Research Article

Characteristics of Corrosion Related to Ash Deposition on Boiler Heating Surface during Cofiring of Coal and Biomass

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In order to investigate the regularity and mechanism of corrosion related to ash deposition on the boiler heating surface during cofiring of coal and biomass, the influence of fuel property, type of metal tubes (heating surface), proportion of blended biomass, and atmosphere in the furnace was studied by using the static corrosion mass gain method with the high-temperature tube furnace system. The results indicated that the effect of biomass property on ash corrosion is greater than that of coal, which was mainly due to high content of alkali metals and chlorine in biomass fuels. The corrosion resistance of metal pipes is $T91 > 12CrMoVG > 20G$. T91 is the most appropriate one, and it can effectively inhibit chlorine corrosion and can be used as the ideal material for the biomass-fired boiler and the biomass and coal cofired boiler. In addition, ash deposition can significantly aggravate the corrosion of metal tubes, and the degree of corrosion tends to become significant with increasing proportion of blended biomass fuels. HCl can aggravate metal corrosion, which can be inhibited by SO_2 .

1. Introduction

Because of the depletion of fossil fuels and their environmental pollution all over the world, the development and utilization of clean renewable energy has gradually drawn more attention, in which biomass energy receives much attention for its characteristics, including easy to burn and low emission of CO_2 , SO_x , NO_x , and other pollutants [1]. However, biomass fuels are generally low in heat value and also difficult to collect, transport, and store. There are problems in utilization of biomass such as high investment costs and low utilization efficiency. These problems can be solved by the biomass and coal co-combustion technology. The volatile content in biomass fuels is generally higher, typically more than 60%. With a small amount of blended biomass fuels, the ignition temperature of coal can be greatly reduced and ignition performance can be improved. Meanwhile, the equipment of cofiring of biomass and coal can be transformed from the original coal-fired equipment, which is more economical [2, 3].

Biomass fuels usually contain more alkali metals, alkali-earth metals, chlorine, and other elements. During biomass combustion, chlorine is released in the form of HCl and Cl_2 , reacting with the metal heating surface, causing severe active oxidation corrosion [4, 5]. Also, it can promote the gasification of the alkali metal elements in the fuel and react with alkali metals to form volatile alkali chloride in the gas phase [6]. The vast majority of gaseous alkali metals are deposited and condensed on the low-temperature metal heating surface. Furthermore, they trap solid particles in flue gas, which leads to serious slagging, fouling, and corrosion. The boiler parameters of an advanced coal-fired power plant are in the supercritical and ultra-supercritical states, and the parameters of a biomass boiler are still limited to high temperature and high pressure, which greatly restrains the improvement of boiler efficiency. High-temperature corrosion has always been a major obstacle to improve the boiler steam parameters. The temperature of a high-temperature superheater in a Danish biomass boiler must always be in control within $580^\circ C$. Main steam parameters of a Chinese biomass boiler

also tend to control within 450°C to avoid high-temperature corrosion, which is a serious disorder in massive scale utilization of the biomass energy [7, 8].

High-temperature chloride corrosion of biomass can be eased by cofiring with coal or additives. A biomass and coal cofiring boiler can reach the same steam parameters as the coal-fired boiler; at the same time, it can ensure the low emission of pollutants [9]. In biomass and coal cofiring boilers, due to the high content of Si and Al in coal, most of the alkali metals exist in the form of aluminosilicate with lower reactivity and higher melting point, thus decreasing the content of chlorine and viscosity of the ash deposition, which means the corrosion related to ash deposition is slowed down [10]. Due to the high content of sulfur in coal, the SO₂ content in the atmosphere increases, which leads to sulfur oxide corrosion. Meanwhile, the composition of the deposition becomes complicated. If the content of alkali in the fuel is high, sulfur oxide will conduct complex reactions with the alkali to form low-melting point compound sulfate, focal sulfate, and other complex low-temperature comelts, which lead to local liquid phase appearance. The protective oxide film on the surface of the tube wall is damaged, thus resulting in more corrosion [11].

Due to the reaction of multiphase gases, liquids, and solids, the combustion mechanism of biomass cofiring with coal is more complicated. The high content of chlorine in the biomass and sulfur in the coal will cause serious ash deposition and corrosion problems on the heat exchange surface of the boiler, which reduce the heat transfer efficiency of the heating surface and even harm the boiler operation safety. It has become one of the most serious problems restricting the application of biomass combustion. Therefore, this research focuses on the corrosion related to ash deposition during biomass and coal cofiring. By simulating the cofiring environment of biomass and coal, the regularity and mechanism of corrosion related to ash deposition during cofiring of biomass and coal under different fuel properties, type of metal tubes (heating surface), proportion of blended biomass, and atmosphere in the furnace were explored. It provides a theoretical basis for the effective utilization of biomass fuels and the optimization of boiler operating parameters.

