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Analysis on Fly Ash Sediment of Biomass Fuel Boiler Heating Surface

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Abstract

According to the fuel properties of biomass (straw), it analysis the element content of the Cl, S in biomass straw and alkali meta such as K, Na and the composition of biomass (straw) and ash, meanwhile it analysis the composition of fly ash deposits sediments on heating surface of straw fuel boiler and determines the components of depositional aggressive medium and its mass ratio. A simulation corrosion test is designed base on the mass ratio and other conditions; it obtains the corrosion morphology and corrosion products by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS). Finally it determines the process of alkali metal chloride deposition corrosion is mainly self catalytic oxidation corrosion.

Keywords: *biomass (straw), heating surface of boiler, deposit corrosion medium, self catalytic oxidation corrosion*

1. Introduction

Ash deposition is an important problem in the process of biomass fuel heat utilization. It is product that volatile substances of biomass in the vapor phase condenses or adhere on the heating surface when it flows through the heating surface with flue gas and fly ash [1].In the biomass energy utilization, the biomass ash is an important factor which has effect on its utilization process, the ash deposition, corrosion and abrasion are closely related to the characters of biomass ash [2-6]. So the analysis on fly ash sediment of biomass fuel boiler heating surface is necessary to study the characteristics of biomass ash and the prevention of heating surface.

2. Analysis on Straw Composition

It chooses the corn straw in Liaoning province as analytic raw material of straw fuel. The raw material is made into specimen after shattering handling to analysis the content of Cl, S, K and Na in the straw. The component analyzed results are shown in table 1 and 2.

Table 1. Proximate Analysis of Straw

Component	Mar/%	Aar/%	Var/%	Fcar/%
Corn Straw	9.40	6.96	66.26	17.38

Table 2 Element analysis of straw

Element	Car/%	Har/%	Oar/%	Nar/%	Sar/%	Clar/%
Corn Straw	40.34	3.08	38.80	1.02	0.12	0.399

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3. Analysis on the Main Fly Ash Product of Straw Combustion

The ash deposition on the heating surface is mainly produced by fly ash deposition of combustion product through burnout in the furnace. The composition of fly ash is directly related to the composition of ash deposition, and the composition of fly ash mostly associated with the morphology of main element migration precipitate through burnout. So it is necessary to discuss the migration precipitation regularity of main element which influences deposition corrosion during the combustion of straw.

According to the content and form of Cl, S, K, Na in the straw, the migration precipitation regularity of main element which influence deposition corrosion during the combustion [7-12] of straw as follows:

When the combustion temperature is lower than 850K, potassium mainly survives in KCl(s), K_2SO_4(s) component form, sodium mainly survives in $Na_2Ca_3Si_6O_{16}$(s) component form and little NaCl(s) component form. There are some reactions conduct during above process: Organic sulfur produces SO_2(g) by oxygenolysis and KCl(s) produces some HCl(g), so the SO_2(g) and HCl(g) exist.

When the combustion temperature reach 850K, KCl(g) and NaCl(g) are produced, with the rise of temperature, the content of KCl(g) and NaCl(g) increase, and KOH(g), NaOH(g) and K, Na ion are produced, K_2SO_4(s) exists at the same time.

When the combustion temperature reach 1300K, K_2SO_4(g) and Na_2SO_4(g) are produced, and NaOH(g) increases and NaCl(g) reduces.

Ca is non-volatile and Si is inert element, they will produce stable compounds, they exit in bottom ash in the solid form.

The main possible reactions are (M is K and Na):

$$\text{Organic sulfur} + O_2 \rightarrow SO_2(g) \quad (1)$$

$$MCl(g)+H_2O(g)\rightarrow MOH(g)+HCl(g) \quad (2)$$

$$2MCl(g)+H_2O(g)+SO_2(g)+0.5O_2(g)\rightarrow M_2SO_4(g)+HCl(g) \quad (3)$$

$$2MOH(g) +SO_2(g)+0.5O_2(g)\rightarrow M_2SO_4(g)+H_2O(g) \quad (4)$$

$$M_2SO_4(g)+H_2O(g)\rightarrow 2MOH(g) +SO_3(g) \quad (5)$$

According to the check analysis of K, Na content in the fuel, the K content is 1~2 orders of magnitude more power than Na[13].And it obtains the result is true after comparison with the actual straw ash composition in table 3.

