Research Progress on High Temperature Corrosion Mechanism of Waste Incineration Power Generation Boiler

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Abstract. Waste incineration power generation is a main method of waste disposal, and high temperature corrosion has always been a key issue restricting the development of this technology. This paper reviews the research progress of high temperature corrosion mechanism of waste incineration boilers. Based on the chemical reaction of high temperature corrosion of chloride, the mechanism of chloride corrosion of boiler metal fittings is discussed. The analysis results show that the high-temperature flue gas corrosion mainly includes HCl gas corrosion, molten salt corrosion and sulfide corrosion. In addition, the analysis of the high-temperature soot corrosion mechanism shows that the corrosion behavior of the heated surface in the presence of sintered ash is stress cracking corrosion. This is the result of the combined effect of the stress destruction of dense sintered ash and the ion diffusion corrosion reaction of chloride in the ash.

Keywords: Waste Incineration, Chlorine Corrosion, Molten Salt, Activated Oxidation

1. Introduction
In 1905, the United States built the world's first waste incineration power plant in New York. From the 1970s to the 1990s, waste incineration power generation developed rapidly. After entering 2010, China's waste incineration power generation has entered a rapid development track. The installed scale and generation capacity of waste incineration power generation has ranked first in the world. In 2019, the waste power generation has exceeded 35 billion kilowatt hours.

The high-temperature corrosion of water-cooled walls and superheaters of garbage incinerators generally includes several types, such as oxidative corrosion, thermal corrosion, and chloride corrosion. Among them, chloride corrosion is the most important. The composition of waste is complex and changeable. Rubber waste is the main source of chlorine. Waste such as kitchen waste and paper are the main sources of sulfur. At the same time, the waste also contains a certain amount of alkali metals and heavy metals (Table 1) [1]. In the high temperature environment of the incinerator,
various corrosive media such as chlorine, sulfur, alkali metals and heavy metals will have complex interactions, which will easily form compounds with low melting points and high vapor pressure, which will cause corrosion of the flue.

Table 1. Proportion of components in domestic waste [1]

| Category              | Proportion (%) | Category             | Proportion (%) |
|-----------------------|----------------|----------------------|----------------|
| Paper                 | 5.42           | Metals               | 5.88           |
| Rubber                | 19.5           | Glass                | 0.15           |
| Bamboo and wood       | 0.77           | Brick and tile ceramics | 0.46         |
| Textiles              | 8.05           | Lime soil            | -              |
| Kitchen waste         | 51.7           | Other                | -              |
| Mixed-type            | 8.05           |                      |                |

2. High-Temperature Corrosion Mechanism of Waste Incineration

2.1 High Temperature Flue Gas Corrosion Mechanism

The burning temperature of municipal solid waste incinerators is generally between 850-950 °C. The main components of the flue gas produced are CO₂, N₂, H₂O, O₂ and harmful gases such as SOₓ, HCl, HF, NOₓ, heavy metals, dioxins, and incomplete combustion gases such as CO. Corrosion between 320-800 °C is high-temperature corrosion. When the metal temperature is in the range of 320-480 °C, ferric chloride and ferric sulfate will be formed. When the temperature further rises in the range of 480-800 °C, ferric chloride and ferric sulfate will decompose, causing the metal material to lose the oxidation protection layer and be corroded, that is, high temperature corrosion.

2.1.1 Chemical Reaction Process of High Temperature Corrosion of Chloride

The generation of HCl during waste incineration is generally considered to be due to the removal of substituents from organic chlorides [2, 3]. The overall reaction result can be expressed as Equ. (1):

\[ \text{C}_n\text{H}_m\text{Cl}_p + \rho\text{O}_2 \rightarrow \text{XCO}_2 \uparrow + \text{YCO} \uparrow + \text{ZH}_2\text{O} \uparrow + \text{W} \text{HCl} \uparrow \]  