2. Materials and Methods

2.1. Experimental Samples. Common crops in Shandong province are used as biomass fuels: straw, corn stalk, and cotton stalk. Lean coal and bitumite are used as blended coal. Proximate and ultimate analysis of fuels is shown in Table 1. Table 2 shows the elemental analysis of ashes. The data in the tables are the weight percentage. Before the experiment, fuels are separately ground to 20 mesh. and dried in the drying oven at a constant temperature of 100°C and then stored under seal. Experimental ash samples are fired according to the standard material (coal ash) using a mixture of biomass fuels and coal by weight ratio [12]. The proportion of blended biomass is 0%, 20%, 50%, 70%, and 100%. The metal samples 12CrMoVG, 20G, and T91 are taken from power plants in Shandong. Through wire

cutting and other metal processing methods, the samples are made into 20 mm × 3 mm × 3 mm standard size. The metal samples are polished before experiment using 200, 500, and 1000 grit sand paper sequentially in order to remove the last traces and get a unified standard sample surface. Their size is measured by a vernier caliper to calculate the surface area, followed by washing in acetone to remove the fouling on the metal surface. After drying with a filter paper, they are placed in the drying oven at a constant temperature 100°C for 20 min. The chemical composition of the metal materials is shown in Table 3.

2.2. Experimental System. The experimental system is shown in Figure 1. Due to the higher content of chlorine in biomass fuels, it mainly exists in the form of HCl in the combustion process, and sulfur in the coal is almost completely oxidized to SO₂. Therefore, this experiment mainly investigates corrosion characteristics of ash deposits under the coexistence atmosphere of sulfur chlorine in the gas phase. In the mixed gas, N₂ is the balance gas. The concentration of O₂ is kept at 6%, while CO₂ is maintained at 12%. The content of HCl and SO₂ is adjusted through a flow meter. They are mixed well in the gas mixing device in order to simulate the flue gas atmosphere in the boiler superheater [13]. The high-temperature reaction part adopts a horizontal tube furnace electric heating system. The temperature is under precise control by using an intelligent PDI temperature controller and solid state relay (SSR). The temperature difference between the constant temperature section in the reaction zone is less than 5°C. Exhaust gas treatment adopts NaOH solution to absorb excess SO₂ and HCl to avoid polluting the environment.

2.3. Experimental Procedure. The metal samples are coated with the synthetic deposits: first, the deposited sample are prepared in a suspension liquid with anhydrous ethanol, smeared evenly it on the surface of metal samples, and the amount of plaster is controlled at 15 mg/cm². Then, the samples are placed into the oven at a constant temperature of 100°C for 20 min to remove the residual ethanol solution. The metal samples covered with synthetic deposits are placed into the constant temperature section of the horizontal tube furnace to carry out the corrosion experiment. The concentration of HCl and SO₂ is changed to investigate the effect of different atmospheres on corrosion. The total air flow is controlled at 120 mL/min, and the temperature is controlled at 600°C. Preliminary experiments show that the corrosion weight gain of samples increases rapidly in the early stage (within 15–20h), but tends to be stable in the later stage. [9]. The whole process presents the regularity of a similar parabola curve. For the convenience of quantitative analysis, the parabola fitting for the corroded weight curve is carried out. The equation is as follows:

$$\Delta G = k\tau^{1/2} + C, \quad (1)$$

where k is a rate constant of the parabolic curve, characterizing the reaction rate of corrosion, and C is the

TABLE 1: Proximate and ultimate analysis of fuels (air-dried) (%).

Fuel	Sample number	Proximate analysis			Ultimate analysis						
		M _{ad}	A _{ad}	V _{ad}	FC _{ad}	C _{ad}	O _{ad}	H _{ad}	N _{ad}	S _{ad}	Cl _{ad}
Straw	B1	8.22	7.05	65.62	19.11	40.87	37.22	5.71	0.78	0.15	0.31
Corn stalk	B2	7.96	8.32	65.46	18.26	40.51	36.58	5.83	0.67	0.13	0.065
Cotton stalk	B3	5.67	4.23	69.74	21.38	44.26	38.94	6.32	0.50	0.08	0.074
Bitumite	C1	4.35	20.69	35.18	39.79	61.02	7.54	4.01	1.18	1.21	–
Lean coal	C2	1.30	34.94	10.15	53.62	55.27	3.27	2.96	0.61	1.65	–

TABLE 2: Major ash constituents in fuels (%).

