Study on high temperature corrosion of super heater in MSW combustion

Zisen Liu, Xin Wang, Guangyao Du

School of Environment and Architecture, University of Shanghai for Science and Technology, 516 Jungong Road, Yangpu District, Shanghai, 200093,China

Abstract: In this day and age, using municipal solid waste (MSW) as fuel to produce heat and electricity has becoming an industry trend. However, compare with other fuels, the flue gas of waste combustion contains a lot of corrosive components such as hydrogen chloride and ash. When the temperature of the steam which inside the boiler is too high, some elements like chlorine, sulfur and its compounds will corrode the pipe, and also lower the power generation efficiency. Therefore, it is necessary to analyze the high-temperature anti-corrosive materials and antisepsis technology for super heaters to improve the steam parameters. Some specific methods about how to prevent high temperature corrosion were illustrated in this report, mechanism and precaution measures related to high temperature are also discussed in this paper.

Keywords: MSW, super heater, corrosion

1. INTRODUCTION

Electric energy is indispensable in modern industrial society. Today, most of electricity production comes from burning fossil fuels such as coal in thermal power plants. Due to the harmful effects of large CO_2 emissions, some developed countries decide to increase the part of renewable energy sources instead of fossil fuels. Therefore, the waste-to-energy (WTE) plant which use municipal solid waste (MSW) and refuse-derived fuel (RDF) to produce electricity and heat is becoming more and more common. Waste combustion is much better than landfilling; it's an excellent substitute for fossil fuels and can destroy toxic organic compounds. What's more, it can save energy and reduce air pollution if the waste is treated in a good way.

However, compared with other fuels, the flue gas of waste combustion contains a lot of corrosive components such as hydrogen chloride and ash. When the temperature of the steam inside the boiler is too high, the superheated steam pipe would be rapidly corroded by high temperature chlorine, sulfur and its compounds[1]. It will lead to material loss, frequent downtime, high operating costs and other problems in WTE plant.

Ordinary method is to reduce the steam temperature to 400℃~420℃, but the boiler energy efficiency will decrease to less than 25% in corresponding [2].

2. CORROSION PHENOMENA

Figure 1 is a schematic diagram of a typical WTE facility which used for combustion of waste, consisting essentially of a waste inlet area, fuel storage, feed section, grate, combustion chamber, heat recovery facility, flue gas cleaning system and ash handling system.

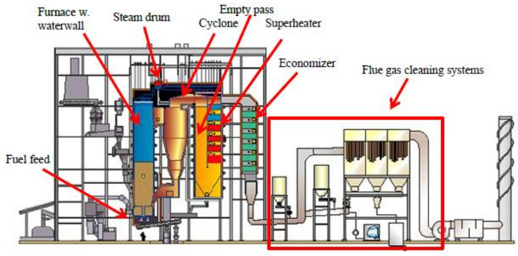

Figure1. Schematic of typical waste-to-energy (WTE) facility [3]

Since the boiler is a facility having a comparatively large heat exchange area, the temperatures of each part is not uniform. The hottest part of the boiler is the furnace, and the hottest stream is produced in the super heater.

When high-temperature gases flow through the water pipes, like super heater tubes or economic tubes, heat is transferred from the gas to water vapor within these tubes, after that, the water vapor is becoming superheated steam; it was used to rotate the turbine for power generation. The higher temperature and pressure of the steam result in higher efficiency of the power generation. However, with the increasing temperature of steam, the heat transfer surfaces which from the pipe are being high temperature corroded. Because of the chloride which is deposited on the pipes and the HCl gas which forms during the combustion process.

The concentration of chlorine in the combustion gas depends on the composition of MSW; different parts have different concentration of chlorine. Generally speaking, the source of chlorine in MSW 50% comes from the natural organic matter; the other part comes from chlorinated plastics, mostly PVC. During combustion, almost all the chlorine element was volatilized and converted to HCl gas.

3. CORROSION MECHANISM

The corrosion mechanism is determined by observing and analyzing various types of deposits on the surface of the etched metal. In general, high temperature corrosion has three main mechanisms [4].

