



Experimental study on adsorption of potassium vapor in flue gas by coal ash



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ABSTRACT

Potassium removal from biomass combustion flue gas is important in power engineering because potassium may cause serious problems such as the agglomeration, contamination, corrosion and deposition of heating surfaces. It is feasible to capture potassium vapor in flue gas by solid adsorbents. Experiments were performed to study the reaction characteristics and mechanism of the potassium adsorption by coal ashes with KCl as the alkali model compound. The influences of adsorption temperature, alkali metal concentration and adsorption atmosphere on potassium removal were analyzed. The experimental results confirm that coal ash has a good ability of potassium adsorption. The potassium adsorption amount by coal ash in initial 2 h increases roughly linearly with the increase of alkali metal concentration. Potassium adsorption by Guizhou coal ash during the fixed adsorption period increases with the increasing temperature in the range of 650–900 °C; while the reaction temperature is over 900 °C, potassium adsorption by Guizhou coal ash begins to decline. The potassium adsorption under the conditions even with a little water vapor content is larger than that under the conditions without water vapor. However the effect of high water vapor content on the alkali adsorption capacity is not obvious. The alkali adsorption by coal ash sorbent at a given period is the highest in reducing atmosphere, the second in the conventional flue gas atmosphere and the lowest in the oxyfuel combustion flue gas. The present experimental results will provide the references for the development of economical efficient sorbent of alkali metal to reduce the harm of the alkali in the biomass combustion or gasification process.

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1. Introduction

Biomass is a kind of renewable energy source with zero CO₂ emissions to atmosphere. Pyrolysis, gasification and combustion are the major methods to use biomass fuels. The total power plant capacity from direct biomass combustion reached 100 Billion Watt in 2015, of which China occupies 10%. Compared to coal fired boiler, the biomass fired boiler encountered the heavy agglomeration [1,2], ash deposition, slagging and high temperature corrosion problems [3] which may threaten the safety operability of the boiler. It has been shown that one important factor to cause those problems is the high contents of K and Cl in biomass. Potassium is usually high in biomass ash [4], both in organic and inorganic types [5]. Potassium tends lower the melting point of biomass ash. In addition, chlorine in biomass may be released to the gaseous phase as KCl in addition to HCl, which enhanced the evolution of potassium elements. Bläsing et al. studied the release of alkali metal, sulphur, and chlorine species from high temperature gasification of different rank coals [6], and Wei et al. [7] investigated behavior of gaseous alkali metals during biomass thermal utilization with chemical

equilibrium method. We have performed the experiments on sodium release from Zhundong coal [5]. Removal of alkali species in flue gas by solid sorbent material in a fixed bed or in a fluidized bed before flue gas enters the convective heating surface is a promising method to solve the alkali problems through physical adsorption or chemical adsorption.

Escobar et al. [8] studied alkali removal from hot flue gas by aluminosilicate sorbents in pressurized pulverized coal combustion qualitatively and quantitatively using high pressure mass spectrometry. Waindich et al. [9] investigated the alkali removal at higher temperature with sorbent bed using molecular beam mass spectrometry (MBMS). Li et al. [10] investigated the absorption of alkali vapor by Kaolin, diatomite, activated bauxite and SiO₂, and they found that Kaolin has the best adsorption performance of four adsorbents, and alkali adsorption by Kaolin was controlled by surface chemical reaction and internal diffusion. Punjak et al. [11] also studied the kinetics of alkali adsorption by Kaolin. Luthra and Leblanc [12] studied the Al₂O₃ adsorption dynamics, and the values of adsorption constants are calculated. Zheng et al. [13] also believed that the adsorption of alkali metal by Kaolin was controlled by the complicated process of diffusion and chemical reaction. In order, Yao et al. [14] modified the morphology of Kaolin by intercalation-exfoliation method to improve the sodium adsorption capacity. Many

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other scholars [15–18] studied the adsorption kinetics of other adsorbents to alkali metal vapor. However, most previous studies are mainly concentrated on materials such as Kaolin, diatomite and alumina, emathlite and so on. Those adsorbents are generally expensive for engineering application in power generation, therefore low-cost sorbent is urgently required. In a review of sorbent materials for fixed bed alkali getter by Turn et al. [19], investigation by Mulik et al. [20] on the alkali adsorption by low-temperature char and coal gasifier ash was mentioned. Our previous study on alkali adsorption by coal chars also demonstrates that ash in char plays an important role in adsorption [21]. In addition to the adsorption of alkali, Wendt et al. [22–26] studied release and adsorption of sodium and toxic trace metals such as lead and cadmium by several solid adsorbent including Kaolin and alumina compounds. However, up to now little is known about the property and capacity of fluidized bed coal ash for the adsorption of alkali metal vapor. For the fact that during a practical combustion process, the gas surrounded the solid sorbents may vary among different atmospheres, the adsorption by solid sorbent at different atmospheres is not clear.