Fuel	K	Na	Ca	Mg	Al	Si	Fe
Straw	1.96	0.78	0.84	0.072	1.69	1.83	0.17
Corn stalk	1.88	0.64	1.20	0.069	3.16	2.24	0.16
Cotton stalk	0.86	0.35	0.84	—	1.65	0.51	0.25
Bitumite	0.081	0.11	1.05	0.50	15.87	21.71	3.99
Lean coal	0.098	0.16	1.61	0.86	15.38	24.36	5.66

integration constant, indicating the deviation of the parabola curve on the initial corrosion reaction caused by kinds of factors. The following experimental cycle is selected: 30 h, weighed every 6 h, in order to obtain a corrosion mass gain curve. For analyzing the cross section of the corrosion layer, the metal sample is first fixed with the epoxy resin and cured at normal temperature for 24 hours. It is cut transversely with a small cutter, and then the cross section is polished with a polisher. The SEM is used to observe the morphological characteristics of the corrosion layer on the cross section of the metal sample; the energy dispersive spectrometer (EDS) is used to detect the elemental composition of several regions in the corrosion layer.

3. Results and Discussion

3.1. Effect of Fuel Property on Deposit Corrosion. Deposit corrosion properties are quite different because of the difference in characteristics of biomass fuels. In this paper, common biomass fuels (wheat straw, corn stalk and cotton stalk) and different types of coals (lean coal and bituminous coal) are blended to combust in the weight ratio of 1:1 to study the effect on deposit corrosion caused by different fuel characteristics under the coexistence atmosphere of sulfur and chlorine. Figure 2 shows the fitting curve of the increased weight for 12CrMoVG metal samples under the coexistence atmosphere of sulfur and chlorine using different synthetic deposits at 600°C. The fitted correlations are shown in Table 4. R^2 in Table 4 represents a coefficient of determination or a goodness of fit, which refers to the degree to which the regression line fits the observed value. The value of R^2 in the table is close to 1, indicating that the regression line fits the observations well.

It can be seen from Figure 2 that the weight of metal samples increases with time. It increases faster in the initial stage and gradually decreases in the later stage. The corrosion weight curve is approximately parabola. This is because, in the initial stage, the oxidative corrosion reaction rate is high and a thin oxide layer is quickly formed on the metal surface. As the corrosion reaction continues, the oxide

layer gradually becomes thicker, preventing the metal from direct contact with the reactants and slowing down the corrosion reaction. The corrosion weight of the metal samples increases with time, and its variation curve is parabola: $\Delta G = k\tau^{1/2}$. The corrosion is intensified when the samples are covered by deposits. And it shows significant difference in the degree of corrosion with the changes in fuel properties. The corrosion performance of biomass fuels from strong to weak is as follows: wheat straw, corn stalk, and cotton stalk. The corrosion of lean coal is more intense than bituminous coal when the same biomass fuel blends with different coals.

From analysis of rate constant k of the parabolic curve in Table 4, it can be seen that the effect of biomass fuels is significantly greater than the effect of coal. The component of deposits varies widely as the fuel characteristics, combustion conditions, and other factors. Lith et al. [13] suggest that the corrosion in the process of cofiring of biomass and coal is mainly based on the alkali metals existed in deposits. They react directly with the wall metal of the heat exchanger, causing the corrosion of the metal matrix. Also, they generate low-temperature eutectic with other compounds. Sometimes, it can even cause serious electrochemical corrosion. So, the damage of deposit corrosion is larger.

Ash deposition mainly exacerbates corrosion through two effects. First, the corrosive salts such as KCl and NaCl directly chemically react with the metal, resulting in intensified active oxidative corrosion at the heating surface; second, the formation of complex low-temperature eutectic melts destroys the oxide film on the metal surface and causes electrochemical corrosion. From the content of major ash constituents in Table 2, it can be seen that the content of alkali metals and chlorine is the highest in wheat straw. The alkali metal content in corn stalk is slightly lower than that in straw. However, the chlorine content is significantly lower than that of wheat straw. The cotton stalk and corn stalk have a similar chlorine content. However, it is lowest for alkali metal content in cotton stalk, even less than half of the two former. So, it is visible that the component of alkali metals and chloride in biomass fuels are the main cause of ash deposit corrosion. The component of alkali metals and chlorine in biomass fuels is obviously higher than that in the coal. Also, there is a large difference. So the effect of the difference between biomass fuels on corrosion is larger than the effect of the coal.

During cofiring of coal and biomass, due to the fixing effect of Al and Si in the ash on the alkali metals, most of the chlorine released in the form of gas phase HCl or Cl₂, the

TABLE 3: Elemental composition of the heating surface metal (%).

