Principle and protective measures of high temperature corrosion of garbage incineration boiler

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Abstract—With the increasing amount of garbage, the environmental pressure is increasing. Waste incineration power generation technology has become the main way to deal with waste. However, due to the complex and variable composition of waste and the large amount of chlorine contained in the waste, the high temperature corrosion of the heating surface of the waste boiler is much more serious than that of the coal-fired boiler. This article sorts out the high-temperature corrosion mechanism of the heating surface of the waste incineration boiler, and summarizes the relevant protective measures.

1. INTRODUCTION

With the continuous expansion of the size of cities and towns and the continuous growth of domestic waste, Municipal solid waste incineration technology is playing an increasingly important role in waste treatment systems worldwide. Municipal solid waste incineration technology has the functions of high volume reduction rate, heat recovery and power generation. However, because the waste incineration boiler is prone to deposition and corrosion problems, the boiler has to use a lower steam temperature and pressure, which results in a power generation efficiency of the waste-to-energy boiler of only 15% to 25%.

The corrosion of garbage boilers mainly includes: gas high temperature corrosion, alkali metal molten salt corrosion, electrochemical corrosion and low temperature corrosion. Among them, high temperature chlorine corrosion (including gas phase corrosion and alkali metal corrosion) is the main reason for the waste power boiler corrosion. The corrosion protection of garbage boilers mainly includes the use of new alloys, coating protection, and reduced corrosion conditions during operation.

2. PRINCIPLE OF BOILER HEATING SURFACE CORROSION

2.1 Gas phase corrosion principle: activation oxidation mechanism

Domestic waste has a high chlorine content, so high temperature chlorine corrosion is the most important cause of garbage boiler corrosion. Plastics in municipal solid waste, especially PVC and food waste, are the main sources of chlorine, which are organic chlorine and inorganic chlorine [1]. Organic and inorganic chloride ion sources release chlorine at high temperatures, thereby forming HCl with hydrogen ions [2]. PVC (organic Cl) releases more HCl than NaCl (inorganic Cl).

During the incineration of Cl-containing municipal solid waste, about 72-80% of HCl is formed from organic sources of Cl, such as PVC, while only 20-28% of HCl is formed from inorganic chlorides.
When the boiler temperature reaches 200°C to 360°C, the PVC plastic begins to release HCl. The chemical reaction is shown in formula 1. When the temperature reaches 500°C, it completely decomposes. KCl and NaCl in MSW volatilize at a temperature of about 800°C and are partially converted to HCl [3]. The chemical reaction is shown in formula 2, 3. But also has some substances, such as SOx, SiO2 and Al2O3, can promote the formation of HCl in inorganic chloride (NaCl and KCl).

\[
PVC = HCl + yC_nH_y. \quad (1)
\]

\[
MSW-Cl = MCl(g) + HCl(g) + Cl_2(g). \quad (2)
\]

\[
MSW-Cl = MCl(s). \quad (3)
\]

\[
M = \text{Na, K.}
\]

In an oxidizing environment at 600°C, HCl undergoes a Deacon reaction, which thermally decomposes to form Cl2 [4]. The chemical reaction is shown in formula 4:

\[
2HCl + \frac{1}{2}O_2 = Cl_2 + H_2O. \quad (4)
\]

The main point of view of the gas phase corrosion mechanism of high temperature chlorine corrosion is the activation oxidation mechanism [5]. The activated oxidation mechanism is as follows: due to the high activity of chlorine, chlorine will react with metal (Fe) on the surface of the heated surface in different forms. The metal chloride produced by the oxidation of the metal surface will diffuse to the outside. Metal chloride reacts with oxygen to form metal oxides and chlorine gas. Chlorine gas will diffuse back to the metal surface, forming a reaction cycle. In the reaction, chlorine gas only needs a small amount to promote the reaction, and chlorine gas acts as a catalyst. The activated oxidation mechanism is shown in Figure 1. The chemical reaction is shown in formula 5-10:

\[
M(s) + Cl_2(g) = MCl_2(s). \quad (5)
\]

\[
M(s) + 2HCl = MCl_2(g) + H_2(g). \quad (6)
\]

\[
MCl_2(s) = MCl_2(g). \quad (7)
\]

\[
2MCl_2(g) + \frac{3}{2}O_2(g) = M_2O_3(s) + 2Cl_2(g). \quad (8)
\]

\[
M = \text{Fe, Cr.}
\]

\[
3FeCl_2(g) + 2O_2(g) = Fe_3O_4(s) + 3Cl_2(g). \quad (9)
\]

\[
FeCl_2 + HCl + \frac{1}{4}O_2 = FeCl_3 + \frac{1}{2}H_2O. \quad (10)
\]

