Study on the Effect of Additives on the Corrosion to Metal Heating Surface Caused by Alkali Metal Chloride and Sulfate in Biomass-fired Boilers

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Abstract. In this paper, the horizontal tube furnace was used to study the inhibition effect of various additives on the corrosion to metal heating surface in biomass-fired boiler. The results showed that the corrosion rate of the metal samples was significantly reduced by kaolin, pulverized coal ash, silica fume, dolomite, limestone and bauxite. When kaolin, pulverized coal ash, silica fume and bauxite are used as additives, the corrosion is obviously inhibited. When dolomite and limestone are used as additives, the inhibition effect is poor, but the corrosion rate is also reduced. The corrosion ability of alkali metal chloride is greater than that of alkali metal sulfate. Different additives have different inhibitory effects on them.

1. Introduction
The effective use of biomass energy is an important way to solve the world energy problems. As a large agricultural country, China has huge reserves of biomass energy[1]. Power production from the biomass have good environmental and economic benefits, but there are also disadvantages, which are mainly caused by the characteristics of biomass fuel[2,3]. Biomass contains high alkali metal elements and chlorine elements, including K, Cl, Na, Ca, S and N, and it will form KCl, NaCl and other alkali metal salts at high temperature. In the process of combustion, alkali chloride and ash particles condense on the heating surface to form deposits. These deposits not only reduce the heat transfer efficiency of the heated surface, but also corrode the tube wall[4,5].

The main factors of the corrosion are: biomass composition, metal material on heating surface, temperature and atmosphere in the furnace[9]. Among them, the key factor is the composition. The alkali metal chloride in the flue gas is the main cause of the corrosion[7,8]. Therefore, adding additives to remove alkali metals and chlorine elements in biomass during combustion can reduce corrosion. Kaolin, pulverized coal ash, silica fume and other materials contain elements such as Al, Si and Ca, which are commonly used in additives[9,10,11]. They are also inexpensive and readily available as additives. In this paper, the horizontal tube furnace is used to simulate the furnace conditions, and the effects of different additives on the corrosion by alkali metal chloride and sulfate were studied.

2. Experimental Section
2.1. Experimental system
The experimental system consists of the gas distribution part, the heating part and the exhaust gas absorption device. The heating part is composed of a horizontal tube furnace, a KSY automatic temperature regulator and a chromel-silicel thermocouple. The experimental temperature is 600°C.
The gas distribution part consists of two steel cylinders A and B, a gas mixing device and a rotameter. The gas in the steel cylinder A is 12% CO₂, 6% O₂ and 82% N₂, and the gas in the steel cylinder B is N₂. The exhaust gas from the experiment was absorbed by saturated NaOH solution and discharged to the outdoor. The experimental system diagram is shown in Figure 1.

**Figure 1.** Horizontal tube furnace experimental system

1—air bottle, 2—flowmeter, 3—gas distributing device, 4—triple valves, 5—temperature controller, 6—horizontal tube furnace, 7—thermocouple, 8—combustion boat, 9—alumina tube, 10—flue gas absorbent solution

2.2. Samples

The ash samples are made of compounds such as NaCl, KCl, Na₂SO₄, K₂SO₄ and Fe₂O₃. The additives are kaolin, pulverized coal ash, silica fume, dolomite, limestone and bauxite. The steel used in this experiment is 15CrMoG, which is a common heating surface material in boilers. The components of the ash samples are shown in Table 1. The components of additives are shown in Table 2.