Steel	C	S	P	Si	Mn	Cr	Mo	V	Cu	Ni
12CrMoVG	0.08~0.15	≤0.03	≤0.03	0.17~0.37	0.40~0.70	0.90~1.20	0.25~0.35	0.15~0.30	≤0.20	≤0.25
20G	0.17~0.24	≤0.03	≤0.03	0.17~0.37	0.35~0.65	—	—	—	—	—
T91	0.08~0.12	≤0.02	≤0.02	0.02~0.50	0.30~0.60	8.00~9.50	0.85~1.05	0.18~0.25	—	≤0.40

FIGURE 1: The schematic diagram of the experimental system. 1, gas cylinder; 2, gas flowmeter; 3, mixing equipment; 4, gas valve; 5, PID temperature controller; 6, tube furnace; 7, thermocouple; 8, porcelain boat; 9, corundum tube; 10, absorber bottle.

FIGURE 2: Curves of corrosion mass gain of different metal samples coated with different fuel ash.

alkali metal was mostly in the form of silicate, aluminosilicate, and sulfate, and only a very small amount of Cl remained in the ash, and the chemical activity of the ash was relatively stable. Generally, Ca and Mg in fuels do not exist in the form of chlorides during combustion, but they still affect the content of active corrosion components in the ash by complex reactions. When the content of Ca or Mg in fuels is high, most of the Al will react with it to form compounds such as MgAl_2O_4 , CaAl_2O_4 , etc., so that the fixation of Al to the alkali metal is weakened, and the content of alkali metal chloride in the ash is correspondingly increased.

There is a high content of ash in lean coal and bitumite. The composition of the oxide in ash is based on SiO_2 and Al_2O_3 [14] and is mostly considered to be inert. Through the study, Li et al. [15] find that the oxide from ash can be divided into basic oxide and acidic oxide, where the basic oxide has lower ionic energy as important composition of low-melting eutectic mostly. Alkali metals and alkali-earth metals content such as Na, K, Ca, Mg, and others in the ash of lean coals is higher than that of bitumite coals. The alkaline component in ash generated by cofiring of the same biomass fuels and lean coals is certainly higher than bitumite coals. So, it results in increase in the content of low-melting point eutectic in deposits, which can accelerate the corrosion. Meanwhile, sulfur content of lean coal is high. It can be also easy to cause the molten salt corrosion of alkali metal sulfate in deposits [11]:

3.2. Effect of Pipe Components on Deposit Corrosion. The deposit corrosion of the superheater varies while the pipe components are different. Under simulated condition, the contents of HCl and SO_2 in the flue gas are both 500 $\mu\text{L/L}$, and blended percent of straw and lean coal is, respectively, 50%. The fitting curve and fitting correlation of the corrosion weight gains of the tube metal materials including 12CrMoVG, 20G and T91 are shown in Figure 3. It can be

TABLE 4: Fitting correlations of corrosion mass gain of different metal samples coated with different fuel ash.

Fuels	Fitting correlations ($\Delta G = k\tau^{1/2} + C$)	k	R^2
No fuel ash	$\Delta G = 0.1695\tau^{1/2} - 0.19802$	0.1695	0.98618
50%B1 + 50%C1	$\Delta G = 0.39923\tau^{1/2} - 0.36598$	0.3992	0.99751
50%B1 + 50%C2	$\Delta G = 0.37439\tau^{1/2} - 0.38188$	0.3744	0.99388
50%B2 + 50%C1	$\Delta G = 0.29955\tau^{1/2} - 0.24879$	0.2996	0.99752
50%B2 + 50%C2	$\Delta G = 0.23953\tau^{1/2} - 0.11091$	0.2395	0.96897
50%B3 + 50%C1	$\Delta G = 0.19297\tau^{1/2} - 0.08606$	0.1930	0.97963
50%B3 + 50%C2	$\Delta G = 0.18106\tau^{1/2} - 0.09793$	0.1811	0.97704

seen that the corrosion resistance of three kinds of metal materials from strong to weak is T91, 12CrMoVG, and 20G. The corrosion resistance of T91 is much higher than that of the latter two. From the beginning of the reaction to about 10 h, the increase in corrosion mass gain appears to be not obvious. The corrosion resistance of 12CrMoVG is slightly better than that of 20G. Nevertheless, from the corrosion reaction rate k , it can be seen that the difference between the two is nonobvious.