![Figure 1. High temperature chlorine corrosion flow chart](image)
2.2 Molten salt deposit corrosion
Waste fuel has a high content of chlorine, which can be present in the form of HCl, alkali metal chlorides, or heavy metal chlorides in furnaces and flues. Domestic garbage will release alkali metals (such as K and Na) and ash particles in the form of gas during the combustion process. In the process of alkali metal deposition, it will generate sulfate with SO2 in the flue gas. When SO2 is not present, it will react with elemental chlorine to form chloride, and when chloride is not present, it will generate hydroxide [6].

Gaseous alkali metal compounds will interact with ash particles to form low melting alkali metal silicates. The alkali metal silicate has a higher viscosity at the furnace temperature, when the temperature of the heated surface is lower than the saturation temperature of the alkali metal and heavy metal chloride. These chlorides will be deposited on the heated surface. Especially in the waste-to-energy boilers with high ash and alkali metal fuel, the problem of deposition corrosion on the heated surface is more serious.

There are two corrosion methods for alkali metal chlorides. One way is the oxidation reaction of alkali metal chlorides to generate HCl and Cl2, and then HCl and Cl2 will diffuse back to the metal surface for activation oxidation cycle. The chemical reaction is shown in formula 11,12:

\[
2\text{KCl}+\text{SO}_2+\text{O}_2(g)+\text{H}_2\text{O}(g)=\text{K}_2\text{SO}_4+2\text{HCl}(g). \tag{11}
\]

\[
2\text{KCl}+\text{SO}_2+\text{O}_2(g)+\text{H}_2\text{O}(g)=\text{K}_2\text{SO}_4+\text{Cl}_2(g). \tag{12}
\]

Another way is that the alkali metal chloride reacts with the metal oxide to destroy the protective layer while releasing chlorine gas to corrode the boiler tube. The chemical reaction is shown in formula 13,14:

\[
2\text{K/NaCl}+\text{Fe}_2\text{O}_3+1/2\text{O}_2=\text{K/Na}_2\text{Fe}_2\text{O}_4+\text{Cl}_2 \tag{13}
\]

\[
4\text{K/NaCl}+\text{Cr}_2\text{O}_3+1/2\text{O}_2=2\text{K/Na}_2\text{CrO}_4+2\text{Cl}_2. \tag{14}
\]

3. OTHER CAUSES OF CORROSION

3.1 Low temperature corrosion
Low temperature corrosion is due to the SO3 in the flue gas, and the temperature of the heated surface wall is lower than the acid dew point. In addition to the above reasons, the low temperature corrosion of garbage boilers is also due to the generation of hydrogen chloride after the burning of plastic products in the garbage. The acid dew point of hydrogen chloride is also determined by its vapor partial pressure. Normally, the metal wall temperature is above 120 °C to avoid acid condensation. Therefore, the temperature of the exhaust gas of the garbage boiler should not be lower than 200 °C.

3.2 Temperature change
The non-uniform physical and chemical composition of domestic waste fuel and the corresponding fluctuations in heating value over time lead to significant fluctuations in the temperature of the gas in the combustion chamber. Experimental studies have confirmed that the corrosion rate caused by large temperature fluctuations can be increased several times.

3.3 Electrochemical corrosion
Stainless steel becomes inactive because it contains metals such as nickel and chromium. The electrode potential is higher than ordinary carbon steel. But when stainless steel is in contact with carbon steel, an electrochemical primary cell can be formed. In this primary battery. Carbon steel is the negative electrode. Stainless steel is the positive electrode. Therefore, carbon steel will corrode due to the accelerated oxidation of stainless steel. Therefore, the vicinity of the part where the superheater tube is in contact with the stainless steel bracket is the most severe.
3.4 Unreasonable boiler design
Some boiler three-stage superheaters are located above the slag tube. The flue gas rushes directly to the support of the tertiary superheater when it turns from the cooling chamber through the slag tube to the entrance of the tertiary superheater. Unreasonable structural design of the boiler leads to the deflection and concentration of flue gas, resulting in the most concentrated heat and the most severe corrosion at this location; at the same time, the location is subject to flue gas scouring toward the fire side. Under the dual action of corrosion and smoke erosion. Causes increased corrosion.

