EXPERIMENTAL STUDY OF ADSORPTION OF ALKALI WITH BED MATERIAL WHEN CO-FIRING BIOMASS WITH COAL

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Abstract–Co-firing biomass and coal has potential problems, such as deposition, high temperature corrosion of the heating surface due to the high content of potassium chloride. Due to the high ash concentration, co-firing is feasible in circulating fluidized bed (CFB), which can capture alkali with bed material. Experiments were performed to study the alkali adsorption ability of the bed material in lab test rig and a 3.3 MW_{th} hot CFB test rig. Firstly, the influences of reaction temperature, alkali concentration on the adsorption of alkali with bed material were investigated. The mixture of NaCl and bed material was heated in Thermogravimetric Analysis(TGA) and fixed bed, respectively. The TG curves (9%NaCl+bed material) show that the alkali adsorption will reach the steady state in less than 135/80/40 minutes at 800/850/900℃. As temperature increases, the mixture weight comes to a steady state more quickly. In capturing time of 135 minutes, the results of fixed bed indicate an decreasing tendency of the alkali adsorption with the increasing temperature at the range of 800-900℃. The alkali adsorption of amount by bed material increases nearly linear while the NaCl mass content in the mixture increasing at the range of 1-8%. In the hot CFB test rig, at certain operating conditions, NaCl was mixed in the feeding coal continuously, at same time, the circulating ash, fly ash were sampled. The alkali capacity of bed material in pilot scale CFB boiler was also analyzed.

INTRODUCTION

With the development of the world economy, the consumption of conventional energy sources such as coal, oil and natural gas greatly increases. Climate issues have become gradually prominent. The demand for efficient and clean utilization of energy and new alternative energy is urgent. Biomass has attracted worldwide attention and plays an important role in the current world energy consumption pattern because of its renewable, low pollution and wide availability. China is a large agricultural country, biomass resources is rich, the theoretical biomass energy is about 5 billion tons of standard coal [Zhou, F., et al, 1999; Zhou, S. Y., 2001].

Substituting biomass for coal in pulverized coal-fired (PC) units is helpful for alleviating pressure from energy shortage and pollution in the word, and it's also a possible way to reduce greenhouse-gas emissions[Yang, G., 2012; Kati, S., 2003]. Biomass direct combustion has been widely applied and developed, but it will cause deposition and high temperature corrosion of heating surfaces in boiler during biomass combustion due to the high content of alkali metals, which may obviously reduce the efficiency and influence the long-time safe operation of the boiler [Gong, B., 2015].The deposition of a 150MWe Utility power boiler in Denmarkare was shown in Fig. 1[Kate, W. H., 2000].

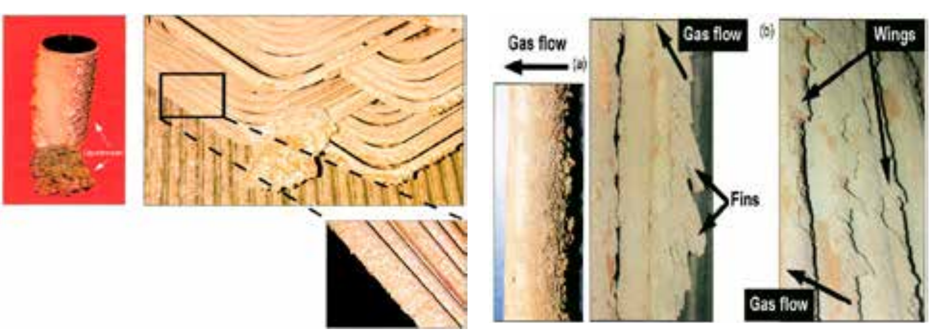


Fig. 1.Probe deposit in superheaters in a 150 MWeUtility power boiler in Denmark

Alkali metals problems especially deposition and high temperature corrosion of the heating surface when co-firing biomass and coal result from the high content of potassium chloride. Aluminosilicate materials are found to be good candidates for use as fouling mitigating additives [Stella, K., 1999]. A number of additives (silica, alumina, graphite, alumina, calcined limestone, et al.) had been studied to prevent fouling but bed material [PUNJAK, W. A., 1987; Shen M. K., 2015;]. Due to the high ash concentration, co-firing is feasible in circulating fluidized bed (CFB), which can capture alkali with bed material. To further study the possibility of using bed material as fouling mitigating additives, experiments were performed to study the alkali adsorption ability of the bed material in lab test rig and a 3.3 MWth hot CFB test rig.

