Analysis on Reaction Kinetics of High Temperature Corrosion to Metal Heating Surface in Biomass-fired Boiler

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Abstract. In this paper, the effect on temperature to biomass boiler corrosion is studied by corrosion weight gain experiment, and the thermal analysis model of high temperature corrosion is established by reaction kinetics using experimental results. The corrosion weight gain curve of the heating surface steel is in accordance with the parabola. The thermal analysis kinetics of T91 corrosion process is studied, and the data is matched with several functional models at 480°C to 680°C. The results show that the corrosion reaction is the two-dimensional diffusion type. The reaction kinetic equation was determined and the corrosion process was quantitatively analyzed.

1. Introduction
Excessive potassium and chlorine in biomass fuels can cause problems such as equipment corrosion and slagging in the furnace. These problems will affect the safety and stability of boiler operation, and also affect the efficiency of biomass boilers [1].

The corrosion of biomass boilers is divided into gas phase corrosion and ash corrosion. Gases such as HCl and Cl₂ cause gas phase corrosion. In an oxidizing atmosphere, the metal surface is oxidized to an oxide film, which prevents corrosion from proceeding further [2]. However, the gas chloride also reacts with the metal to form a metal chloride. The metal chloride is oxidized and releases Cl₂ again, and Cl₂ diffuses into the gas for a new round of reaction, which is named active oxidative corrosion [3]. In a reducing atmosphere, the metal oxide film is absent, and the Cl₂ can directly react with the metal.

Ash deposition is the main cause of high temperature corrosion of biomass boilers [4], due to the large amount of KCl in the ash. The sedimentary layer of ash is divided into three layers, wherein the innermost main component is KCl, the middle layer is K₂SO₄, and the outermost layer is mainly SiO₂ [5]. It was found that the precipitation of K in wheat straw, rice straw and rice husk was higher, and the precipitation of Cl in corn stalk and cotton stalk was higher [6]. KCl can directly react with the oxide film on the metal surface to form Cl₂, metal oxides and potassium compounds [7,8].

The corrosion weight gain experiment is used to investigate the influence of ash deposition on the corrosion of biomass boiler superheater at different temperatures. The thermal analysis kinetics of the biomass corrosion reaction was used on the basis of experiment results, to determine the reaction function and the corrosion rate, which quantitatively characterize the corrosion reaction process.
2. Experimental

2.1. Experimental Samples

The straw grown in Shandong is selected as biomass fuel. The composition of biomass fuel is shown in Table 1. Before the experiment, the biomass was made into ash samples, and the corrosive medium was prepared according to the ratio of KCl: NaCl of straw. The ratio of the corrosive medium and biomass ash is 1:4, which increases the corrosion effect and made the results more obvious. The pipe steel used in this experiment is T91. It is used as the superheater, reheater and import and export container materials of power station boiler. The composition is shown in Table 2.

| Table 1. Biomass ash composition /%.
| Fuel | Na₂O | K₂O | SiO₂ | Al₂O₃ | SO₃ | Cl⁻ | CaO | MgO | Fe₂O₃ | P₂O₅ |
|------|------|------|------|-------|-----|-----|-----|-----|-------|------|
| Straw | 0.52 | 24.73 | 24.11 | 7.53  | 2.34 | 7.65 | 1.95 | 4.31 |

| Table 2. Chemical composition of T91 /%.
| Steel | C     | Si    | Mn    | Mo    | Cr    | V     | P    | S    | Ni    |
|-------|-------|-------|-------|-------|-------|-------|------|------|-------|
| T91   | 0.08~0.12 | 0.20~0.50 | 0.30~0.60 | 0.85~1.05 | 8.00~9.50 | 0.15~0.30 | ≤0.02 | ≤0.01 | ≤0.40 |

2.2. Experimental System

The experimental system is shown in Figure 1. The high-temperature reaction part is composed of a tube furnace and a temperature control device. The sample is placed in a small porcelain boat. The gas mixture is controlled by a ratio of 6% O₂, 12% CO₂, and 82% N₂. The test is carried out in a corundum tube, and the ends are sealed with rubber stoppers to simulate the actual heating surface in boiler. The exhaust gas is absorbed by the NaOH solution to avoid environmental pollution.

