metal vapor by solid sorbents is also not well-understood.^{11–5} Although the application of sorbents seems very promising and versatile, there are still major challenges left. Most studies have focused on the removal process with respect to one type of contaminant, and it is difficult to control the combined removal of various contaminants in a reactor.¹⁶

The amounts of HCl and alkali metal vapor in hot gas are generally small. Thus, the simultaneous or combined removal of two contaminants is potentially important and becomes very attractive. This study was first focused on evaluating solid sorbents for the removal of HCl and alkali metal vapor. In addition to understanding the single removal process of contaminants, the objective was to develop and evaluate the combined removal process of two contaminants.

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Table 1. Composition and Properties of the Sorbents

	sorbent	composition wt %	surface area (m ² /g)	pore volume (mL/g)	pore diameter (Å)
HCl removal	E1	MgO, 30%; MMt, 70%	136.2	0.20	89.8
	E2	commercial catalyst	127.9	0.15	47.3
	E3	MgO, 50%; MMt, 50%	12.1	0.05	300.8
	E4	MgO, 70%; MMt, 30%	16.4	0.07	289.2
alkali metal vapor (NaCl) removal	Al ₂ O ₃	commercial catalyst	258.3	0.20	45.0
	kaoline	natural minerals	16.6	0.11	257.9
	bauxite		10.2	0.09	188.3
	clay		8.7	0.04	356.9

2. Experimental Section

The experiments were designed to determine the remove characteristics of HCl and alkali metal vapor. Thermodynamic calculations by some studies have shown that NaCl and KCl are the major alkali metal vapor species in hot gas.¹¹ Thus, NaCl was used as the model alkali metal vapor compound in this work. The errors from the balance data of HCl and NaCl vapor in a typical experiment were estimated to be less than 4.2%.

2.1. Preparation of Sorbents. Sorbents E1, E3, and E4 for the removal of HCl were prepared by pelletizing the powder of montmorillonite (MMt; 30~70 wt %) and the Mg(OH)₂ substance. MMt is a kind of natural mineral, and SiO₂ and Al₂O₃ are its main components. In addition, glycol and amine (10%) were added as texturizing agents. The pellets were dried at the a temperature of 100 °C for 2 h and calcined at 550 °C in air for 6 h. Sorbent E2 was commercially obtained and calcined at 550 °C for 4 h prior to being used. It was prepared with alkali or alkali-earth compounds on Al₂O₃ by wet impregnation.

Four sorbents of bauxite, kaoline, clay, and activated Al₂O₃ were used to capture NaCl vapor in the experiments. The activated Al₂O₃ was commercially obtained. The others are natural minerals. The natural minerals were calcined at 900 °C for 4 h prior to being used as sorbents.

Surface areas of the sorbents were determined with a Brunauer–Emmett–Teller method using a Micrometric Acusorb 2100E apparatus. The X-ray diffraction patterns of the sample were obtained with a PW3710 Philips X'pert diffractometer. Table 1 shows the compositions and properties of the sorbents. All the sorbents were used in the form of particles 0.45~0.90 mm in diameter.

2.2. Apparatus Approach. The experiments for the removal of HCl were carried out in a vertical fixed-bed reactor.⁷ This system consisted of a gas manifold, a reactor, and a chlorine analysis section. In the gas manifold, the gas mixture was prepared by entraining HCl vapor with N₂. When N₂ passed through a vessel containing a 20~30% concentration HCl solution, a simulated gas with an acceptably stable HCl concentration could be obtained. The sorbent was supported by quartz wool in the center of the reactor tube. A thermocouple inserted into the sorbent bed was used to measure the temperature of the bed. The gaseous effluent from the sorbent bed was analyzed for HCl content by dissolving the HCl vapor in a solution of NaOH. At the end of the experiment, the sorbent is cooled, removed from the reactor, and analyzed to determine its chlorine content. The HCl concentration in a solution of NaOH is measured by AgNO₃ titration. The chlorine content of the sorbent is analyzed according to the method of determination of chlorine in coal.¹⁷ During the reaction process, the HCl concentration in the effluent gas rose rapidly when the sorbent reached a certain capacity. The rapid change was termed breakthrough. The chlorine content of the sorbent was based on the amount of fresh sorbent and the amount of HCl absorbed by the sorbent.^{8,9}