LAB SCALE EXPERIMENTAL

Preparation of Experimental Sample

Bed material collected from a 300 MWe CFB in Longyan Fujian was chosen as the experimental sample. Fig. 1 shows the particle size distributions of bed material. The particle size analysis indicates that the main particle size distribution is 68~180 μm, d(0.1)=60.2 μm，d(0.5)=114.0 μm，d(0.9)=214.9 μm. The XRF analysis of the bed material is listed in tab. 1.

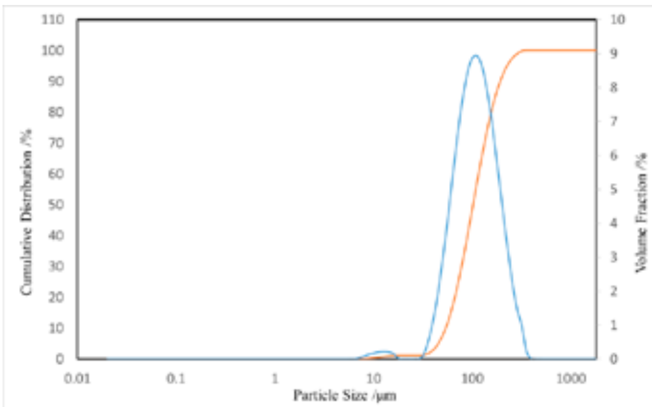


Fig.2. Particle size distribution of bed material.

Table 1:X-ray fluorescence results of bed material.

Analyte	Result	Analyte	Result
SiO_2	52.43%	MnO	0.23%
Al_2O_3	20.54%	P_2O_5	0.12%
Fe_2O_3	15.97%	ZrO_2	0.09%
K_2O	2.96%	Cr_2O_3	0.09%
CaO	3.74%	SrO	0.07%
TiO_2	1.47%	Rb_2O	0.05%
MgO	0.81%	ZnO	0.04%
SO_3	1.07%	Co_2O_3	0.03%
Na_2O	0.23%	NiO	0.04%

The samples are rich of SiO_2 and Al_2O_3, which were considered the main composition that react on Alkali.

Experimental Apparatus and Procedure

Experimental procedure

The investigation mainly focused on the adsorption properties of bed material. Specific experimental steps were as follows:

(1) Carry out a slow ash treatment on the bed material to remove carbon residue and pulverize the NaCl into powders which have an average particle size of 75 μm;

(2) Put samples (m_{NaCl} : $m_{Bed\ material}$ = 9:100) into a thermogravimetric analyzer (TGA) at 800/850/900℃ respectively. It can determine the experimental time for stabilizing the weight of bed material samples at different temperatures.

(3) Blend bed material and NaCl in the proportion of 0% (without salt), 1%, 2%, 3%, 5% and 8%.

(4) Calcinate the samples in step 3 in a muffle furnace at 800℃, the calcination time is determined by the step 2;

(5) The changes of the quality of the sample before and after calcination were measured, and the weight gain of the bed material was obtained, and the experiment was repeated three times.

(6) Change the calcination temperature, repeat steps 3 to 5 at 850 ° C and 900 ° C respectively.

Experimental Apparatus

The TGA test was used to measure the temperature-mass relationship of the materials. The thermogravimetric analysis was performed on the TGA/DSC1/1600HT simultaneous thermal analyzer. The experimental conditions are listed in Tab.2.

Table 2: Test conditions of TGA.