Table 3. Component Analysis of Straw Ash

Composition	SiO_2/%	Al_2O_3/%	Fe_2O_3/%	CaO/%	MgO/%	SO_3/%
Content	49.83	9.90	3.04	9.19	7.01	2.80
Composition	TiO_2/%	K_2O/%	Na_2O/%	P_2O_5/%	MnO_2/%	Cl/%
Content	0.30	10.27	1.34	1.33	0.16	9.27

It follows that fly ash product during the combustion of straw is mostly potassium compound.

4. Analysis on Fly Ash Sediment

According to the characteristic analysis of straw ash, the volatile constituents in straw enters gas phase at high temperature, its gas phase products are the main component of fly ash, its elemental composition is the important matter that affect the fly ash component. According to the temperature conditions and combustion temperature field in the furnace, it obtains the composition and distribution of gaseous material of combustion products:

The solid state constituent material (the compounds of potassium KCl, K2SO4) and the complex salt (Na2Ca3Si6O16) are main in fire grate, the gas state constituent material are main in the middle of furnace, but KCl, NaCl, SO2 and a spot of K2SO4, Na2SO4 (gaseous) are main exit in the area near the boiler heating surface (the area A in figure 1).

According to the temperature of steam (hot water) in boiler heating surface pipe in area A of Figure 1, it is usually between 400℃ and 535℃ in different boiler settings. So the KCl(g), NaCl(g) and little K2SO4, Na2SO4 in the fly ash will accumulate on the pipe and form the sediment. Meanwhile, the reference [14-16] confirmed the KCl, NaCl and little K2SO4, Na2SO4 are the main sediment on the biomass boiler heating surface. As shown in research, if a certain S in the fuel burn and produce the SO2 or SO3, the alkali chloride KCl, NaCl on the heating surface will be sulphating at high temperature and produce K2SO4, Na2SO4 in the deposition layer. It shows that the fly ash sediments on biomass boiler heating surface are KCl, NaCl and K2SO4, Na2SO4.

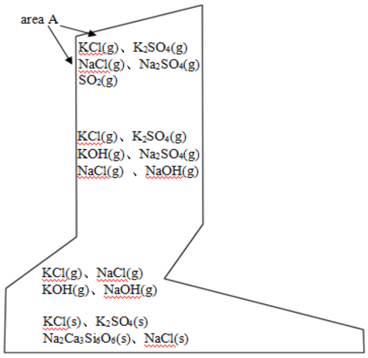


Figure 1. Main Ash Compound Distribution of Furnace Burner

In order to check above result of fuel theory analysis, it analysis the corrosion pipe which was cut from some biomass boilers in Liaoning province, the fuel of that boiler is corn straw, the corrosion pipe cut from the boiler pipe where the flue gas temperature is 850～950℃. Table 4 is the element analysis result of deposition corrosion product layer. As shown in table 4, Fe is the main deposition corrosion product in the inner layer, the content of K, Na and Cl is less, and there are some Si, Al, Mg and Ca in it, they may be the heating product that contained when the deposition of fly ash. In the corrosion product of middle layer, K, Na and Cl, S are enriched, the corrosion product content of Fe declined dramatically, the content of Si, Al, Mg and Ca increases slightly. In the deposition corrosion product of outermost layer, Si, Al, Mg and Ca are enriched, the content of K, Na and Cl, S decreased obviously.

The XRD analyzed result of corrosion deposition in table 5 provides a guarantee for the further analysis of occurrence state. As shown in table 5, it only detects the K_2SO_4, the reason may be the Cl has evaporated by corrosion reaction, the low content of Cl causes that KCl cannot be detected, and the Na content in the straw fuel is low, Na_2SO_4 and NaCl also cannot be detected. In the middle layer of corrosion product it detects the KCl, NaCl, K_2SO_4 and $K_3Na(SO_4)_2$, without Na_2SO_4. The reason is the Na content is low and the Na_2SO_4 which produced reacts with K to form the $K_3Na(SO_4)_2$. In the outermost layer of corrosion product it detects the KCl, SiO_2, $CaSO_4$.