Tests of different sorbents for the removal of alkali metal vapor were carried out by a horizontal laboratory-scale, fixed-bed reactor.¹⁰

In this system, NaCl was vaporized at the high-temperature section of the reactor. The alkali metal vapor was carried downstream by the carrier gas through the sorbent and finally was completely condensed on a cold trap system with cooling water. The temperature of the alkali source was always about 10 °C lower than that of adsorption. Under this condition, there was no physical condensation of alkali on the outer surface of the particles. At last, sorbent powder is leached with 5% HCl solution at 95 °C. The reactor tube and cold traps are leached with distilled water at 95 °C. The water and the acid leaching solutions are analyzed for sodium ion concentration by atomic absorption spectroscopy. Adsorption efficiency and sodium content are used to evaluate the sorbents' capacity for capturing alkali metal vapor. The adsorption efficiency is calculated by the amount of Na⁺ captured by the sorbent and Na⁺ concentration in inlet gas. The sodium content of the sorbent is calculated by the amount of fresh sorbent and the amount of Na⁺ absorbed by the sorbent.

Some studies have indicated that the adsorption of alkali metal vapor by silicate and alumina sorbents could lead to HCl emission. In combined removal experiments of HCl and alkali metal vapor, we first designed to remove alkali metal vapor, then remove HCl in a reactor. Due to sintering of the solid at higher temperatures, the best performance of the sorbent for the removal HCl is with temperatures less than 600 °C. Alkali metal vapor condensation greatly takes place at this temperature. Thus, a multifunctional reactor having automatic differential temperature control along the tube axis was developed, and the removal of HCl and alkali metal vapor was conducted in different temperature zones. This multifunctional reactor is shown in Figure 1.

The reactor setup mainly consisted of a heated-flow channel housed in a furnace with four independent heating zones. The inner diameter of the tube in the reactor is 20 mm, and the total length of the tube was 1000 mm. The alkali source (NaCl) was positioned 250 mm upstream of the bed at 800 °C. The sorbent for the removal of alkali metal vapor was inserted into the tube at 840 °C between the alkali source and the sorbent for the removal of HCl. The part of the reactor downstream of the alkali source to the sorbent for the removal of alkali metal vapor was kept at a higher temperature, relative to the source temperature. This prevented the alkali species from condensing on the tube walls downstream from the source.

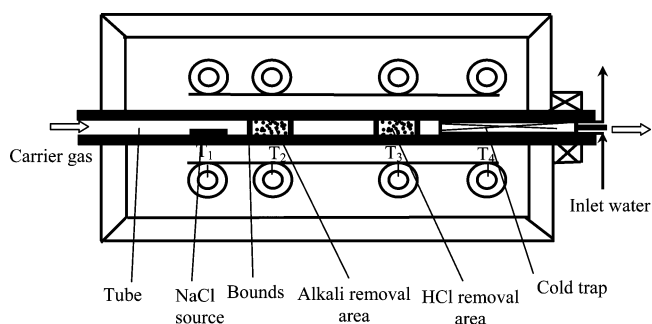


Figure 1. Schematic representation of the four-zone reactor used for the combined removal of HCl and alkali metal vapor experiments.

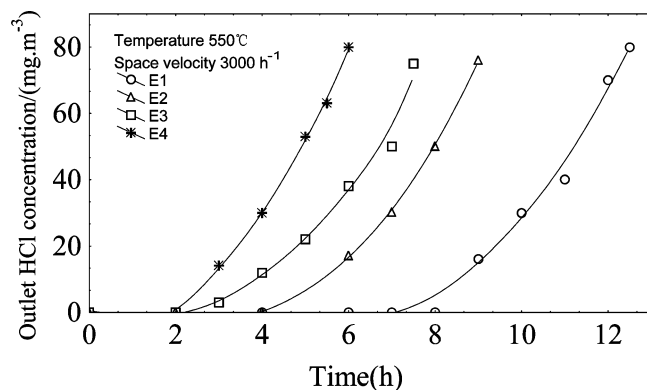


Figure 2. HCl-breakthrough curves of various sorbents.