**Table 1.** The components of ash samples/%

| ash samples | KCl | K₂SO₄ | Na₂SO₄ | NaCl | Fe₂O₃ |
|-------------|-----|-------|--------|------|-------|
| D1          | 60.7| 4.8   | 1      | 12.5 | 20    |
| D2          | 60.7| 4.8   | 1      | 12.5 | 20    |
| D3          | 60.7| 4.8   | 1      | 12.5 | 20    |
| D4          | 60.7| 4.8   | 1      | 12.5 | 20    |
| D5          | 60.7| 4.8   | 1      | 12.5 | 20    |
| D6          | 60.7| 4.8   | 1      | 12.5 | 20    |
| D7          |     | 40    | 40     | 13.6 | 20    |
| D8          | 66.4|       | 13.6   | 20   | 13.6  |
| D9          |     | 66.4  | 13.6   | 20   | 13.6  |

**Table 2.** The components of additives/%

| additives        | SiO₂ | CaO | Al₂O₃ | MgO | Fe₂O₃ | SO₃ | TiO₂ | Na₂O | K₂O |
|------------------|------|-----|-------|-----|-------|-----|------|------|-----|
| kaolin           | 44.39| 0.23| 38.7  | /   | 0.89  | /   | 1.6  | /    | /   |
| limestone        | 1.2  | 51.5| 1.3   | 1.3 | 0.95  | /   | /    | /    | /   |
| dolomite         | 0.85 | 31.85| 0.22  | 20.86| 0.24  | 0.0041| /    | /    | /   |
| silica fume      | 86.5 | 0.3 | 1     | 0.7 | 0.9   | /   | /    | 0.9  | /   |
| bauxite          | 23.84| 57.88| 1.34  | 1.73 | 0.05  | 0.13| /    | /    | /   |
| pulverized coal ash | 50.8 | 3.7 | 28.1  | 1.2 | 6.2   | 0.8 | /    | 0.2  | 0.06|

2.3. Experimental procedure

The change in weight of the metal sample can reflect the corrosion rate. The ash sample was smeared on the steel at the content of 30 mg/cm². Then the combustion boat containing the sample was heated for 30 minutes and taken out in a drying dish. The sample was weighed and recorded as the initial weight of the experiment. The experimental system was ventilated for 30 minutes every 2.5...
hour after the start of the experiment. The combustion boat was taken out every 5 hours and weighed. The experiment was continued for 30 hours.

3. Results and Discussion

3.1. Effect of kaolin on corrosion

D1, D7 and D8 were mixed with kaolin, and the corrosion weight gain curve of 15CrMoG is shown in Fig. 2. Table 3 is the equation of the fitting curve, and $R^2$ is greater than 0.95, which means the curve conforms to parabola. It can be seen that the corrosion weight gain rate of the metal sample coated with D8 is larger, and the rate is increased by 27.4% compared with D1; the metal coated with D7 has a lower rate of corrosion growth and a 54.3% reduction in corrosion rate relative to D1. This indicates that the corrosion effect of alkali metal chloride is stronger than that of alkali metal sulfate, and alkali metal chloride plays a major role in corrosion of metal on the heated surface.

Kaolin reacts with alkali metal chloride as follows\cite{12}, M stands for Na or K:

$$2MCl+Al_2O_3\cdot2SiO_2\cdot2H_2O=2MAlSiO_4+H_2O+2HCl$$ (1)

Kaolin reacts with alkali metal chloride in ash to release chlorine element in the form of HCl gas, which reduces the content of Cl in sediments and thus reduces the corrosion on the heating surface.

Kaolin reacts with alkali metal sulfate as follows\cite{13}:

$$2M_2SO_4+2Al_2O_3+2SiO_2=4MAI_{SiO_4}+2SO_2+2O_2$$ (2)

Although kaolin can react with alkali metal sulfate, the spontaneous temperature of the reaction (2) is 597°C, so it is difficult to conduct the reaction on the heating surface in biomass-fired boilers. Kaolin as an additive has a significant inhibitory effect on the corrosion of alkali metal chloride, but not on the corrosion of alkali metal sulfate.