	Starting temperature /℃	Air flow rate /(ml/min)	Heating rate /(℃/min)	Maintain time /(min)
Heating process	25	100	30	-
Adiabatic process	800/850/900	100	-	150/120/90
Cooling process	800/850/900	100	-30	-

The pretreated bed material was calcinated in a GW-300C muffle furnace, which can operate stable within 1000 degree Celsius. Specific experimental steps were as follows:

(1) A dedicated slow ash program in muffle was performed to extract carbon residue in bed material;

(2) In order to avoid volatilization of the sodium salt vapor in the furnace influence the accuracy of the experimental results, experiments of different blending ratio should be performed respectively;

(3) The original and calcinated sample should be cooled in the dryer to prevent the samples absorbing water vapor in the air. The experimental conditions are listed in Tab.3.

Table 3: Test conditions of meffle experiment.

Temperature /℃	Blending ratio (NaCl/Bed material) /%	Calcination time /min
800	0、1、2、3、5、8	135
850	0、1、2、3、5、8	80
900	0、1、2、3、5、8	40

Evaluation Criteria

The evaluation criterion, which is the adsorption amount of alkali, namely alkali capacity of the sorbent, is expressed as follows:

(1)

Blending ratio is expressed as follows：

$$Blending\ ratio = \frac{m_1}{m_2} \times 100\% \quad (1)$$

Results and Discussion

TGA Test – Determination of Calcination Time

Weight loss of NaCl and bed material mixed with NaCl (mNaCl : mBed material = 9:100) at 800/850/900 ℃were shown in fig. 3-4, respectively. It can be found that almost all the NaCl can change from solid to gas between 800-900 ℃, and the complete adsorption process of bed material takes less than 135/80/40 min.

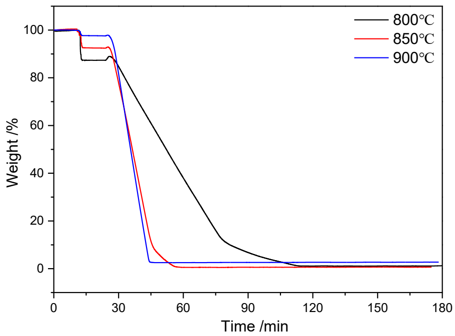


Fig.3. Weight loss curve of NaCl.

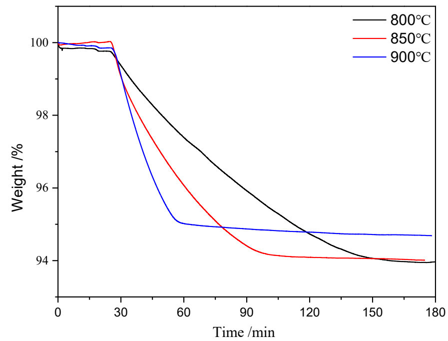


Fig.4. Weight loss curve of bed material.

The TG curves (9%NaCl+bed material) show that the alkali adsorption will reach the steady state in less than 135/80/40 minutes at 800/850/900℃. As temperature increases, the mixture weight comes to a steady state more quickly.

Fixed bed experiment – Alkali Capacity of Bed Material

The experiment results were listed in tab. 4.The alkali capacity of the bed material (mixed with 8 % of its own weight) is up to 5.51%, 4.34 %, 3.02% when calcinated at 800/850/900 ℃ respectively.

Table 4: Test results of muffle experiment.

Blending ratio (NaCl/Bed material) /%	Alkali capacity /%		
	800℃	850℃	900℃
0	0.053±0.01	0.03±0.02	-0.09±0.01
1	0.57±0.03	0.55±0.05	0.36±0.02
2	1.14±0.01	1.02±0.03	0.84±0.01
3	1.72±0.03	1.45±0.04	1.11±0.02
5	3.12±0.09	2.49±0.12	1.96±0.01
8	5.51±0.04	4.34±0.71	3.02±0.03

Fixedbed experiment – Effect of calcination Temperature on Alkali Capacity

Experiment is carried out by changing the adsorption temperature from 800-900 ℃ using Longyan bed material to get the effect of calcination temperature on alkali adsorption, which is shown in Fig.5. Obviously, the results of fixed bed indicate an decreasing tendency of the alkali adsorption with the increasing temperature at the range of 800-900℃, because higher calcination temperature promotes adsorption reaction rate and volatilization rate of NaCl significantly, and the impact on volatilization rate of NaCl is greater than that of promotes adsorption reaction.