Table 2. Breakthrough Time and Chlorine Content of Sorbents

sorbent	E1	E2	E3	E4
breakthrough time (h)	7.2	4.0	2.1	2.0
breakthrough chlorine content (%)	8.6	3.6	3.2	3.0
saturation chlorine content (%)	48.3	32.15	19.7	19.2

The last zone inside the furnace was kept at a constant temperature of 30 °C by cold traps, making alkali species for condensing in this region.

The gas derived from coal gasification consists of many components including CO, H₂, H₂O, H₂S, and others; considering experimental convenience, the feed gases which were mixed with contaminants mainly consisted of 70% N₂ and 30% H₂. In a typical experiment, first, the composition of the inlet gas and, then, the temperatures of the reactor and the contaminant concentrations were stabilized. During the startup stage, the gas flow was directed away from the sample to prevent any reaction. To start the removal process, the gas flow switched and directed to the sample section of the reactor.

3. Results and Discussion

3.1. Removal of HCl. The experimental conditions for the removal of HCl were a temperature of 550 °C, a space velocity of 3000 h⁻¹, and an inlet HCl concentration of 1000 mg/m³. Under these operating conditions, the HCl breakthrough curves of various sorbents are shown in Figure 2. The HCl breakthrough time, chlorine content at 1 mg/m³ breakthrough time, and the saturation chloride content at 550 °C are also shown in Table 2.

The allowable HCl concentration in the feed gas to such a fuel cell must be less than 1 mg/m³. Thus, when the HCl concentration in reactor effluent gas reaches 1 mg/m³, the sorbents are regarded as spent. Then, the experiments were stopped. The results show that all sorbents can react rapidly with HCl vapor at 550 °C and reduce the HCl vapor concentration to 1 mg/m³ within the initial 2 h. After a 1 mg/m³ breakthrough of outlet HCl concentration, the HCl concentration in the reactor effluent gas increased rapidly. It is found that sorbent E1 is the best sorbent for HCl removal, which indicates that the better adsorption capacity may be due to a combination of a necessary amount of reactive component and favorable structure.

The X-ray diffraction patterns of the E1 sorbent sample (Figure 3) indicate a typical structure of clay pillared. The layer thickness of E1 is estimated to be equal to 10.0 Å, and the distance between layers is about 12.0 Å using the Scherrer equation. The reflection peak for the sorbent has transferred from $2\theta = 6.820$ to 8.818 , and this corresponds to a distance between layers that was decreased to 6.0 Å after reaction. The physical properties of the fresh E1 and E1 after reaction are

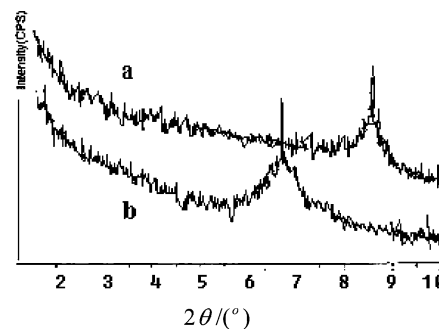


Figure 3. XRD patterns of the samples of E1 sorbent: (a) after reaction and (b) before reaction.

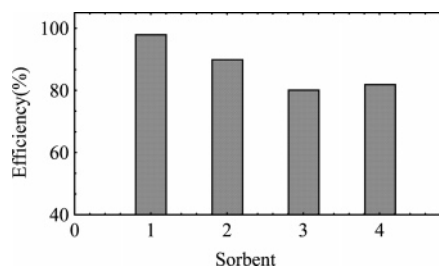


Figure 4. Comparison of adsorption efficiency of NaCl vapor for four sorbents: (1) activated Al₂O₃, (2) bauxite, (3) kaoline, and (4) acidic white clay.