In the initial corrosion reactions, each of elements in metals participates in the corrosion reaction. Cr can react preferentially with oxygen in the atmosphere as a crucial element in alloy, form the oxide film with dense and adhesive properties, and produce the passivation phenomenon, so that the corrosion resistance of metals can be enhanced. However, when the temperature rises, the diffusion velocity of C in the interior of the metal grain is greater than that of Cr. The formation and precipitation of carbides make the chrome poor locally near the grain boundary. NaCl from deposits is easy to react with metal carbide generated Cl_2 , which can increase the susceptibility to intergranular corrosion and cause serious intergranular corrosion. The reaction equation is as follows (M represents the metal of the heat transfer surface) [16]:

The sectional micromorphology of 20G after the deposit corrosion experiment is shown in Figure 4. The corrosion resistance performance of 20G is the worst as plain carbon steel without any addition of other alloying elements. The surface of the corrosion layer is loose and porous, and there is a large gap in the surface of the metal substrate. The adhesion of the corrosion layer is poor and cannot effectively prevent the corrosive medium HCl/SO_2 in the gas phase from further erosion of the metal. Because of the major Cl element in the biomass fuel, the content of gaseous HCl and Cl^- of deposits increases while cofiring of biomass and coal. As very small atom radius, Cl atom tends to agglomerate to the location of the defects on the metal heating surface, even directly pass through the oxide film on metal surface, and lead to pitting corrosion. When deposits contain alkali metal chlorides, they will directly react with the metal oxide film and continue to cause corrosion. The reaction equations are as follows:

FIGURE 3: Curves and fitting correlations of corrosion mass gain of metal samples coated with ash.

FIGURE 4: Sectional topography of 20G after deposition corrosion.

12CrMoVG is superior to use as stainless steel in terms of corrosion resistance than 20G. But it is not very perfect in corrosion resistance to use for biomass-fired boiler due to the high Cl content in biomass fuel. Wang et al. [17] found that adding Mo and Ni elements into alloy can improve the microeutectic structure of metals, suppress the intergranular corrosion and pitting corrosion effectively, and improve the adhesion of protective oxide film, thereby improving the corrosion resistance of metals. When the Mo content is more than 3% in steel, it can significantly inhibit the penetration of Cl into metallic matrix.

FIGURE 5: Sectional topography of T91 after deposition corrosion.

The sectional micromorphology of T91 is shown in Figure 5. For T91, Cr content is more than that of 12CrMoVG by an order of magnitude. The content of trace elements such as Mo and Ni in T91 is also higher than that in 12CrMoVG. A dense protective film is formed between the metal matrix and the deposit corrosion layer. The corrosion film is thin and has a good combination with the metal matrix. It can isolate the metal matrix from the surrounding corrosive environment. So, the corrosion resistance is the strongest. In addition, it can be used as the ideal material for the cofiring boiler of biomass and coal.

3.3. Effect of Proportion of Blended Fuel on Deposit Corrosion.

Figure 6 shows the fitting curve of the increased weight for 12CrMoVG under the coexistence atmosphere of sulfur and chlorine, using synthetic deposits with different blending ratios of wheat straw. The fitted correlations are shown in Table 5. The relation curve between the coefficient indicating corrosion rate k and the proportion of blended biomass λ is shown in Figure 7. From Figure 6, final corrosion weight of metal samples increases with the proportion of blended biomass. However, this increase does not show regularity of weighted average according to the proportion of blended biomass and coal.

When the proportion of blended wheat straw is more than 20%, the ash deposit shows the obvious accelerated corrosion phenomenon on the metal samples. From 50% to 70%, it changes little for the increased corrosion weight. When the proportion of blended biomass is more than 70%, the value of k increases obviously. When the proportion of blended wheat straw is 100%, the corrosion degree is most serious. Compared with the sample with ash added, the weight of the metal sample with ash added increases slightly, but not significantly, while the ash is pure lean coal ash. Therefore, each composition of the ash generated by combustion of pure coal works little for the metal corrosion. In addition, the addition of lean coal in the combustion effectively inhibits the corrosion caused by wheat straw.

As shown in Table 6, from the analysis of EDS elements of different gray samples, it was found that there were significant differences in the content of the corrosive key elements in ash when different proportion of blended biomass was burning. When the proportion of blended wheat straw is 100%, the content of alkali metals and chlorine in deposits is high. In addition, it is mainly in the

FIGURE 6: Curves of corrosion mass gain of metal samples coated with ash under different proportion of straw biomass blended to coal.

form of chlorides and other substances with a strong chemical reaction activity. The corrosion is the most severe: on the one hand, it can directly cause severe active oxidation corrosion; on the other hand, as the reaction is prolonged, alkali metal chloride such as KCl can react with the corrosion products FeCl_2 and CrCl_2 and produce the eutectic with a melting point of 355°C and 470°C , respectively. Also, the melting point of the eutectic formed with FeCl_3 is even as low as $202\text{--}220^\circ\text{C}$ [18], thereby enabling ash deposition to appear liquid phase and resulting in more severe corrosion. The deposit corrosion activity declines significantly with the adding of the lean coal. The Cl content has decreased obviously while blending 50% lean coal into wheat straw. There is a high content of sulfur in lean coal. While cofiring of wheat straw and lean coal, the partial pressure of SO_2 increases in the atmosphere, and the activity of alkali metal chloride decreases because of the sulfate reaction in deposits [19]. The corrosion was obviously reduced. Meanwhile, Si and Al elements in the coal can react with alkali metal chloride and form aluminosilicate [20], so that the corrosion of deposits has a further reduction.