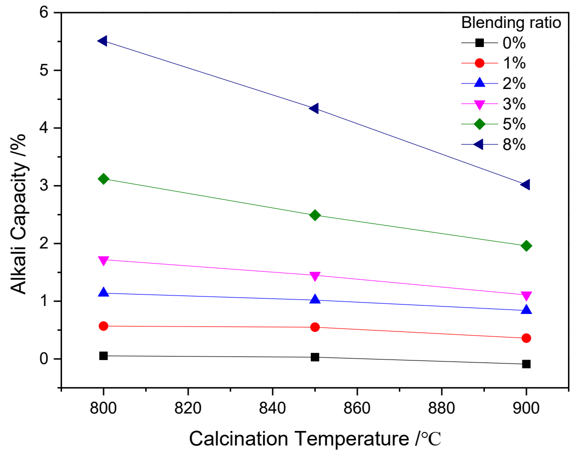


Fig. 5. Influence of calcination temperature on alkali capacity of bed material.

Fixed bed experiment – Effect of alkali concentration on Alkali Capacity

The effect of alkali concentration on alkali capacity was investigated by varying the calcination temperature. Fig. 6 shows the influence of calcination temperature on the alkali capacity of Longyan bed material exposed at 800/850/900°C for 135/80/40 min. The alkali adsorption of amount by bed material increases nearly linear while the NaCl mass content in the mixture increasing at the range of 1-8%.

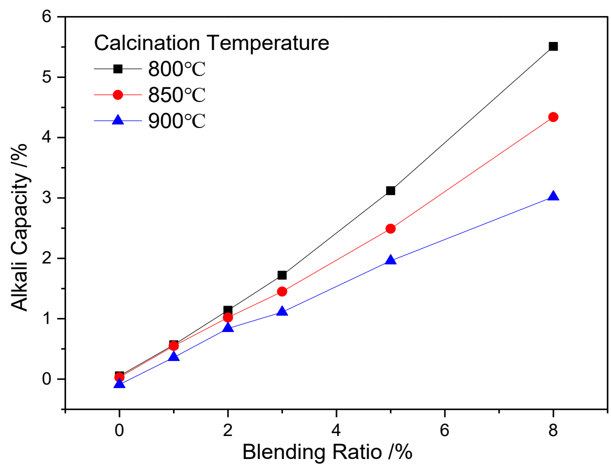
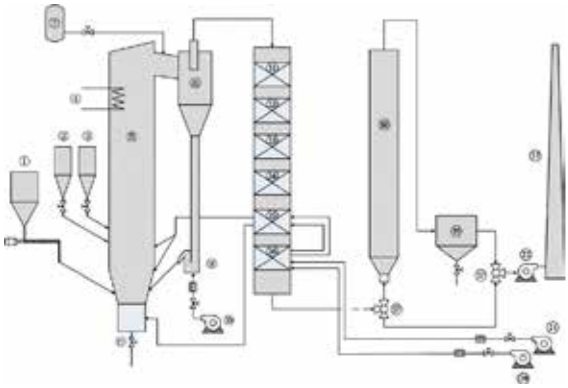


Fig. 6. Influence of blending ratio on alkali capacity of bed material.

PILOT SCALE EXPERIMENTAL

Experimental Apparatus and Procedure

As shown in Fig.7, the 3.3 MWth pilot scale CFB boiler, built in Taiyuan Boiler Group, has whole set of CFB device and one heat insulated cyclone separator.



1.Coal bunker 2.Limestone bunker 3.Sand bunker 4.Water-cooled tubes 5.Furnace 6.Slagging pipe 7.Ammonia 8.Seperator 9.Loop seal 10.Material-returning air fan 11-12.High temperature economizer 13-14.Low temperature economizer 15-16.Air pre-heater 17.Valve 18.Half dry desulfurization 19.Precipitator 20.Primary air fan 21.Secondary air fan 22.Induced draft fan 23.Chimney

Fig.7. 3.3 MWth pilot scale CFB boiler.

The experiment was performed after the combustion parameters were stable, which provide a relatively stable combustion environment for the adsorption of NaCl in the CFB boiler. Fig.8 shows the temperature distributions along the furnace. At certain operating conditions, NaCl was mixed in the feeding coal continuously at a mass flow rate of 10.8 kg/h, at same time, the circulating ash, fly ash were sampled. The mass flow rate of feeding coal is 500 kg/h. The alkali capacity of bed material in pilot scale CFB boiler was analyzed.