3.2. Effect of pulverized coal ash on corrosion

D2, D9 and D10 were mixed with pulverized coal ash, and the corrosion weight gain curve of 15CrMoG is shown in Fig. 3. Table 4 is the equation of the fitting curve. It can be seen that the corrosion weight gain rate of the metal sample coated with D10 is larger, and the rate is increased by 30.91% compared with D2; the metal coated with D9 has a lower rate of corrosion growth and a 17.5% reduction in corrosion rate relative to D2.
The reaction of pulverized coal ash with alkali metal chloride and sulfate is similar to kaolin[14]:

\[
2\text{MCl} + \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + \text{H}_2\text{O} = 2\text{MAlSiO}_4 + 2\text{HCl} \tag{3}
\]
\[
2\text{M}_2\text{SO}_4 + 2\text{Al}_2\text{O}_3 + 2\text{SiO}_2 = 4\text{MAlSiO}_4 + 2\text{SO}_2 + 2\text{O}_2 \tag{4}
\]

The effect of pulverized coal ash on the corrosion inhibition of alkali metal sulfate is not as good as that of kaolin, but it has obvious inhibitory effect on the corrosion of alkali metal chloride.

### 3.3. Effect of silica fume on corrosion

D3, D11 and D12 were mixed with silica fume, and the corrosion weight gain curve of 15CrMoG is shown in Fig. 4. Table 5 is the equation of the fitting curve. It can be seen that the corrosion weight gain rate of the metal sample coated with D12 is larger, and the rate is increased by 15.7% compared with D3; the metal coated with D11 has a lower rate of corrosion growth and a 8.6% reduction in corrosion rate relative to D3.

Silica fume contains SiO2, which reacts with alkali chloride as follows[15,16]:

\[
2\text{MCl} + \text{SiO}_2 + \text{H}_2\text{O} = 2\text{M}_2\text{SiO}_3 + 2\text{HCl} \tag{5}
\]
\[
2\text{MCl} + 2\text{SiO}_2 + \text{H}_2\text{O} = 2\text{M}_2\text{Si}_2\text{O}_5 + 2\text{HCl} \tag{6}
\]
\[
2\text{MCl} + 4\text{SiO}_2 + \text{H}_2\text{O} = 2\text{M}_2\text{Si}_4\text{O}_9 + 2\text{HCl} \tag{7}
\]

The temperature of reaction (5) is 544 °C, and the reaction can take place on the deposit layer of the heating surface. However, the temperature of reaction (6) and (7) is all over 900 °C, and it is difficult to conduct the reactions on the heating surface in biomass-fired boilers. Silica fume only releases part of the alkali chloride from the deposit.

Silica fume reacts with alkali metal sulfate as follows[17]:

\[
2\text{M}_2\text{SO}_4 + 2\text{SiO}_2 = 2\text{M}_2\text{SiO}_3 + 2\text{SO}_2 + 2\text{O}_2 \tag{8}
\]
\[
2\text{M}_2\text{SO}_4 + 4\text{SiO}_2 = 2\text{M}_2\text{Si}_2\text{O}_5 + 2\text{SO}_2 + 2\text{O}_2 \tag{9}
\]
\[
2\text{M}_2\text{SO}_4 + 8\text{SiO}_2 = 2\text{M}_2\text{Si}_4\text{O}_9 + 2\text{SO}_2 + 2\text{O}_2 \tag{10}
\]

The temperature of these reactions is more than 800 °C, which is difficult to occur on the heating surface in biomass-fired boilers. Therefore, silica fume has poor inhibitory effect on corrosion caused by alkali metal sulfate.

![Figure 4. Corrosion curve of silica fume](image1)

![Figure 5. Corrosion curve of dolomite](image2)

### Table 5. Fitting relation of silica fume

| Ash samples | Fitting relation | \( R^2 \) |
|-------------|-----------------|----------|
| D3          | \( \Delta G = -1.5441 + 3.3611 \tau^{1/2} \) | 0.9547   |
| D11         | \( \Delta G = -1.1215 + 3.0738 \tau^{1/2} \) | 0.9726   |
| D12         | \( \Delta G = -1.6658 + 3.8876 \tau^{1/2} \) | 0.9637   |