![Figure 1. The schematic diagram of experimental system.](image)

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2.3. Experimental Procedure

The surface area of the sample was measured, and the sample was uniformly covered by ash and dried, to make sure the ash content of 30 mg/cm² before the test. The porcelain boat containing the sample was pre-fired for 30 min, and weighed after cooling as the initial weight of the test. The porcelain boat was taken out every 4 h, placed in a drying dish to cool and weigh. The process was controlled within 10 minutes and continuously tested for 32 h.

3. Effect of temperature on biomass ash corrosion

Figure 2 shows the constant temperature corrosion weight gain curve of synthetic wheat straw ash to T91 at different temperatures. The fitting correlation is shown in Table 3. When the temperature exceeds 630°C, the corrosion reaction is rapidly increased. Because when the temperature is low, the reactant molecules have lower energy; and the metal surface slowly forms an oxide film to isolate the
metal substrate from the external environment, so the corrosion reaction proceeds slowly. When the temperature rise, the proportion of activated molecules also rises, the gas molecules pass through the oxide film gap easily; and the oxide film to crack and fall off, so the weight gain rate has a significant rise process. The integrity of the oxide film is affected by the volume ratio of the metal to the corrosion product. When the ratio of the two is approximately equivalent, the metal surface can form a dense oxide film; but when the ratio is much smaller than 1, due to the corrosion product is bulky, the internal stress of the oxide film gradually increases. When the internal stress is greater enough, the oxide film is cracked and peeled off, so that the corrosion reaction continues. T91 is an iron-based alloy. The volume of iron oxidation products is much larger than that of metal. The repeated cracking and spalling of the metal surface cannot resist corrosion and results in higher corrosion rates [9].

Figure 2. Corrosion weight gain fitting curve of T91 at different temperatures.

Table 3. Correlation of corrosion weight gain of T91 at different temperatures.

| Temperature/°C | Fitting correlations | k_p | Ra^2 |
|---------------|----------------------|-----|------|
| 480           | Δw=0.25301t^{1/2}-0.10881 | 0.25301 | 0.97779 |
| 530           | Δw=0.42724t^{1/2}-0.20903 | 0.42724 | 0.96742 |
| 580           | Δw=0.54363t^{1/2}-0.23410 | 0.54363 | 0.97421 |
| 630           | Δw=2.20159t^{1/2}-0.91001 | 2.20159 | 0.97013 |
| 680           | Δw=4.25330t^{1/2}-2.09820 | 4.25330 | 0.98188 |

4. Thermal Analysis Kinetics of High Temperature Corrosion on Heating Surface

4.1. Thermal analysis kinetic theory

The corrosion reaction on the heated surface is heterogeneous reaction, and each set of experiments is controlled at a constant temperature, so the kinetic equation of the fixed temperature heterogeneous reaction is used [10]:

\[
\frac{d\alpha}{dt} = f(\alpha) \cdot k(T)
\]

(1)

Where \( t \) is the reaction time; \( \alpha \) is the percentage of reactants converted to product at time \( t \); \( k(T) \) is the reaction rate constant; \( f(\alpha) \) is the differential form of the reaction mechanism function.

The reaction rate \( k \) is an important dimensionless constant characterizing the chemical reaction rate. \( k \) varies with temperature. Arrhenius proposes a relationship between temperature and reaction rate:

\[
k(T) = k_0 \exp\left(-\frac{E}{RT}\right)
\]

(2)

Substituting equation (2) into equation (1) gives the kinetic equations under constant temperature heterogeneous conditions:
\[
\frac{d\alpha}{dt} = k_0 \exp\left(-\frac{E}{RT}\right)f(\alpha)
\]  

(3)

Let \(G(\alpha)\) be the integral form of the reaction function, and the corresponding definition is:

\[
G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}
\]

(4)

Substituting equation (4) into equation (3) yields:

\[
G(\alpha) = \int_0^\alpha k_0 \exp\left(-\frac{E}{RT}\right)dt = k(T)t
\]

(5)

Since the test is carried out under constant temperature, \(k(T)\) is a constant, \(G(\alpha)\) and \(t\) are straight lines with a slope of \(k\), so \(f(\alpha)\) with the best linear relationship is selected as the best model function.