Table 3. Physical Properties of E1 Sorbent Fresh and after Reaction

sample	specific surface area (m ² /g)	pore volume (mL/g)	pore diameter (Å)	crush strength (N/cm)
E1 (fresh)	136.2	0.20	89.8	104.0
E1 (after reaction)	76.8	0.12	62.2	65.0

also shown in Table 3. Table 3 shows that the specific surface area, the average pore diameter and crush strength decrease after reaction. Gas–solid reaction and diffusion inside the particle is essentially dependent on porosity. This parameter can be affected by the temperature and degree of reaction. However, our experimental work was carried out at 550 °C, so that thermal sintering could not occur. Thus, porosity changes are solely due to the effect of the chemical reaction. This may be the result of the great difference existing between the molar volumes of the solid reagent and the product. The decrease in the overall reaction rate is due to the decrease of particle porosity owing to the high molar volume of the solid product in comparison with that of the solid reagent. This similarity behavior has been widely studied for CaO sulfation.

3.2. Removal of Alkali Metal Vapor. The removal of alkali metal vapor by a solid sorbent depends on many factors. In general, the important characteristics for a desired sorbent are high adsorption efficiency and a high loading capacity of alkali metal. The evaluation tests of sorbent are carried out under conditions of 840 °C, a capturing time of 3 h, and a space velocity of 1000 h⁻¹. The adsorption efficiency of four sorbents is shown in Figure 4. The sodium content of the sorbents is shown in Figure 5.

Figure 4 shows that these sorbents including activated Al₂O₃, bauxite, kaoline, and acidic white clay present a high adsorption efficiency. They remove respectively 98%, 90%, 80%, and 82% of the NaCl vapor in a high-temperature inlet gas. The results show that activated Al₂O₃ has the highest sodium content among the four sorbents tested. In a capturing time of 3 h, the sodium content absorbed by activated Al₂O₃ is up to 6.2 mg/g.

The adsorption of gaseous contamination on solid sorbents

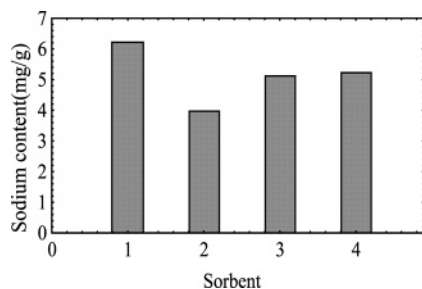


Figure 5. Comparison of sodium content of four sorbents: (1) activated Al_2O_3 , (2) bauxite, (3) kaoline, and (4) acidic white clay.

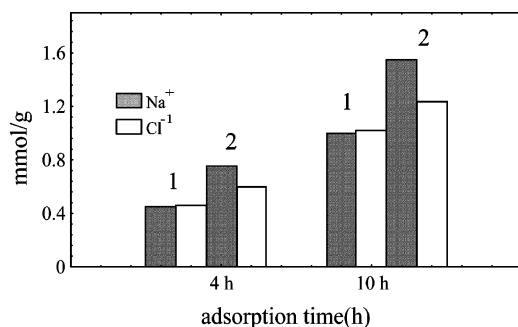
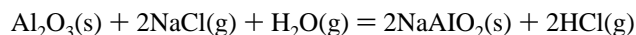
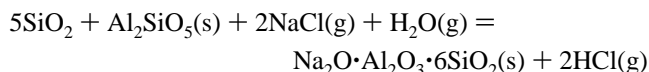
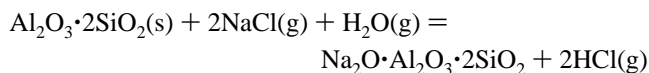


Figure 6. Comparison of Na^+ and Cl^- content of the sorbent after adsorption (1) in the absence of water vapor and (2) in the presence of water vapor.

involves physical and chemical forms. However, there is a difference between chemical and physical adsorption. If adsorption is predominated by the physical form, the molar amount of sodium absorbed by the sorbent is equivalent to that of chloride absorbed by the sorbent. If adsorption is predominated by chemical adsorption or physical and chemical adsorption in combination, the molar amount of sodium absorbed by the sorbent may be higher than that of chloride absorbed by the sorbent. If using Al_2O_3 and silicate resulted in a chemical reaction, one mechanism may be as follows:



The water vapor seems to play a significant role in the removal



of alkali metal vapor. Thus, experiments were conducted to remove alkali metal vapor under two different conditions: one is an absence of water vapor in the inlet gas; the other is presented water vapor. The Na^+ and Cl^- contents of activated Al_2O_3 after a capturing time of 4 and 10 h at 840°C are shown in Figure 6. Figure 6 shows that the molar amount of sodium absorbed by the sorbent is more than that of chloride absorbed by the sorbent if the inlet gas contains water vapor. The tests indicate that the removal of alkali metal vapor with activated Al_2O_3 is not a physical adsorption process in the presence of moisture. Chemical adsorption exists mostly in water vapor environments and results in HCl emissions. Furthermore, the structure of sorbents could also be altered.