Table 4. SQX Analyzed Results of Corrosion Deposits

Composition	K_2O	Na_2O	Fe_2O_3	SO_3	Cl
Inner layer	3.67	0.17	49.19	6.13	0.98
Middle layer	17.11	1.34	9.19	7.88	10.19
Outermost layer	4.11	0.16	3.01	2.74	0.19
Composition	Al_2O_3	SiO_2	CaO	MgO	P_2O_5
Inner layer	6.37	15.89	1.58	8.49	1.66
Middle layer	9.12	25.14	3.77	9.53	1.91
Outermost layer	12.12	59.38	7.67	7.29	1.52

Table 5. XRD Analyzed Results of Corrosion Deposits

Position	Main substance
Inner layer	Fe_2O_3、K_2SO_4
Middle layer	KCl、NaCl、K_2SO_4、$K_3Na(SO_4)_2$
Outermost layer	KCl、SiO_2、$CaSO_4$

As shown in above analysis, the result of fuel theoretical analysis is in line with fly ash sediment of actual straw boiler combustion product, the fly ash deposition at the temperature of 850～950℃(about 1100K) are main KCl, NaCl, K_2SO_4 and Na_2SO_4. It needs to determine the ratio relationship of each content after the corrosion medium is determined. The corrosion medium quality ratio relationship is determined base on the proximate analysis of straw (table 1) and component analysis of straw ash (table 3). According to component analyzed data of straw fuel ash, the content of K_2O in the fly ash is 10.27%, Na_2O is 1.34%, SO_3 is 2.8%, Cl is 9.27%. As most inorganic substances in the ash exists in the form of oxide when the component detection and analyzing, it cannot be shown in the form of chlorides and sulfide, it can be considered the K, Na, Cl, S in the ash all form the alkali metal chlorides and sulfide, the content ratio of the alkali metal chlorides and sulfide is the maximum of alkali metal ratio, the maximum of corrosion sediment content approach. According to above contents, it obtains the mass ratio of KCl, NaCl, K_2SO_4 and Na_2SO_4 is 63:13:5:1 by the conversion relation of the mass ratio and molar ratio.

5. Analysis on the Micro Morphology and Element

According to the mass ratio of deposit corrosion medium and operation status of biomass boiler, the corrosion simulation experiment is designed. The experiment material is 20G which commonly used in biomass boiler, the mass ration of corrosion medium that smeared on the specimen is KCl: NaCl: K_2SO_4: Na_2SO_4=63: 13: 5: 1, it reacts at four temperature: 500℃, 550℃, 600℃ and 650℃, the reaction cycle is 20h.

The surface morphology of 20G that reacted 20h at two temperatures is shown in figure 2. As shown in figure 2:

(1)The specimen surface is dense after corrosion, but it still produces some invisible granular corrosion product at 500℃.

(2)The corrosion products connect into a sheet and there are distinct thickening and bulge in the corrosion layer at 650℃.

The EDS analyzed result is shown in figure 3 and table 6.As shown in figure 3 and table 6, there are Fe, Cr, O, and a few K, Na, Cl on corrosion layer surface at 500℃, without Ni, S. The element detection result is Fe, Cr, Ni, O and little K, Cl. As shown in table 6, the content of Fe reduces, and the content of O, Cr, Ni increases during the reaction temperature change from 500℃ to 650℃. It shows that the corrosion of specimen aggravates with the temperature rising. According to the atomic percentage of Fe and O in table 6, the corrosion products at 500℃ main are FeO and little Cr_2O_3, without NiO. The corrosion products at 650℃ are FeO, Cr_2O_3 and a few NiO. According to the atomic percentage of K, Na, Cl and S, corrosion surface still exists un corroded salt, it also be seen from figure 2 (b) and (d), the bright spot particles and whiskers state material on the corrosion layer are the un cleaned salt.