4. BOILER CORROSION PROTECTION MEASURES
For the protection of garbage boiler corrosion, it is mainly divided into main measures and secondary measures. The main measures are the use of optimized combustion conditions, co-firing and the use of additives to eliminate boiler corrosion. The secondary measures in terms of materials reduce the impact of boiler corrosion. The secondary measures mainly include thermal spraying technology, surfacing welding technology and laser cladding technology.

4.1 Thermal spraying technology:
Thermal spraying technology is the most basic and most comprehensive measure to solve the high temperature corrosion of thermal power plants. Due to different heating acceleration principles, thermal spraying technology is divided into supersonic flame spraying, atmospheric plasma spraying, explosive spraying, and arc spraying.

4.1.1 Supersonic flame spraying
Supersonic flame spraying is the use of high-temperature and high-pressure flame sprayed from the nozzle to melt the material to be sprayed and impact the workpiece at high speed to form a coating. The coating has the characteristics of high density and low oxygen content, so it has become the main protection method of foreign waste-to-energy boilers. At the same time, supersonic spraying also has many shortcomings, such as high cost, large gas consumption, high powder requirements, and slow spraying speed.

4.1.2 Atmospheric plasma spraying
The nozzle and electrode of plasma spraying are respectively connected to the positive and negative poles of the power supply. Working gas is passed between the nozzle and the electrode. The working gas is ionized under the action of the arc and generates a plasma arc. The plasma jet sprayed from the nozzle will spray The powder is heated and melted and sprayed onto the surface of the workpiece to form a layer. Plasma spraying has high spray temperature, high coating quality, and wide range of applicable materials. At the same time, the high cost, high consumption, and complicated operation also limit the application of this technology to waste boilers.

4.1.3 Explosive spraying
Explosive spraying is to use the detonation wave generated by the explosion to provide the initial velocity of the sprayed material to bombard the substrate, and the sprayed powder hits the substrate to form a dense coating. The coating has fewer defects and is dense, and has good corrosion resistance. Under similar conditions, the coating prepared by explosive spraying has better corrosion resistance than supersonic flame spraying. However, due to technical limitations, there are few domestic researches and applications on explosive spraying.

4.1.4 Arc spraying
Arc spraying uses two continuously fed metal strips as consumable electrodes. The two electrodes are connected to the positive and negative electrodes of the power supply respectively. After contacting each other, an arc is generated and the ends of the metal strip are melted into droplets. The temperature can reach 6000℃. The molten filamentous metal is atomized by the action of compressed air and
sprayed onto the surface of the substrate at a very high speed to form a sprayed layer. Because of the high initial velocity and high temperature of the droplet generated by arc spraying, the coating produced by spraying has a high bonding strength. At the same time, arc spraying also has the advantages of high productivity and simple equipment. The current research shows that adding an appropriate amount of deoxidizing elements to the wire can inhibit the formation of sprayed oxides and can effectively improve the coating's ability to resist high temperature corrosion. According to this principle, arc spraying can be applied to the corrosion protection of waste-to-energy boilers.

4.2 Surfacing technology
The surfacing technology is the most widely used for anti-corrosion of garbage boilers. Surfacing is the use of Cr, Ni alloys and CMT automatic surfacing mode to surfacing a 2mm alloy layer on the heated surface. The texture of the surfacing layer is quite clear, and the effect is good. The hardness of the heat-affected zone of the surfacing layer is less than 250HV. The surfacing is carried out by lamination, the dilution rate is extremely low, the percentage of Fe is about 3%, and the highest is not more than 7%. The surface dilution rate requirements of the surfacing layer are as follows: Cr ≥ 20.5%, Fe ≤ 6%, Nb ≥ 3.2%, Mo ≥ 8% [7]. The surfacing technology is suitable for the heated surface around 400℃, and it does not have a good protection for higher temperatures. For medium-temperature and medium-pressure garbage boilers using surfacing technology, the service life can reach about 6 years.