Hydrogen chloride gas is very harmful to human health and plants. In addition, many documents have pointed out that hydrogen chloride gas has a strong corrosive effect on the body of the incinerator. It is generally believed that the corrosion reaction of chlorine on metal pipes in the incinerator is shown in Equ. (2) to Equ. (11):

\[ \text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2 \]  

(2)

\[ 2\text{Fe} + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2 \]  

(3)

\[ 2\text{FeCl}_3 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3 \]  

(4)

\[ 2\text{Fe} + 3\text{Cl}_2 \rightarrow 2\text{FeCl}_3 \]  

(5)

\[ 4\text{FeCl}_3 + 3\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3 + 6\text{Cl}_2 \]  

(6)

\[ 4\text{FeCl}_2 + 3\text{O}_2 \rightarrow 3\text{Fe}_2\text{O}_3 + 4\text{Cl}_2 \]  

(7)

\[ \text{Fe}_2\text{O}_3 \text{(protective film)} + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \]  

(8)

\[ 4\text{FeCl}_2 + \text{O}_2 \rightarrow 2\text{FeCl}_3 + 2\text{FeCl}_4 \]  

(9)

\[ 4\text{FeCl}_3 + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + 2\text{Cl}_2 \]  

(10)

As long as HCl and Cl₂ are continuously replenished, the corrosion reaction continues. In addition, the melting point of FeCl₃ is 282 °C, which is more volatile and damages the protective film more seriously. In addition to the erosion of Fe and Fe₂O₃, chlorine and chloride can also corrode the Cr₂O₃ protective film under certain conditions, such as Equ. (11) to Equ. (14) [3]:
When chlorine and sulfur compounds coexist, a reaction process such as Equ. (15) and Equ. (16) may occur:

\[
\begin{align*}
2\text{MCl} + \text{SO}_3 + \text{H}_2\text{O} &\rightarrow \text{M}_2\text{SO}_4 + 2\text{HCl} \\
2\text{NaCl} + \text{SO}_3 + \text{O}_2 &\rightarrow \text{Na}_2\text{SO}_4 + \text{Cl}_2
\end{align*}
\]

It can be seen that the simultaneous existence of chlorine and sulfides and the help of H\(_2\)O and O\(_2\) can not only accelerate the formation of sulfate, but also facilitate the formation of HCl and Cl\(_2\), and then accelerate the high-temperature corrosion process [3]. The chemical reaction process of corrosion in the waste incinerator is shown in Figure 1.

![Figure 1. Chemical reaction process for corrosion in a waste incineration boiler][2]

### 2.1.2 Mechanism of Chloride Corrosion of Boiler Pipes

The "activated oxidation" mechanism was widely cited [4]. According to this mechanism, metal chloride can be generated at the oxide film/substrate interface due to the presence of HCl, Cl\(_2\), etc. in the incinerator flue gas. Under the effect of vapor pressure gradient, the metal chloride will evaporate, diffuse and transport outward, oxidizing to form metal oxide and chlorine gas. Chlorine gas will diffuse into the oxide film and generate new metal chloride. As shown in Figure 2, element chlorine plays an autocatalytic role, this process requires only a small amount of chlorine to maintain.

During the outward transport of metal chlorides, there will be many defects and holes in the protective film, which provides many channels for the inward transmission of chloride elements and the diffusion of chlorides and accelerates the movement of gaseous substances and the rate of corrosion.

![Figure 2. Autocatalysis of chlorine][5]

![Figure 3. System diagram of corrosion caused by Cl\(_2\)(g)'][3]

HCl and Cl\(_2\) in flue gas can accelerate metal corrosion. When the steel on the heating surface of the boiler water wall, superheater, etc. is exposed to a high temperature oxidizing atmosphere, it will gradually form a stable oxide, and finally the oxide scale is wrapped on the metal surface. Chlorine
has the ability to invade the oxide film, especially through the holes and cracks to reach the interface between the metal and the oxide layer and react with the alloy to form chlorides (Figure 3). HCl and/or Cl\(_2\) react with metals as follows:

\[
\begin{align*}
M(s) + \text{Cl}_2(g) &\rightarrow M\text{Cl}_2(s) \\
M(s) + 2\text{HCl}(g) &\rightarrow M\text{Cl}_2(s) + \text{H}_2(g) \\
\text{MCl}_2(s) &\rightarrow \text{MCl}_2(g)
\end{align*}
\]