When the proportion of blended wheat straw reduced from 70% to 50%, the deposition corrosion degree decreased slightly, but not obvious. With the increase in lean coal blending ratio, alkali metal compounds will form low-melting eutectics with SiO_2 , aluminosilicate, sulfate, etc. For example, the melting temperature of $\text{K}_2\text{O}\cdot 4\text{SiO}_4$ is 764°C , and $\text{KCl}\text{--}\text{K}_2\text{SO}_4\text{--}\text{Fe}_x\text{O}_y$ will melt at 557°C . The appearance of some trace elements such as Pb, Zn, and Ni will also lead to the increase of low-temperature eutectic materials in the ash, and the local liquid phase will appear and lead to serious electrochemical corrosion [19, 21]. With increasing proportion of blended wheat, the corrosion rate has an unobvious change when the proportion of blended wheat straw is lower than 20%. Montgomery et al. [22] find

TABLE 5: Fitting correlations of corrosion mass gain under different proportion of straw biomass blended to coal for metal samples coated with ash.

Proportion of straw biomass blended to coal (%)	Fitting correlations ($\Delta G = k\tau^{1/2} + C$)	k	R^2
100	$\Delta G = 1.2737\tau^{1/2} - 1.6477$	1.2737	0.9945
70	$\Delta G = 0.3913\tau^{1/2} - 0.2843$	0.3913	0.9967
50	$\Delta G = 0.3992\tau^{1/2} - 0.3659$	0.3992	0.9975
20	$\Delta G = 0.2221\tau^{1/2} - 0.1707$	0.2221	0.9894
0	$\Delta G = 0.1906\tau^{1/2} - 0.2145$	0.1906	0.9969
No fuel ash	$\Delta G = 0.1695\tau^{1/2} - 0.1980$	0.1695	0.9862

FIGURE 7: Curves of coefficient indicating corrosion rate versus proportion of straw biomass blended to coal.

TABLE 6: Content of elements in different ash.

Element	Na	Al	Si	S	Cl	K
Straw ash	0.433	7.602	10.855	2.54	13.521	21.529
Lean coal	0.612	28.169	33.481	0.837	0.412	0.262
50% straw and 50% lean coal ash	0.498	17.635	25.282	3.911	0.649	7.076

FIGURE 8: Curves and fitting correlations of corrosion weight gain of the metal samples coated with ash under different atmospheres. (a) HCl: 500 $\mu\text{L/L}$, not containing SO_2 . (b) SO_2 : 500 $\mu\text{L/L}$, not containing HCl.

that all KCl transform into noncorrosive alkali aluminosilicate while cofiring blended with 20% biomass. Then, sulfate corrosion plays a main role, but the corrosion is weakened dramatically. It is also consistent with the experimental results of this paper.

3.4. Effect of Atmosphere in Furnace on Deposit Corrosion.

The effect of the change of the atmosphere in the furnace on deposit corrosion is shown in Figure 8. The increased weight curves and the fitting correlations when the blended proportion of wheat straw is 50%, 70%, and 100% under the simulating flue atmosphere containing 500 $\mu\text{L/L}$ HCl only are shown in Figure 8(a) while the simulating flue only contains 500 $\mu\text{L/L}$ SO_2 in Figure 8(b). With the increase of wheat straw ratio, it tends to be severe for the corrosion of samples when the flue gas only contains HCl. Comparing with the situation under the coexistence atmosphere of sulfur and chlorine (Figure 6), it can be found that the degree of corrosion is intensified significantly when the proportion of blended wheat straw increases from 50% to 70% under the atmosphere of HCl merely. Once the SO_2 is mixed, the corrosion will be inhibited obviously. Also, the increased weight of the metal samples covered with combustion ash by 70% wheat straw and lean coal is even less than 1/2 of that under the HCl atmosphere. The corrosion rules of samples under the atmosphere containing only 500 $\mu\text{L/L}$ SO_2 are similar with the rules under the coexistence atmosphere of sulfur and chlorine. There is a further reduction in the increased corrosion weight. However, the reduction is not obvious, and the corrosion rate does not appear to be significant. So, when the SO_2 content in the atmosphere is certain, the corrosion effect of HCl on samples is obviously weakened.