### 4.2. Determination of the best mechanism function of corrosion reaction

To determine the optimal reaction function, it is necessary to determine \(\alpha\). The experiment cannot be carried out for a long time because of the experimental conditions. It is assumed that the reaction will not proceed after 32 h, so that the definition of \(\alpha\) can be expressed as:

\[
\alpha = \frac{w_t - w_0}{w_{32} - w_0} = \frac{\Delta w}{\Delta w_{32}}
\]

(6)

Where \(w_t\) is the mass of the sample at time \(t\), \(w_0\) is the mass of the sample at the initial of the reaction, \(w_{32}\) is the mass of the sample after 32 h of reaction, \(\Delta w\) is the weight of the sample at the time of reaction \(t\), and \(\Delta w_{32}\) is the total weight of the sample at the end of the test.

The reaction kinetic model functions often used in the fitting calculation is shown in Table 4.

| Model functions | Symbol | \(G(\alpha)\) | \(f(\alpha)\) |
|-----------------|--------|----------------|----------------|
| One-dimensional diffusion model | D1 | \(\alpha^2\) | 1/2\(\alpha^2\) |
| Two-dimensional diffusion model | D2 | \(\alpha+(1-\alpha)\ln(1-\alpha)\) | \([-\ln(1-\alpha)]^{1/2}\) |
| Three-dimensional diffusion model (Jander) | D3 | \([1-(1-\alpha)^{1/3}]^2\) | 3/2\((1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]\) |
| Three-dimensional diffusion model (G-B) | D4 | \(1-2/3\alpha-(1-\alpha)^{2/3}\) | 3/2\([1-\alpha]^{1/3}-1\) |
| Secondary nucleation and growth reaction | A2 | \([-\ln(1-\alpha)]^{1/2}\) | 2\((1-\alpha)[-\ln(1-\alpha)]^{1/2}\) |
| Secondary phase interface reaction (Spherical) | R2 | \(1-(1-\alpha)^{1/2}\) | 2\((1-\alpha)^{1/2}\) |
| Secondary phase interface reaction (Cylindrical) | R3 | \(3(1-\alpha)^{2/3}\) | 1\((1-\alpha)^{1/3}\) |

The relative error SD [11] of the calculated and measured values of \(G(\alpha)\)-t fit curve is defined as:

\[
SD = \sqrt{\frac{\sum_{i=1}^n [G(\alpha)_{ni} - G(\alpha)_{ce}]^2}{n}}
\]

(7)

Where: \(G(\alpha)_{ni}\) is the calculated fit value, and \(G(\alpha)_{ce}\) is the calculated measurement value.

Based on the experimental data given in Fig. 2, the thermal kinetic analysis is carried out, and the conversion fraction \(\alpha\) of samples at each temperature and time period can be obtained by the formula (6). By substituting the \(\alpha\) value into the integral form function \(G(\alpha)\) in the reaction kinetic function in Table 4, the relationship between \(G(\alpha)\) and time \(t\) can be obtained. The calculation results are shown in Table 5. The relative errors SD and goodness to fit of each reaction kinetic model is shown in Figures 3 and 4. It is known that D1, D2, D4 and R2 have smaller SD values and fit better.
### Table 5. Functional relationship $G(\alpha)$ fitting to different models at different temperatures.