Where \(M \in \{\text{Fe, Cr, Ni}\}\). As the distance from the metal layer increases, the oxygen concentration increases, further causing oxidation, and the metal chloride is transformed into a solid metal oxide, causing the metal oxide layer to become loose:

\[
\begin{align*}
3\text{MCl}_2(g) + 2\text{O}_2(g) &\rightarrow \text{M}_3\text{O}_4(s) + 3\text{Cl}_2(g) \\
2\text{MCl}_2(g) + 3/2\text{O}_2(g) &\rightarrow \text{M}_2\text{O}_3(s) + 2\text{Cl}_2(g)
\end{align*}
\]

In a reducing atmosphere, since there is no oxide film, the metal chloride directly invades the metal surface, and the reaction of the following Equ. (22) occurs:

\[
\begin{align*}
M(s) + \text{Cl}_2(g) &\rightarrow \text{MCl}_2(s)
\end{align*}
\]

At high temperatures (> 800 °C), the metal loses its protective film. If only the effect of HCl is considered, severe corrosion will only occur after reaching the melting point of the metal oxide, and the corrosion rate is linear with time. The corrosion rate of iron by HCl increases in a reducing atmosphere due to the disappearance of the protective oxide film. Gaseous NaCl can also corrode metal pipes. The following reactions occur at 500 ppmv NaCl vapor at 850 °C:

\[
\begin{align*}
\text{Cr}_2\text{O}_3(s) + 4\text{NaCl}(g) + 5/2\text{O}_2(g) &\rightarrow 2\text{Na}_2\text{CrO}_4(s.l) + 2\text{Cl}_2 \\
\text{Cr}(s) + 2\text{NaCl}(g) + 2\text{O}_2(g) &\rightarrow \text{Na}_2\text{CrO}_4(s.l) + \text{Cl}_2
\end{align*}
\]

The effect of the deposition of NaCl gas in the alloy pipeline causes the total corrosion depth in the alloy to increase sharply above 550 °C. Chromium in alloy steel accelerates corrosion at a NaCl melting point below 810 °C, but reduces internal corrosion. The results show that NaCl accelerates corrosion at 650–900 °C, and high-temperature corrosion increases 30-120 times when NaCl is present.

2.1.3 Mechanism of Sulfide Corrosion of Boiler Pipes [1]

Corrosion products generally contain a certain amount of sulfur element. In the case of insufficient combustion, sulfur in the garbage is reduced to generate hydrogen sulfide, thereby promoting the occurrence of sulfide corrosion. The presence of chloride will promote the formation of H\(_2\)S and further enhance the corrosion process [5]:

\[
\text{FeS(s) + 2HCl} \rightarrow \text{FeCl}_2(g) + \text{H}_2\text{S(g)}
\]

In addition, sulfide is also more likely to cause local corrosion on the pipe wall. S in the waste incineration environment will penetrate into the oxide film/metal interface to form sulfides, and react with alloying elements to form holes in the alloy boundary.

Gaseous SO\(_2\), SO\(_3\) will react with KCl to form K\(_2\)SO\(_4\) deposition salt. Relevant scholars believe that the thin and dense K\(_2\)SO\(_4\) layer formed by this reaction can effectively hinder the diffusion of HCl and Cl\(_2\), thereby hindering its corrosion. Davidsson [6] pointed out that the additional addition of SO\(_2\) will promote the formation of K\(_2\)SO\(_4\) deposition salts, while the additional addition of HCl will aggravate the corrosion of metals.