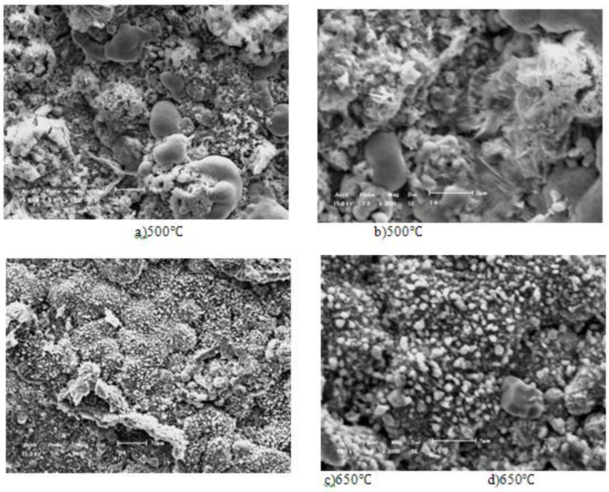
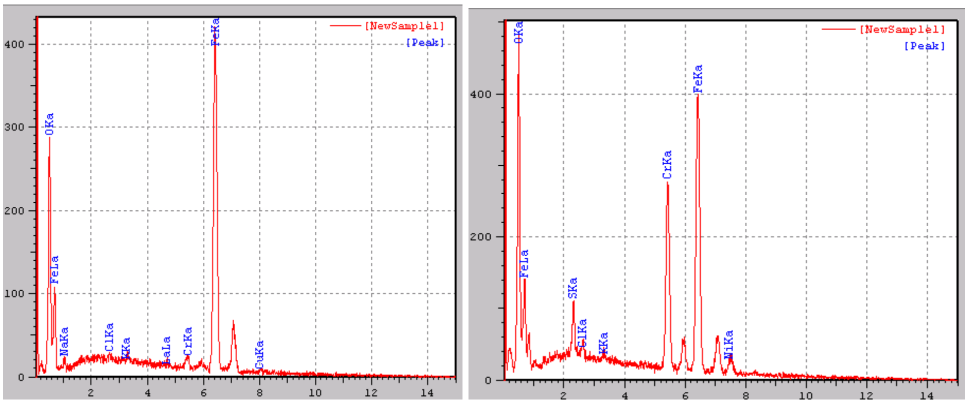


Figure 2. Surface Morphologies of 20g at Different Temperature after Corrosion for 20h



a) 500℃ **b) 650℃**

Figure 3. Surface EDS Spectra of 20g at Different Temperature after Corrosion for 20h

Table 6. Element Analysis of 20g Surface after Corrosion for 20h

temperature	Element atomic percentage							
	O	Fe	Cr	Ni	Cl	S	K	Na
500℃	48.827	47.697	0.854	/	0.517	/	0.152	1.333
650℃	52.865	29.207	12.392	2.528	0.356	2.429	0.223	/

6. Analysis and Discussion

At present, the deposit corrosion mechanism of biomass boiler heating surface pipe has not formed a unified understanding. It combines experiment and corrosion product analyzed to obtain the deposit corrosion process is roughly:

(1)Self catalytic oxidation reaction of chloride

The fly ash sediment on the biomass boiler heating surface reacts with Fe (some material also contains Cr) in the base material of heating surface tube in the condition of high temperature and aerobic environment, and releases stronger corrosive Cl_2, its response equation is:

$$2ACl(s) + yFe(Cr)(s) + (x/2)O_2(g) \rightarrow A_2Fe(Cr)_yO_x(s) + Cl_2(g) \quad (6)$$

In the equation: A is K and Na.

The Cl_2 reacts directly with base material of heating surface tube and produces metal chloride, its response equations are:

$$M+Cl_2 \rightarrow MCl_2 \quad (7)$$
$$2M+3Cl_2 \rightarrow 2MCl_3 \quad (8)$$
$$2MCl_2+Cl_2 \rightarrow 2MCl_3 \quad (9)$$

In the equation: A is Fe, Cr and Ni.

As the vapor pressure of metal chloride is usually higher, it readily penetrates the alkali metal chloride salt film on the heating surface tube, and diffuses outward. Along with the diffusion, oxygen potential rises. A part of metal chloride is oxidized again and produces metal oxide film and Cl_2, when oxygen reaches a specified level.