4.3 Laser cladding technology
Laser cladding technology is to use high-energy laser to heat the pre-cladding material and the workpiece, so that the cladding material and the surface layer of the workpiece melt and form a metallurgical combination. The metal cladding layer formed in this way has the characteristics of low dilution rate, and also makes the performance of the metal cladding layer not to be greatly changed by the substrate. Because the laser cladding technology uses metallurgical bonding, the applicable materials are very wide, and ceramics, metals and their composite materials can be applied. The laser cladding layer applied to the garbage power generation boiler can adapt to the corrosion of 800 ℃ furnace temperature, which is the highest temperature that can withstand the various protective measures. But at the same time, laser cladding technology also has many limitations, such as huge initial investment, the technology is not very mature, and thermal deformation.

4.4 Co-firing and additives
Co-firing is an anti-corrosion measure that burns waste fuel and additives together to prevent alkali metal chloride from depositing on the boiler tube surface. Adding fuel rich in sulfur and aluminosilicate is mainly used in fluidized bed boilers or boilers with powder burners. Aluminum silicate and sulfur dioxide react with chlorides of alkali metals or alkaline earth metals [8], releasing HCl while capturing alkali, which will not condense on boiler tubes [9]. By studying the effects of adding NaCl, PVC, ammonium sulfate and kaolinite additives on co-combustion, it was found that the addition of NaCl promoted the burnout of the fuel, and the remaining additives inhibited the burnout of the fuel; ammonium sulfate has the effect of releasing NO obviously inhibit the effect. Among the additives that inhibit chlorine corrosion, calcium-based additives are very common. Common calcium-based additives include Ca(OH)₂, CaO, and CaCO₃. According to research, the inhibitory effect of Ca(OH)₂ and CaO is stronger than CaCO₃ [10], and the level of Ca(OH)₂ and CaO is still controversial. . In studying the efficiency of Ca(OH)₂ dechlorination of PVC and NaCl, it was found that when the temperature increased from 650℃ to 800℃, the dechlorination effect of Ca(OH)₂ was greatly reduced.

4.5 Optimize combustion conditions
Reasonable choice of integrated waste heat boiler and incinerator; excess air coefficient adopted; rational arrangement and design of secondary air and secondary air nozzles, so that the flue gas produced by combustion is uniform, the temperature fluctuation of the furnace outlet is small and
hidden. In waste classification, plastic wastes are divided into chlorine-depleted plastics and chlorine-rich plastics according to the chlorine content. The chlorine-depleted plastics are used as fuel for garbage incinerators, and the chlorine-rich plastics are landfilled.

Garbage classification The fuel for garbage power plants is municipal solid waste, which contains plastics, tires, metals, textiles and other substances. The composition is complex, and the flue gas produced by combustion will contain a variety of acid gases, salt substances, and fly ash particles. The flow of these substances along with the flue gas is usually deposited on the metal tube wall that is subjected to high temperature and pressure, which is very easy to cause the metal tube wall wear in the furnace. Therefore, the garbage needs to be sorted, which can reduce the amount of garbage that needs to be treated, and can remove recyclable garbage, non-combustible garbage, and garbage that will produce toxic and harmful gases after combustion. This will make garbage boiler combustion more stable and safe.

Strengthening operation control and adjusting ash deposit coking and furnace outlet temperature are two important factors that affect the corrosion process. The corrosion process can be slowed down by appropriately adjusting the operating conditions. For example: try to make the garbage mix evenly, reduce the accumulation of garbage with strong viscosity and low ash melting point to reduce coking; adjust the air volume and air temperature of the primary and secondary air to ensure the outlet temperature of the furnace and the flue gas velocity to make the flue gas be fully disturbed to avoid dead zones and to prevent serious local corrosion; regular deashing work to prevent excessive external opportunities for the water wall.

4.6 New alloy materials
Cr can produce a dense oxide layer Cr₂O₃ on the surface of the material, Cr₂O₃ has high corrosion resistance. Cl and Ni will synthesize high-melting NiCl₂ and can react with Fe to form FeCl₂, FeCl₃ and other high-melting substances. Therefore, Ni-based alloys can be used as materials in Cl-rich environments.