3.3. Combined Removal of HCl and Alkali Metal Vapor.

The chemical adsorption of alkali metal vapor by sorbents displays a higher sodium capability of the sorbents. However,

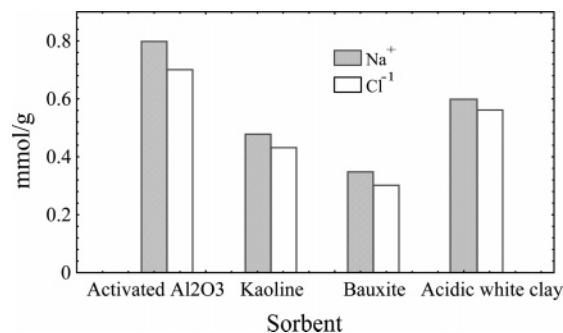


Figure 7. The Na^+ and Cl^- content of the sorbent in the experiments of combined removal of alkali and HCl vapor.

Table 4. Removal Efficiency of NaCl Vapor and Outlet HCl Concentration

sorbent	activated Al_2O_3	kaoline	bauxite	acidic white clay
removal efficiency of NaCl (%)	89.4	80.0	70.1	83.2
chlorine content of E1 (%)	7.2	6.5	6.3	7.0
outlet HCl concentration (mg/m^3)	0.32	0.58	0.76	0.50

it inevitably leads to HCl emission. It is very profitable to remove HCl after the chemical adsorption of alkali metal vapor in a reactor. This combined removal of alkali and HCl vapor has received very little attention in the purification of hot gas so far. In most cases, the interaction of various compounds during combined removal is complex and not understood. In this study, any one of the four sorbents including activated Al_2O_3 , bauxite, kaoline, and acidic white clay was placed in the alkali removal area in the tube of the reactor for capturing NaCl vapor; at the same time, sorbent E1 was used to remove HCl in the reactor. The experimental conditions are a removal time of 4 h, a space velocity of 3000 h^{-1} , inlet gas containing a small amount of moisture, and NaCl and HCl concentrations of $0.8\sim 1.0 \times 10^3\text{ mg}/\text{m}^3$. Under these operating conditions, the removal efficiency of NaCl vapor and outlet HCl concentration results are shown in Table 4; the molar amount of sodium and chlorine absorbed by the sorbent for the removal of alkali metal vapor is shown in Figure 7. The results show that the removal efficiencies of NaCl vapor for activated Al_2O_3 , bauxite, kaoline, and acidic white clay are 89.4%, 80.0%, 70.1%, and 83.2%, respectively. Compared to the single removal of alkali metal vapor, HCl in inlet gas affects the chemical adsorption equilibrium of sorbents in the process of removing alkali metal vapor and decreases the removal efficiency of NaCl vapor. Under the combined removal conditions, E1 sorbent almost removes 100% of HCl and decreases the outlet HCl concentration to less than $1\text{ mg}/\text{m}^3$. It indicates that the combined removal of HCl and alkali metal vapor is feasible in a reactor by different solid sorbents.

4. Conclusion

Using different solid sorbents, the removal of HCl and alkali metal compound (NaCl) vapor in hot gas was studied. It is found that the E1 sorbent based on montmorillonite and $\text{Mg}(\text{OH})_2$ is the best sorbent for HCl removal, and activated Al_2O_3 shows the highest adsorption efficiency and sodium content for the removal of alkali metal vapor. The tests indicate that the removal of NaCl with activated Al_2O_3 is not a physical adsorption process in the presence of moisture. The experiment was designed to remove metal alkali vapor and HCl in a combined or simultaneous method by developing a multifunctional reactor

with four independent heating zones, and the results indicate that the removal of HCl and alkali metal vapor with higher efficiency is feasible.

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