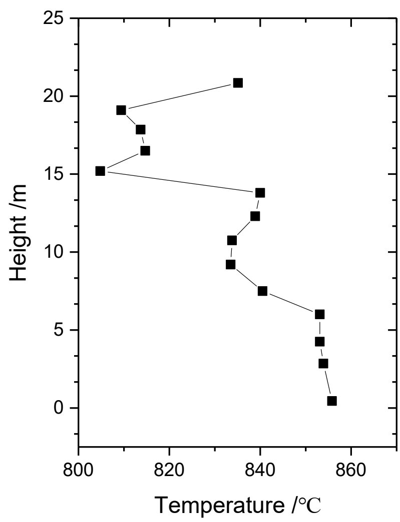


Fig.8. Temperature distribution along the furnace.

The dense phase temperature is about 855 ℃, and the dilute phase temperature is about 810 ℃ when NaCl was mixed in the feeding coal.

Results and Discussion

Fig. 9 shows the sodium content as a function of time in a 3.3 MWth pilot scale CFB boiler for NaCl was mixed in the feeding coal continuously for 3 hours with the dense phase temperature is about 855 ℃. Obviously, the results indicate an increasing tendency of the sodium content over time both in bed material and fly ash, which indicate that sodium content in bed material can be up to 1.5% of the weight of the bed material, while sodium content in fly ash can be up to 1.2% of the weight of the fly ash.

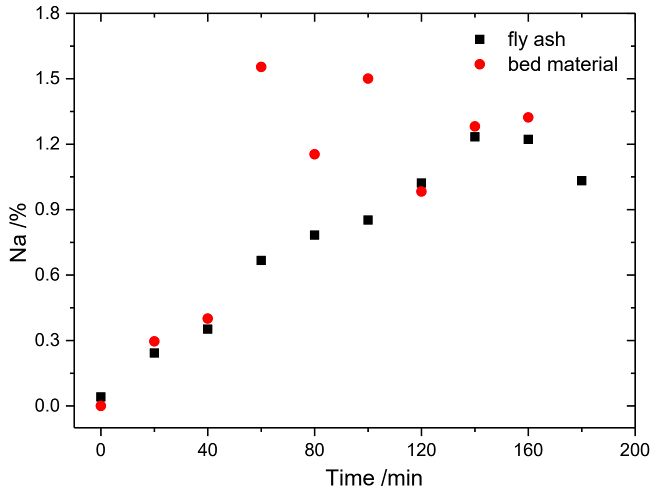


Fig. 8. Chang of sodium content in fly ash and bed material over time.

CONCLUSIONS

To further study the possibility of using bed material as fouling mitigating additives, experiments were performed to study the alkali adsorption ability of the bed material in lab test rig and a 3.3 MWth hot CFB test rig. The main results are as follows:

(1)The TG curves (9%NaCl+bed material) show that the alkali adsorption will reach the steady state in less than 135/80/40 minutes at 800/850/900℃. As temperature increases, the mixture weight comes more quickly to a steady state.

(2)The alkali capacity of the bed material (mixed with less than 8 % of its own weight) is up to 5.51%, 4.34 %, 3.02% when calcinated at 800/850/900 ℃ respectively. The results of fixed bed indicate an decreasing tendency of the alkali adsorption with the increasing temperature at the range of 800-900℃.The impact of calcination temperature (800-900℃) on volatilization rate of NaCl is greater than that of promotes adsorption reaction.

(3)The alkali adsorption of amount by bed material increases nearly linear while the NaCl mass content in the mixture increasing at the range of 1-8%.

(4)The sodium content in bed material can be up to 1.5% of the weight of the bed material, while sodium content in fly ash can be up to 1.2% of the weight of the fly ash.

ACKNOWLEDGMENT

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NOTATION

m_c	weight of the calcinated sample, g	m_o	weight of the original sample, g
m_1	weight of NaCl, g	m_2	weight of the Longyan bed material, g

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