Boiler heating tube alloy materials mainly include Ni-Fe based high Cr alloy, high Cr-Mo-Ni based alloy and high Si-Cr-Ni alloy. The introduction of the three alloys is shown in Table 1.

| Alloy categories | Ni-Fe base high Cr alloy | High Cr-Mo-Ni base alloy | High Si-Cr-Ni base alloy |
|------------------|--------------------------|---------------------------|-------------------------|
| Kinds            | 310S, NF709              | 625 alloy                 | QSX3, QSX5              |
| Applicable boiler temperature | 400°C                   | 450°C                     | 500°C                   |

Ni-Fe-based high Cr alloys mainly include 309S, 310S, 25Cr-14-20Ni alloys and 310HcBN and NF709, which are suitable for waste heat boilers with a furnace temperature of 400°C.

High Cr-Mo-Ni based alloys mainly include 625 alloy, HC-22 and JHN24. The Mo content of HC-22 and JHN24 is higher than that of 625 alloy. Suitable for waste heat boiler with furnace temperature 450°C. Due to its excellent high-temperature strength, corrosion resistance, resistance to intergranular corrosion and stress corrosion cracking, alloy 625 has become the main material of superheaters in waste-to-energy boilers in Europe. But the disadvantage is that the alloy with high Mo content will produce composition changes under high temperature environment, leading to material degradation and aging.

The characteristic of high Si-Cr-Ni-based alloy is that a certain amount of Si is added. If 310S alloy is added with about 3% Si to improve it, QSX3 and QSX5 can be obtained. The high-Cr-Ni-Fe-Si (4%) alloy can be applied to 500 °C/9.8 MPa superheater pipes, and it can be safely operated for 4 years [11].
4.7 Summary of protective measures:
The advantages of surfacing and thermal spraying technology are mature technology and low cost. The disadvantage is that the applicable temperature of the surfacing technology is reduced, and it is not suitable for higher temperature boiler corrosion. The disadvantage of thermal spraying technology is that there is no metallurgical bonding between the sprayed layer and the substrate, and the bonding strength is not high. The advantages of laser cladding technology are metallurgical bonding and high bonding strength. The laser beam melting pool is small, so the dilution rate of the cladding layer is smaller than that of the surfacing, which also ensures the strength of the cladding layer. But the disadvantage is that the laser cladding technology is not very mature. Now the domestic productivity is low and the thermal deformation is high. Therefore, in general, surfacing and thermal spraying technologies are suitable for medium capacity boilers, while laser cladding technology is more suitable for high capacity boilers.

5. SUMMARY
The main WTE boiler is still a medium-capacity unit, which limits the efficiency of the waste boiler. In order to improve the power generation efficiency of the WTE boiler, increasing the unit capacity has become the development trend of the WTE boiler. As the capacity of the boiler increases, the corrosion of the heated surface of the boiler will also increase dramatically.

The corrosion problem of WTE boiler is mainly high temperature chlorine corrosion, which has the following characteristics:

- Correlation between the corrosion rate of high-temperature chlorine corrosion and the concentration of chlorine is not particularly large
- The corrosion strength of alkali metal in high temperature chlorine corrosion is greater than that of vapor phase corrosion
- The temperature has a great influence on the corrosion rate. As the temperature increases, the corrosion rate greatly increases.

Because of the above three characteristics, the method of protecting the heating surface of the boiler by changing the structure of the furnace is very limited. Therefore, the secondary measures to prevent corrosion on the heating surface of the waste-to-energy boiler are more effective than the main measures.

The research and application of this important measure are as follows:

- The traditional protective measures thermal spraying technology and surfacing technology have the advantages of mature technology and low cost, and are suitable for waste heat boilers with medium capacity and furnace temperature below 450 ℃.
- Co-firing and the use of additives are suitable for circulating fluidized bed boilers. Commonly used co-combustion additives to reduce chlorine content are ammonium sulfate, aluminosilicate and calcium-based additives (Ca(OH)₂, CaO and CaCO₃); NaCl has a promoting effect on fuel burnout; Ammonium sulfate has a significant inhibitory effect on NO release.
- Laser cladding technology or new alloys can adapt to high temperature (500 ℃) anti-corrosion requirements of boilers. The defect is that the price is higher and the technology is not mature enough.

The current protective measures still limit the improvement of WTE boiler parameters. The development of new alloys and the research of new surface coating technologies similar to laser cladding technology are very necessary.

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