The analysis of the above test results shows that the corrosion of the metal samples caused by the change of the atmosphere is affected by the characteristics of the deposits in the metal wall. The corrosion degree of the samples under different atmospheres tends to be severe with the increase of the blending ratio of biomass. When the simulated flue gas contains only HCl, both KCl from the deposits and HCl from the gas can cause metal corrosion. The corrosion of the metal by SO_2 is mainly reflected in the early rapid corrosion stage. As the reaction proceeds, SO_2 reacts with the alkali metal salts in the ash to form products with lower activity, such as sulfate, chromate, and oxide, which can evenly cover the metal surface, and a similar passivation state appears between the metal and the gas phase interface, which inhibits further corrosion.

However, under different atmospheres, it can be seen that the corrosion of the metal samples covered with wheat straw burning ash is still very serious and is not under the control obviously with the adding of SO_2 . Broström et al. found that sulfation of alkali chlorides is mainly based on SO_3 content in the atmosphere [23, 24]. When the KCl content in deposits is high enough, the inhibitory effect of SO_2 on corrosion is weakened, and the corrosion is mainly based on KCl from deposits. When SO_2 forms a metal protective layer on the metal surface, it will undergo a sulfation reaction with KCl in the ash deposit, which will increase the partial pressure of HCl at the wall, and the active

oxidative corrosion reaction of chlorine will intensify. KCl will also destroy the protective layer of the metal surface and intensifies the corrosion reaction.

4. Conclusions

- (1) During cofiring of different biomass fuels with coals, characteristics of corrosion show obvious differences. Effect of corrosion from strong to weak is as follows: wheat straw, corn stalk, and cotton stalk, because the content of alkali metals and chlorine in wheat straw is significantly higher. During cofiring of the same biomass fuels with different coals, the corrosiveness of lean coal is stronger than that of bituminous coal. The content of alkaline metal oxides and sulfides in coal ash is relatively high, and it will also cause ash melt corrosion.
- (2) The corrosion resistance on three kinds of common boiler metal materials is as follows: T91, 12CrMoVG, and 20G. This is because T91 contains more Cr, which can form a dense oxide film to slow down corrosion. The content of Mo and Ni is more than that in the other two metals, which improves the microeutectic structure of the metal. The corrosion resistance of 12CrMoVG is not much better than that of 20G. T91 can effectively inhibit the rate of corrosion, and it can be used as the ideal metal materials of the heat transfer surface in biomass and coal cofired boilers.
- (3) The degree of ash deposit corrosion enhances with the increase in the proportion of blended wheat straw. Under the atmosphere with coexistence of sulfur and chlorine, when the proportion of blended wheat straw is greater than 70%, the corrosion rate decreases significantly with the addition of coal. When the proportion decreases from 70% to 50%, the metal corrosion weight reduces slightly. When the proportion is as low as 20%, it can be regarded that alkali metal chlorides in deposits are all converted into aluminosilicate and sulfate, and the corrosion rate shows no obvious change with the increase in the proportion of blended biomass.
- (4) The metal corrosion caused with the atmosphere change is influenced by the ash property. HCl in atmosphere can aggravate the metal corrosion. The presence of SO_2 significantly inhibits HCl corrosion through the sulfate reaction. Especially when the proportion of blended wheat straw is below 70%, the inhibitory effect of SO_2 on deposit corrosion is more significant. When the proportion of blended wheat straw is 100%, the presence of SO_2 does not significantly inhibit corrosion due to the high KCl content in deposits.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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References