The diffusion process of metal chloride is: Mainly to explain by chloride of Fe. The high volatility metal chloride builds the concentration gradient of outward migration from metal internal of cation, and provides the power of migration which from the oxide film/metal interface of low O_2 partial pressure to gas phase/oxide film interface of high O_2 partial pressure. The holes which are formed by accumulation of the reverse flow holes keep the balance of migration of this ion [17]. Therefore, the chloride in oxide film/metal interface cooperates with the collective holes to make the continuous evaporation and diffusion of metal chloride at high temperature. Along with the diffusion, the partial pressure of O_2 rises, some chlorides are oxidized again during the diffusion process when the partial pressure reaches a specified level, its response equations are:

$$4MCl_2\,(g) + 3O_2\,(g) \rightarrow 2M_2O_3(s) + 4Cl_2(g) \quad (10)$$
$$4FeCl_3\,(g) + 3O_2(g) \rightarrow 2Fe_2O_3(s) + 6Cl_2(g) \quad (11)$$

In the equation: M is Fe, Cr and Ni.

The fly ash sediment on the boiler heating surface will reacts with metal oxide which is produced by above reactions [18], and it releases the strong corrosive Cl_2, its response equations are:

$$2ACl(s) + Fe_2O_3(s) + (1/2)\,O_2\,(g) \rightarrow A_2Fe_2O_4(s) + Cl_2(g) \quad (12)$$
$$2ACl(s) + (1/2)\,Cr_2O_3(s) + (5/4)O_2(g) \rightarrow A_2CrO_4(s) + Cl_2(g) \quad (13)$$

In the equation: A is K, Na.

The released Cl_2 return to heating surface tube and continue reacting with matrix surface until the alkali metal chloride is consumed.

The reactions that releases Cl_2 in equation (6) and (12) (13) are simultaneous, so the generation of Cl_2 is faster and the partial pressure of Cl_2 is higher.

The outward diffusion of metal oxide from equation (10) (11) and metal chloride from equation (7) (8) (9) will produce new stress. It will destroy the integrity of oxide film on heating surface; it causes the lamination of metal oxide film and desquamates of heating surface matrix. The outward diffusion of metal chloride is easier, Oxygen is easier to reach the matrix interface of heating surface from outside, and the corrosion is faster. Therefore, the existence of alkali metal chloride will promotes the corrosion reaction; the chloride in the sediment of biomass straw boiler heating surface has self-catalysis. So, the process of alkali metal chloride deposition corrosion is mainly self catalytic oxidation corrosion, it is similar to the active oxidation mechanism [19, 20].

(2)Low melting point eutectic corrosion

There is also following reaction in this experiment condition:

$$Fe+A_2SO_4 \rightarrow FeS+Fe_2O_3/\ Fe_3O_4/\ FeO+A_2O \quad (14)$$

In the equation: A is K, Na.

According to reference [21], this reaction belongs to second low temperature thermal corrosion reaction, producing the low melting point eutectic of A2SO4+A2O. The Fe2O3 which produced by above reaction will deposits on melt/gas interface from the side of oxide/melt where oxygen ion has high activity, and generates the osteoporosis corrosion layer.

7. Conclusion

(1) According to the analysis of S, Cl, K, Na content and the straw combustion characteristic, it obtains that the fly ash products are main alkali metal chloride (KCl, NaCl) during the combustion of straw fuel.

(2) According to the XRD analyzed result of corrosion tube in certain straw boilers, it determines the fly ash sediment are main KCl, NaCl, K_2SO_4, Na_2SO_4.

(3) According to above industry analysis and fly ash content analysis, it obtains the mass ratio of KCl, NaCl, K_2SO_4 and Na_2SO_4 is 63:13:5:1 by the conversion relation of the mass ratio and molar ratio.

(4) According to the corrosion morphology and corrosion products by scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) , it determines the process of alkali metal chloride deposition corrosion is mainly self catalytic oxidation corrosion.

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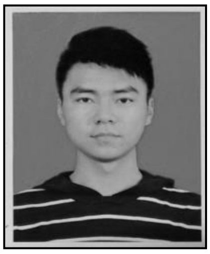

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