With the wide application of biomass energy, effective controls of the vapor phase potassium arouse people's attention. In present study, experiments were carried out to investigate the potassium capacity of coal ash in biomass utilization through fluidized bed combustion. The factors that may influence potassium capacity of coal ash were taken into account, including sorbent type, adsorption temperature, potassium concentration, steam content, adsorption atmosphere etc. The traditional recognized promising alkali sorbent kaolinite was also tested as a reference for comparison.

2. Experiment

2.1. Experimental apparatus and procedure

Potassium adsorption experiments were carried out in a packed bed. A schematic diagram of the experimental setup applied in present study is shown in Fig. 1. The reactor consists of a vertical corundum tube with an internal diameter of 41 mm and the length of 900 mm located in a two-zone heating furnace. The heating furnace includes two segments which are controlled by digital temperature controllers separately. The lower one is for potassium evaporation and the upper one is for potassium adsorption. As shown in Fig. 1, two stainless steel wires are fixed correspondingly, so as to support the potassium source holder and adsorbent ceramic holder.

KCl was used as the potassium model compounds. Potassium is added to the primary flow in vapor phase evaporated at high temperature from potassium source ceramic holder and carried downstream

by gas. The potassium vapor concentration is controlled by varying the evaporation bed temperature. The potassium released to the gas flow is measured by weight change of potassium chloride in ceramic holder before and after experiment. The gas stream flows through a packed bed of silica wool below the alkali source to guarantee the proper preheating and alkali evaporation. The potassium concentration variation with the evaporation temperature in present experiment is shown in Fig. 2. Compared to the saturation pressure of KCl in Lange's Handbook of Chemistry (16th Edition), the potassium vapor in gas stream in Fig. 2 is not saturated in present study, however it is in the range of the alkali vapor concentration in typical biomass combustion.

About 200 mg sorbent was paved on the holder in adsorption section. The temperature of adsorption is at least 10 °C higher than that of evaporating section to prevent the gaseous potassium metal from condensation or desublimation at adsorption section.

The carrier gases including pure N₂, CO₂ and CO from gas cylinders mix first with the total flowrate of 500 ml/min and then go into the reactor. The addition of water vapor was accomplished by the heated water bath for low steam concentration condition or using a controllable micro flow pump (0.001–18 ml/min) instead of water bath for high steam concentration condition as shown in Fig. 1. The steam concentration is adjusted by varying the temperature of water bath or by changing in controllable micro flow pump. The gas path after water vapor introduced was heated by ribbon heater to maintain the tube wall temperature over 100 °C.

The main gas path and normal vent are closed and the gas stream flow downward over the adsorbent and alkali source in turn and then exit from the auxiliary vent before the furnace is heated to the preset temperature. The main gas path as well as normal vent is opened and the bypass as well as auxiliary vent is closed to initiate adsorption. At the end of each run, the gas was turned off and the furnace was shut off. The adsorption duration is 2 h in present experiment.

The sorbent after adsorption experiments was soaked in the mixed acid (HNO₃:HCl:HF for 3:1:1) for 6 h before leaching in order to guarantee alkali metal compounds fixed to the adsorbent completely dissolved. PH value was adjusted by using diisopropylamine to satisfy measurement requirements and then the alkali ion concentration in filtrate was measured by PXSJ-216 Ion Meter. The relative measurement uncertainty of the K ion is within 0.5%.

In addition, SEM images of adsorbents after adsorption were collected on a JSM-6390A scanning electron microscope equipped with an energy dispersive spectrometer (EDS) manufactured by JEOL Ltd., operating at 30 kV. Samples were set up horizontally and uniformly on the sample stage for examination. The magnification of the microscope (5–300,000) is large enough to satisfy our experimental requirement.

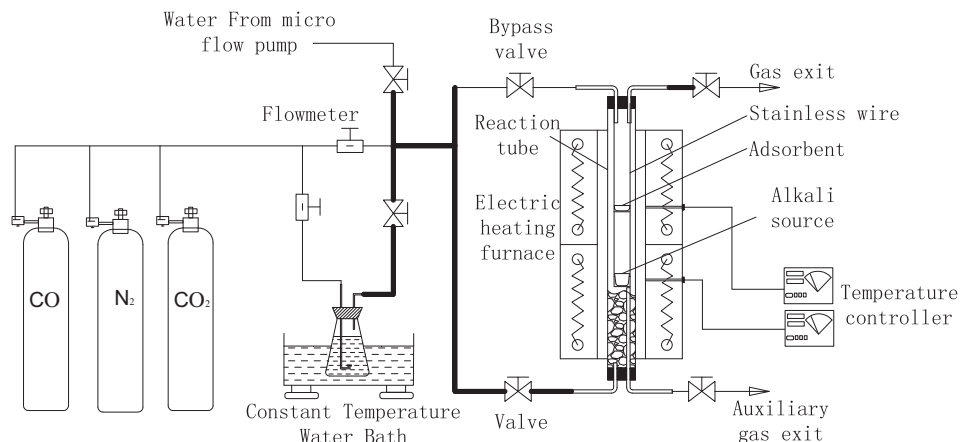


Fig. 1. Schematic diagram of the experimental setup.

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