- [1] H. Raclavska, D. Juchelkova, V. Roubicek, and D. Matysek, "Energy utilisation of biowaste-sunflower-seed hulls for co-firing with coal," *Fuel Processing Technology*, vol. 92, no. 1, pp. 13–20, 2011.
- [2] Z. Ma, S. Wu, and Y. Bai, "Technical analysis on cofiring of coal and biomass," *Power System Engineering*, vol. 25, no. 6, pp. 1–4, 2009.
- [3] T. Wang, T. Kuang, Q. Fang et al., "Experimental study of coal/biomass mixture combustion in O₂/CO₂ atmosphere," *Thermal Power Generation*, vol. 46, no. 4, pp. 16–21, 2017.
- [4] Y. Wang, K. Zhang, L. Jiang et al., "Research on the co-corrosion characteristics of sulfur chloride in the combustion process of biomass mixed coal," *Journal of University Chemical Engineering*, vol. 6, pp. 1422–1429, 2015.
- [5] H. J. Grabke, E. Reese, and M. Spiegel, "The effects of chlorides, hydrogen chloride, and sulfur dioxide in the oxidation of steels below deposits," *Corrosion Science*, vol. 37, no. 7, pp. 1023–1043, 1995.
- [6] P. A. Jensen, F. J. Frandsen, K. Dam-Johansen, and B. Sander, "Experimental investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis," *Energy & Fuels*, vol. 14, no. 6, pp. 1280–1285, 2000.
- [7] Z. Wang, Y. Cao, and Z. Zhang, "Analysis and countermeasures of corrosion of high temperature superheater of biomass boiler," *Zhejiang Power*, vol. 35, no. 9, pp. 53–56, 2016.
- [8] W. Wei, F. Huang, C. Yu et al., "Primary investigation of high-temperature corrosion problems in biomass combustion equipment," *Energy Engineering*, vol. 2, pp. 23–28, 2011.
- [9] Y. Wang, L. Jiang, M. Yue et al., "Study on sulfur-chlorine synergistic corrosion in biomass and coal co-firing," *Proceedings of the CSEE*, vol. 29, no. 26, pp. 118–124, 2009.
- [10] A. L. Robinson, H. Junker, and L. L. Baxter, "Pilot-scale investigation of the influence of coal-biomass cofiring on ash deposition," *Energy & Fuels*, vol. 16, no. 2, pp. 343–355, 2002.
- [11] Y. Zhang, L. Shi, X. Li et al., "Alkali sulfate deposits induced hot corrosion of iron based alloys at intermediate temperatures," *Corrosion Science and Protection Technology*, vol. 4, no. 4, pp. 250–257, 1992.
- [12] X. Dong, R. Li, Z. Liu et al., "Investigation on the ash characteristic during co-firing of coal and biomass," *Proceedings of the CSEE*, vol. 29, no. 26, pp. 118–124, 2009.
- [13] S. C. V. Lith, F. J. Frandsen, M. Montgomery, T. Vilhelmsen, and S. A. Jensen, "Lab-scale investigation of deposit-induced chlorine corrosion of superheater materials under simulated biomass-firing conditions. Part 1: exposure at 560°C," *Energy & Fuels*, vol. 23, no. 7, pp. 3457–3468, 2009.
- [14] X. Li, Y. Wang, M. Yue et al., "Study on corrosion and influencing factors during co-combustion of coal and biomass," *Power Station System Engineering*, vol. 27, no. 6, pp. 13–15, 2011.
- [15] R. Li, Y. Nie, A. Li et al., "Study on physical chemical characteristics of fly ash from municipal solid waste incinerator," *Journal of Fuel Chemistry and Technology*, vol. 32, no. 2, pp. 175–179, 2004.
- [16] M. Mobin and A. U. Malik, "Studies on the interactions of transition metal carbides and sodium chloride in the temperature range 900–1200 K in oxygen," *Journal of Alloys and Compounds*, vol. 186, no. 1, pp. 1–14, 1992.
- [17] J. Wang, G. Zhang, and S. Li, "Investigation of microstructure and corrosive behavior of NiAl-31Cr-3Mo alloy at high temperature," *Mining and Metallurgical Engineering*, vol. 30, no. 6, pp. 93–96, 2012.
- [18] Y. Shinata, "Accelerated oxidation rate of chromium induced by sodium chloride," *Oxidation of Metals*, vol. 27, no. 5–6, pp. 315–332, 1987.
- [19] H. P. Nielsen, F. J. Frandsen, and K. Dam-Johansen, "Lab-scale investigations of high-temperature corrosion phenomena in straw-fired boilers," *Energy & Fuels*, vol. 13, no. 6, pp. 1114–1121, 1999.
- [20] M. Montgomery and O. H. Larsen, "Field test corrosion experiments in Denmark with biomass fuels. Part 2: co-firing of straw and coal," *Materials and Corrosion*, vol. 53, no. 3, pp. 185–194, 2002.
- [21] L. Jiang, Y. Wang, T. Yu et al., "Study on synergy corrosion mechanism of sulfur-chlorine during biomass and coal co-firing," *Power System Engineering*, vol. 29, no. 3, pp. 1–4, 2013.
- [22] M. Montgomery, T. Vilhelmsen, and S. A. Jensen, "Potential high temperature corrosion problems due to co-firing of biomass and fossil fuels," *Materials and Corrosion*, vol. 59, no. 10, pp. 783–793, 2008.
- [23] M. Broström, H. Kassman, A. Helgesson et al., "Sulfation of corrosive alkali chlorides by ammonium sulfate in a biomass fired CFB boiler," *Fuel Processing Technology*, vol. 88, no. 11–12, pp. 1171–1177, 2007.
- [24] K. Lisa, Y. Lu, and K. Salmenoja, "Sulfation of potassium chloride at combustion conditions," *Energy & Fuels*, vol. 13, no. 6, pp. 1184–1190, 1999.