The 20G steel used for water wall usually forms three continuous and protective oxide films at high temperature, which are FeO-Fe\(_2\)O\(_3\)-Fe\(_2\)O\(_4\) from inside to outside. However, because H\(_2\)S and S have a strong destructive effect on the metal oxide film, they penetrate directly through the oxide film, and
continue to penetrate along the metal boundary, which makes the metal internal matrix sulfide, and the oxide film becomes loose, cracked, or even directly peeled off.

2.1.4 Molten Salt Corrosion Mechanism
Alkali metal oxides in waste incineration are also an important factor for high temperature corrosion of boilers. These alkali metal oxides react with HCl to form alkali metal chlorides, which then condense and precipitate on the surface. Nielsen [7] described the mechanism of alkali metal chloride sulfation in sedimentary salts, which can be seen in the following Equ. (26) to Equ. (27):

\[
2\text{KCl} + \text{SO}_2(g) + 1/2\text{O}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{SO}_4 + 2\text{HCl}(g)
\]
\[
2\text{KCl} + \text{SO}_2(g) + \text{O}_2(g) + \text{H}_2\text{O}(g) \rightarrow \text{K}_2\text{SO}_4 + \text{Cl}_2(g)
\]

The HCl generated from the Equ. (26) can be further oxidized to Cl\(_2\), which further corrodes the metal. The specific process is similar to the high temperature corrosion of HCl [8]. High-temperature molten alkali metal chlorides can also react with metal oxides, as shown in the following Equations:

\[
2\text{NaCl} + \text{Fe}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow \text{Na}_2\text{Fe}_3\text{O}_4 + \text{Cl}_2
\]
\[
4\text{NaCl} + \text{Cr}_2\text{O}_3 + 5/2\text{O}_2 \rightarrow 2\text{Na}_2\text{CrO}_4 + 2\text{Cl}_2
\]

These chemical reactions, while destroying the metal oxide film, also release Cl\(_2\), and further vapor-phase corrode the metal. In addition, the molten salt contains a plurality of mixed chlorides, such as an alkali metal and a heavy metal chloride, when blended, their eutectic points become low. In a high-temperature environment, the molten salt becomes a liquid phase. This liquid phase corrosion reaction further accelerates molten salt corrosion, because liquid phase chemical reactions tend to be faster than solid phase reactions. Furthermore, the electrolyte is electrochemically corroded in the liquid phase.

2.2 Ash Deposition Corrosion Mechanism
The heating surface arranged in the high-temperature flue gas is mostly covered with ash deposits [9]. Corrosion under this condition is a complex process involving multiphase interactions of gas, liquid, and solid. It is generally believed that chlorine, sulfur, and alkali metals are closely related to the occurrence of corrosion [10]. The corrosivity of chlorides in the heated surface deposits is manifested in two aspects: one is that a reaction similar to gaseous chlorine corrosion occurs near the wall surface, that is, activated oxidation; the other is that the chlorides in the ash deposits easily form low-melting eutectic melts. The formation of a molten phase at the wall can promote the progress of the corrosion reaction [11-13]. The melting of alkali metal sulfate film accelerates the corrosion more obviously [14, 15]. In actual operation, HC and SO\(_2\) often act simultaneously on the corrosion process. Grabke et al. [16] used thermogravimetry to study the corrosion behavior of alloy steel by NaCl and waste incineration ash in the presence of SO\(_2\) in the oxidizing atmosphere, and considered that the corrosion caused by gaseous HCl and chloride in ash deposits was the main [17].

Traces of corrosion or mechanical action can be seen on the detached surface of the metal oxide layer. Above the bottom ash deposit can be considered as the growth section of ash deposit. The composition of the ash deposit in the growth section can be divided into brittle ash deposit and dense ash deposit, and the dense ash deposit is the main one [18]. The brittle ash is dark in color, easy to break, there are a few cracks and voids inside, and the sintering degree is medium. Dense ash is as hard as rock, light in color, difficult to break, and tight and solid internal structure. This structural feature of sintered ash and its corrosion tendency may be related in the following two aspects: sintered ash has high strength, so it will produce a large stress impact when the temperature fluctuates, causing an increase in metal defects on the heating surface; The loose structure of the ash deposited on the bottom layer can provide a channel for the infiltration and diffusion of reactants and products for the corrosion reaction.