### Table 6. Fitting relation of dolomite

| Ash samples | Fitting relation | \( R^2 \) |
|-------------|-----------------|----------|
| D4          | \( \Delta G = -2.8800 + 4.4037 \tau^{1/2} \) | 0.9119   |
| D13         | \( \Delta G = -0.7302 + 3.5057 \tau^{1/2} \) | 0.9889   |
| D14         | \( \Delta G = -2.3738 + 5.7396 \tau^{1/2} \) | 0.9672   |
3.4. Effect of dolomite on corrosion

D4, D13 and D14 were mixed with dolomite, and the corrosion weight gain curve of 15CrMoG is shown in Fig. 5. Table 6 is the equation of the fitting curve. It can be seen that the corrosion weight gain rate of the metal sample coated with D14 is larger, and the rate is increased by 30.3% compared with D4; the metal coated with D13 has a lower rate of corrosion growth and a 20.4% reduction in corrosion rate relative to D4. As an additive, dolomite has a certain inhibitory effect on the corrosion of alkali metal chloride and alkali metal sulfate, and the corrosion inhibition effect on alkali metal sulfate is more significant.

3.5. Effect of limestone on corrosion

D5, D15 and D16 were mixed with limestone, and the corrosion weight gain curve of 15CrMoG is shown in Fig. 6. Table 7 is the equation of the fitting curve. It can be seen that the corrosion weight gain rate of the metal sample coated with D16 is larger, and the rate is increased by 41.2% compared with D5; the metal coated with D15 has a lower rate of corrosion growth and a 37.7% reduction in corrosion rate relative to D5. As an additive, limestone has a certain inhibitory effect on the corrosion of alkali metal chloride and alkali metal sulfate, and the corrosion inhibition effect on alkali metal sulfate is more significant.

| ash samples | fitting relation | Ra² |
|-------------|------------------|-----|
| D5          | ΔG=−3.0739+5.1368τ¹/₂ | 0.9317 |
| D15         | ΔG=−1.4205+3.2016τ¹/₂ | 0.9589 |
| D16         | ΔG=−1.9572+7.2541τ¹/₂ | 0.9824 |

3.6. Effect of bauxite on corrosion

D6, D17 and D18 were mixed with bauxite, and the corrosion weight gain curve of 15CrMoG is shown in Fig. 7. Table 8 is the equation of the fitting curve. It can be seen that the corrosion weight gain rate of the metal sample coated with D18 is larger, and the rate is increased by 54.2% compared with D6; the metal coated with D17 has a lower rate of corrosion growth and a 6.9% reduction in corrosion rate relative to D6.

Bauxite is mainly composed of alumina and silica, and the content of alumina is higher than that of pulverized coal ash and kaolin. The reaction between bauxite and ash is shown in formula (3) and (4). Bauxite has a certain inhibitory effect on the corrosion of alkali metal chloride and alkali metal sulfate. Since the silica content in bauxite is much lower than that of alumina, there is a phenomenon that the alumina component is excessive and the silica component is insufficient after the reaction, which restricts the inhibition effect of bauxite on corrosion. The corrosion inhibition effect of bauxite can be improved by blending silica fume.
4. Conclusion

This paper studies the corrosion regularity of the heating surface material of biomass-fired boilers by using kaolin, pulverized coal ash, silica fume, dolomite, limestone and bauxite as additives, and discusses the effect of additives on corrosion caused by alkali metal chloride and sulfate.

1. The corrosion rate of the metal samples was significantly reduced by kaolin, pulverized coal ash, silica fume, dolomite, limestone and bauxite. When kaolin, pulverized coal ash, silica fume and bauxite are used as additives, the corrosion is obviously inhibited. When dolomite and limestone are used as additives, the inhibition effect is poor, but the corrosion rate is also reduced.

2. The corrosion ability of alkali metal chloride is greater than that of alkali metal sulfate. Additives have a certain degree of inhibition on alkali metal chloride and alkali metal sulfate corrosion. Kaolin, pulverized coal ash and silica fume can inhibit the corrosion of alkali metal chloride better than alkali metal sulfate, while dolomite and limestone can inhibit the corrosion of alkali metal sulfate more significantly.

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