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Origination and formation of NH_4Cl in biomass-fired furnace

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ABSTRACT

Biomass slagging is widely affected by various factors. NH_4Cl verified by TG/DSC and XRD is found in the exit of bag filters in a cotton stalk biomass-fired furnace in northwest of China. The TG/DSC curves of the sample are well in agreement with standard NH_4Cl. The peaks of sample are also well consistent with standard NH_4Cl identified by XRD and with a purity of almost 100%. Based on the concentration of Cl in cotton stalks (0.44 wt.%) and cropland soil (6.834 wt.%), and balance calculation based on SiO_2 and Al_2O_3 trace method, it is deduced that partial NH_4Cl is from soil doped into the cotton stalks. In boiler, NH_4Cl decomposes into $NH_{3(g)}$ and $HCl_{(g)}$ at 337.8 °C, and then partial $HCl_{(g)}$ reacts with metal oxides in ash, or NH_4Cl reacts with hydroxide directly and generates $NH_{3(g)}$. All the chlorides as reaction products cause serious slagging in the boiler. Together with the $NH_{3(g)}$ and $HCl_{(g)}$ generated from biomass, the remaining $HCl_{(g)}$ gets through bag filters and re-combines with un-oxidized $NH_{3(g)}$ into NH_4Cl accumulated in tail flue. Therefore, inevitable impurities in biomass, especially element Cl, should highly attract attention in the biomass-fired boilers.

1. Introduction

Knowledge of biomass slagging is important for an efficient and economically viable large-scale utilization of field crop residues and energy crops. Biomass-firing often leads to unmanageable deposits on fireside surfaces, especially on a superheater [1,2]. Such deposits depending on chemical and mineralogical compositions of fly ash as well as combustion conditions including temperature and velocity distribution, reducing or oxidizing atmosphere, etc. [3,4] destruct aerodynamic field, deteriorate combustion, inhibit heat transfer, reduce boiler efficiency, and accelerate corrosion of metal surface, even cause superheater tube explosion [5,6]. All these units will affect the safety, reliability and economy of power plants.

Fig. 1 is a schematic mechanism of slagging referring to Patumsawad [7] and our latest research, which also shows the influence of co-firing, additive and leaching. In biomass-fired furnace, Cl and K are combined into $KCl_{(g)}$ firstly, which is then condensed on heating surfaces by various mechanisms such as diffusion, electrophoresis, thermophoresis, inertial impaction and gravity [8–10], and as adhesive bonding coarse fly ash or mineral salt on tube [11]. Meanwhile, partial KCl may be sulfated [12,13], which promotes slagging. While partial KCl can be aluminosilicate and inhibits slagging [14]. Anyway, co-firing, additive and leaching can change the components of fuels and further affect combustion and slagging. In the process of co-firing, additive or leaching, when the (K+Cl)/(Si+Al) ratio in fuels goes up, the KCl concentration increases and slagging exacerbates; while (K+Cl)/(Si+Al) ratio goes down, more KCl is trap by Si and Al and slagging weakens [15,16]. Of course, slagging only accounts for a small part of KCl and other mineral salts, and most are as fly ash and trapped by filters.

Although the slagging problem has been studied widely, the nature for slagging is still uncertain or incompletely understood; especially the effect of various unpredictable compounds on slagging. Further investigations are therefore essentially required.

In this paper, NH_4Cl will be presented to us, which was found in a serious slagging biomass-fired furnace by accident. The origination and formation mechanism of NH_4Cl and the influence on slagging will be discussed. In the coal-fired boiler with the SNCR system it is also found [17], and I.H. Hwang, etc. [18] studied the influences of gas temperature, retention time, $HCl_{(g)}$ and $NH_{3(g)}$ concentrations on the formation in a municipal solid waste incinerator with the SNCR system. NH_4Cl generation increases with decreasing reaction temperature [18]. S. Zandaryaa [19] reported that about 12.3% of total injected NH_3 was detected at bag filter as a form of ammonium salt in an incinerator.

NH_4Cl as a neutral fertilizer with slow nitrification and high utilization rate of nitrogen was widely used in cropland, especially in a cotton field. NH_4Cl significantly evaporates at 100 °C and decomposes into $NH_{3(g)}$ and $HCl_{(g)}$ at 337.8 °C (Eq. (1)) [20]. Then $NH_{3(g)}$ and $HCl_{(g)}$ re-combine into NH_4Cl at low temperature (Eq. (2)) [20], corresponding reactions are as follows:

$$NH_4Cl_{(s)} = NH_{3(g)} + HCl_{(g)} \tag{1}$$

$$NH_{3(g)} + HCl_{(g)} = NH_4Cl_{(s)} \tag{2}$$

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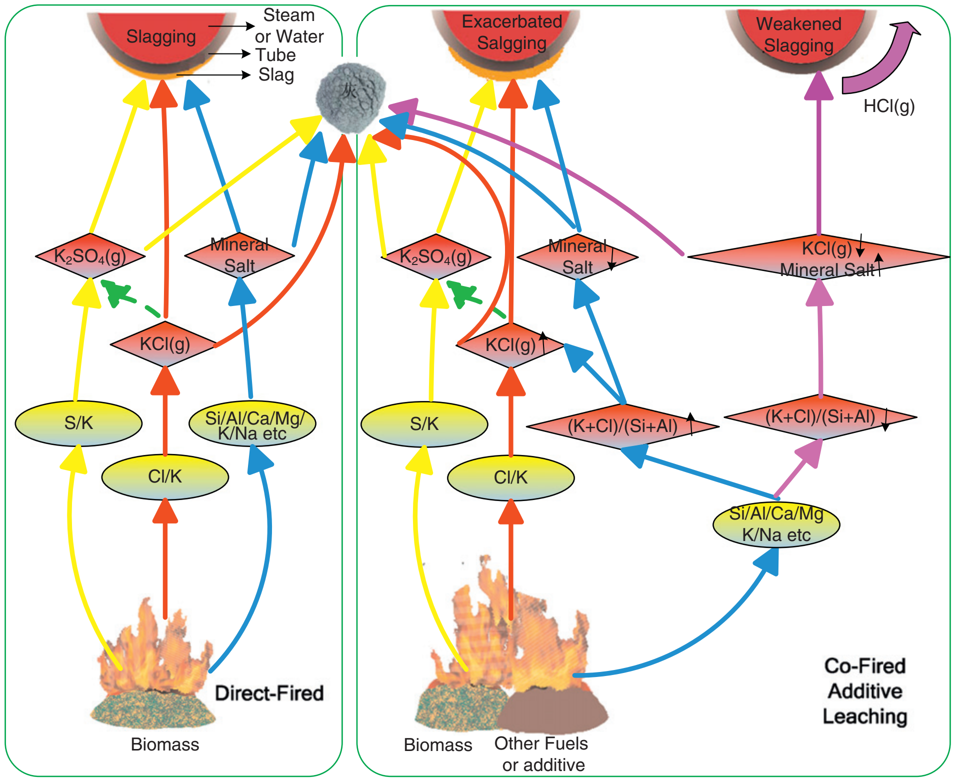

Fig. 1. Schematic diagram of slagging mechanism in biomass-fired furnace.

2. Experimental

2.1. Experimental methods

The TG/DSC test could be used as a tool to measure melting point and decomposition temperature. As TG curve drops and DSC curve has a downward or upward peak, it means that there is decomposition, while when TG curve keeps level and DSC curve has a downward or upward peak, it means that there is a melting behavior or crystal transition. Thermal balance (NETZSCH-490PC, Germany) is applied in the TG/DSC test. The mass of sample is approximately 10 mg and the temperature range is from room temperature to 600 °C at a constant heating rate of 10 °C/min. Flow rate of N_2 (99.999%) is 100 ml/min.

The main crystalline compounds of the sample are identified by qualitative X-ray powder diffractometry (XRD), which is described in detail in previous papers [21,22].The reproducibility of the experiments is acceptable and the experiment is carried out three times.

2.2. Sample

The sample used in the TG test and XRD analysis is obtained from a 12 MW biomass-fired furnace, which is a typical M-type nature circulation boiler. The system schematic can be seen in previous papers [2,21]. Flue gas passes through four-stage superheaters, an economizer and an air preheater in turn. At last, after passing through the bag filters it is discharged into the air. Table 1 shows the gas temperature along the flue gas flow. The temperature in the combustion zone is below 1500 °C, and the temperatures upstream and downstream of the bag filters are about 134–147 °C and 110–138 °C, respectively. The biomass fuels used in the furnace are dominant cotton stalks; the corresponding ultimate analysis, proximate analysis and ash composition are listed in Table 2.

In the biomass-fired boiler where the NH_4Cl sample is obtained, the slagging is very serious and the boiler is forced to shutdown to clean the slagging each 15–20 days. The severity of slagging could be seen in Fig. 2. In the exit of bag filters, white NH_4Cl (Fig. 3a) with salty and slightly bitter flavor as well as pungent odor, is presented. The amount of NH_4Cl was huge and the thickness could reach 10–15 mm (Fig. 3b).

Table 1
Gas temperature along flue gas flow.

Temperature/°C	Inlet	Outlet
Waterwall	<1500	
Third superheater	<900	
Fourth superheater		
Secondary superheater	~703	505–645
Primary superheater	505–645	378–465
Economizer	337–380	192–215
Flue gas cooler	192–215	140–153
Air preheater	49–61	183–190
Bag filters	134–147	110–138

Table 2
Analysis results of cotton stalk.[a]

Component	Content/wt.%	Oxides	Content/wt.%
W_{ad}	2.63	SiO_2	12.28
A_{ad}	4.22	Al_2O_3	3.60
V_{ad}	72.61	Fe_2O_3	1.04
FC_{ad}	20.54	CaO	22.48
C_{ad}	45.86	MgO	9.82
H_{ad}	5.53	TiO_2	0.19
O_{ad}	40.96	SO_3	5.14
N_{ad}	0.61	P_2O_5	6.24
S_{ad}	0.19	K_2O	22.70
Cl_{ad}	0.44	Na_2O	5.88

[a] Subscript 'ad' means air-dry basis.