According to the analysis of the microscopic morphology and structure of the ash deposit, it is
known that the metal oxide layer on the heating surface generates cracks and defects under the stress impact of the high-intensity sintered ash deposit, and some tiny ash deposit particles can slowly penetrate into the crack. The more mobilized Cl\(^{-}\) in the bottom ash deposit diffuses into the metal oxide layer under the promotion of concentration gradient and temperature gradient, and reacts with the metal to form loose chloride [19]. In addition, the volatilization and out-diffusion of chloride at high temperature cause further aggravation of defects and the reaction continues. Ultimately, the combination of these factors leads to the shedding of the oxide layer. The corrosion reaction is mainly caused by the diffusion of Cl\(^{-}\) in the dust deposit to the metal oxide layer. The defect of dust accumulation at the bottom creates favorable conditions for the diffusion of Cl\(^{-}\). The Cl\(^{-}\) diffused into the oxide layer reacts with Fe\(_{2}\) or Fe\(_{3}\) to form FeCl\(_{2}\) or FeCl\(_{3}\). The corrosion reaction product at high temperature diffuses outwards so that the chlorine content of the dust deposits penetrating into the cracks of the oxide layer is very low. The possible reactions during the ash deposition corrosion process are as follows:

\[
\text{The production of Cl}^{-}: \quad \text{CaCl}_2(s,l) \rightarrow \text{Ca}^{2+}+2\text{Cl}^{-} \quad (30)
\]

or

\[
\text{NaCl(l)} \rightarrow \text{Na}^{+}+\text{Cl}^{-} \quad (31)
\]

Ionic reaction:

\[
\text{Fe}^{2+}+2\text{Cl}^{-} \rightarrow \text{FeCl}_2(s) \quad (32)
\]

or

\[
\text{Fe}^{3+}+3\text{Cl}^{-} \rightarrow \text{FeCl}_3(s) \quad (33)
\]

High temperature volatilization:

\[
\text{FeCl}_2(s) \rightarrow \text{FeCl}_2(g) \quad (34)
\]

or

\[
\text{FeCl}_3(l) \rightarrow \text{FeCl}_3(g) \quad (35)
\]

Chlorine cycle:

\[
\text{FeCl}_2(g)+\text{CaO(s)} \rightarrow \text{FeO(s)}+\text{CaCl}_2(s) \quad (36)
\]

\[
2\text{FeCl}_3(g)+3\text{CaO(s)} \rightarrow \text{Fe}_2\text{O}_3(s)+3\text{CaCl}_2(s) \quad (37)
\]

Therefore, improving the corrosive environment may be a feasible method to reduce the risk of corrosion during the waste incineration process, including improvement of heating surface and ash accumulation.

3. Conclusion

(1) When the concentration of HCl in waste incineration flue gas is 600~1300 ppm, it will cause the chlorination of the material under high temperature environment to produce low melting point FeCl\(_3\), which makes the metal lose its protective layer.

(2) The cause of molten salt corrosion is that the HCl and SO\(_2\) gases in the waste incineration waste gas react with the ash on the heating surface to form chloride salts and sulfates are deposited on the surface of the boiler tubes. They melted the oxide film of the steel, causing S and O to further invade to form oxides, which accelerated corrosion.

(3) The corrosion behavior of the heated surface under the condition of sintered ash deposit in the process of garbage incineration is stress cracking corrosion, which is the result of the combined effect of the stress destruction of dense sintered ash and the ion diffusion corrosion reaction of chlorine in the ash.

Acknowledgements

This work was supported by the Special Fund for Shenzhen Basic Research Institute (Shenzhen Clean Energy Research Institute) CERI-KY-2019-002, Shenzhen Energy Environmental Protection Co., Ltd. Commissioned R & D Project (0309-HBZB-Service-2019-2246) and the Fundamental Research Funds for the Central Universities (2020JG003).

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