| Model | 480°C       | 530°C       | 580°C       | 630°C       | 680°C       |
|-------|-------------|-------------|-------------|-------------|-------------|
| D1    | -0.0748+0.0326t | -0.0900+0.0316t | -0.0741+0.0335t | -0.0641+0.0324t | -0.0870+0.0327t |
| D2    | -0.0850+0.0219t | -0.0828+0.0235t | -0.0936+0.0252t | -0.0768+0.0271t | -0.0914+0.0287t |
| D3    | -0.1583+0.0227t | -0.1598+0.0220t | -0.1592+0.0234t | -0.1545+0.0226t | -0.1610+0.0227t |
| D4    | -0.0469+0.0094t | -0.0049+0.0090t | -0.0472+0.0097t | -0.0445+0.0093t | -0.0400+0.0093t |
| A2    | 0.1921+0.0509t | 0.1880+0.0479t | 0.1824+0.0533t | 0.2006+0.0508t | 0.1759+0.0509t |
| R2    | -0.0203+0.0282t | -0.0315+0.0275t | -0.0197+0.029t | -0.0140+0.0281t | -0.0302+0.0284t |
| R3    | 2.9255-0.882t  | 2.9677-0.8864t | 2.9222-0.0902t | 2.9055-0.0880t | 2.9616-0.0888t |

**Figure 3.** Relative error of each reaction kinetic model function.

**Figure 4.** Goodness to fit of each reaction kinetic model function.

### 4.3. Determination of three factors of kinetics

Take the logarithm of the two sides of equation (2):

$$\ln k = \ln k_0 - \frac{E}{RT} \tag{8}$$

It can be seen from equation (8) that $1/T$ is linear with $\ln k$, the slope is $-E/(RT)$, the intercept is $\ln k_0$, let $y = \ln k$, $x = 1/T$, $a = -E/R$, $b = \ln k_0$, then equation (8) can be transformed into the form of the equation $y = ax + b$.

From Table 6 and Figure 5 that the goodness to fit under the D2 model is 0.97632, which is significantly better than the other three reaction models. It is calculated that $k_0=0.079497s^{-1}$, $E=8100.40715J\cdot mol^{-1}$, the optimal reaction model mechanism function $f(\alpha)=\left[-\ln(1-\alpha)\right]^{-1}$ and the values of $k_0$ and $E$ are substituted into equation (3) to obtain the kinetic equation of the corrosion:

$$\frac{d\alpha}{dt} = 0.079497 \exp(-974.32728/T)\left[-\ln(1-\alpha)\right]^{-1} \tag{9}$$

**Figure 5.** Lnk-1/T fitting results of samples in D2 model.
Table 6. Fitting relationship.

| Model | Fitting correlations | $R^2$ |
|-------|-----------------------|-------|
| D1    | $y=-3.3712-46.0104x$  | -0.25309 |
| D2    | $y=-2.5320-974.3273x$ | 0.97632 |
| D4    | $y=-4.6195-47.0222x$  | -0.28282 |
| R2    | $y=-3.5155-44.4420x$  | 0.04274 |

Note: A negative value for $R^2$ indicates a fitting failure.

5. Conclusions

(1) The corrosion weight gain curve of straw on the heating surface steel T91 conforms to the parabolic form. Corrosion reaction is greatly affected by temperature change. As the temperature rises, the energy of the reactant molecules increases, and the reactant molecules are more likely to pass through the oxide film to participate in the reaction. With the reaction proceeding, the reaction product increases, causing the internal stress of the oxide film to increase. The oxide film is cracked and peeled off, and the reaction continues.

(2) The heterogeneous reaction kinetics model under constant temperature conditions was used in this paper. Substituting the conversion rate at each temperature into the integral form mechanism function $G(\alpha)$, and the relationship between $G(\alpha)$ and time $t$ is obtained. The error and goodness to fit of the fitting relationship determine the possible reaction model, and the best reaction model is finally determined by the relationship between $k$ and temperature. At 480 °C to 680 °C, the corrosion of T91 in wheat straw ash is more consistent with the D2 model. The pre-factor $k_0=0.079497s^{-1}$, the corrosion activation energy $E=8100.40715J\cdot mol^{-1}$, and the final kinetic equation is:

$$
d\alpha/dt = 0.079497 \exp(-974.32728/T)\left[-\ln(1-\alpha)\right]^{1/4}
$$

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