3.1 Corrosion caused by chlorine and its chloride

This corrosion mechanism, also known as active oxidation, occurs at temperatures above 450 ° C (840 °F), including several steps:

Hydrogen chloride (HCl) reacts with oxygen which in the flue gas to form chlorine (Cl_2); or chlorides such as NaCl has the reaction with the metal oxides on the surface of the tube to form chlorine (Cl_2).

$$2HCl + 0.5O_2 \rightarrow Cl_2 + H_2O$$

$$2NaCl(g) + Fe_2O_3 + 0.5O_2 \rightarrow Na_2Fe_2O_4 + Cl_2$$

1. The chlorine reaches the oxide interface by osmosis and reacts with iron or the other metal components of tube to form metal chlorides.

$$Fe + Cl_2 \rightarrow FeCl_2(s)$$

$$Fe + 2HCl \rightarrow FeCl_2(s) + H_2(g)$$

2. Due to the high temperature effect, the metal chloride is present in the form of steam, which gradually diffuses and covers the entire tube, and then it reacts with the oxygen to form metal oxides and chlorine (Cl_2).

$$FeCl_2(s) \rightarrow FeCl_2(g)$$

$$3FeCl_2 + 2O_2 \rightarrow Fe_3O_4 + 3Cl_2$$

$$2FeCl_2 + 1.5O_2 \rightarrow Fe_2O_3 + 2Cl_2$$

3. In step 3, the chlorine is released and diffuses into the flue gas. However, some of the released chlorine diffuses back to the oxide/metal interface and reacts with the metal and forms the volatile metal chloride again. Therefore, a cycle has been formed in the corrosion of chlorine and its compounds, which lead to more serious situation of the corrosion of super heater.

3.2 Corrosion caused by sulfate and molten salt deposition

When the volatile chlorides in the combustion gases come into the surface of tube which has been cooling down, they are condensed and form liquid or solid deposit that may contain sulfate and alkali metal chlorides. Subsequently, the deposit of metal chloride reacts with SO_2 or SO_3 to form a concentrated alkali metal sulfate.

$$2NaCl(s,l) + SO_2 + O_2 \rightarrow Na_2SO_4 + Cl_2$$

$$2KCl(s,l) + SO_2 + O_2 \rightarrow K_2SO_4 + Cl_2$$

The corrosion caused by deposition is reflected in two aspects: (1) chloride in the deposits leads to a reactive gas-phase oxidation which is similar with what is described above; (2) The presence of chloride in the deposit can lead to the formation of a low-melting point eutectic (i.e., a salt solution characterized by the lowest possible melting point) that can dissolve the protective oxide film which cover the metal surface.

3.3 Corrosion caused by reaction with protective oxide layer

Many researches have shown that corrosion can be caused by the reaction between protective oxide and other components. Such as chlorine, which can breakdown the oxide layer and transfer to other compounds that make super heater easy to be corrode. For example, a study shows that a protective oxide layer Cr2O3 can react with KCl and produce K2CrO4, which is badly productive of corrosion [5].

$$2KCl_{(s)} + \frac{1}{2} Cr_2O_{3(s)} + H_2O_{(g)} + \frac{3}{4} O_{2(g)} \leftrightarrow K_2CrO_{4(s)} + 2HCl_{(g)}$$

This reaction is not only produce K_2CrO_4, which is badly protective; but also accelerate the breakdown of Cr_2O_3, which is good protective of metal.

3.4 Impact factors

There are many factors affecting the corrosion rate of WTE boilers, such as the concentration of chlorine and sulfur in the MSW, the operating temperature in the combustion chamber, the temperature fluctuation in the metal pipe, and the design of the boiler (for example, horizontal and vertical arrangement of super heater tubes). Four main factors will be introduced as follows.

3.4.1 Metal surface temperature

Generally, the temperature of the water wall and super heater tubes is maintained at the temperature that less than 300℃ (570℉) and 450 ℃ (840℉), respectively[2]. However, as what mentioned above, the thermal efficiency of the steam turbine will increase when the super heater is at a higher temperature. If the metal surface temperature is raised, the radiant heat of the metal will increase and the convective heat transfer to the tube will reduce, causing the deposit melts and accelerates the corrosion rate.

3.4.2 Flue gas temperature

The temperature of flue gas can affect the deposition rate and the composition of deposit, thereby accelerating the corrosion. The temperature gradient between flue gas temperature and metal surface temperature is the driving force for the condensation of evaporation material (e.g., metal chlorides) which on the cooling surface [6]. If the temperature gradient is large, the chloride concentration in the deposit will increase and the melting point of the salt will decrease. In addition, the thermal stress caused by the temperature gradient between the deposit and the metal walls can affect the adhesion of the oxide on the metal surface, thereby causing the rupture of the protective oxide coatings [7].

3.4.3 Temperature fluctuation

Due to the heterogeneous physical and chemical components of the MSW fuel and the fluctuation of calorific value with time, the gas temperature in the combustion chamber fluctuates significantly. Experimental studies confirmed that the corrosion rate increases several times by the factor of unstable gas temperature.

3.4.4 Characteristics of molten salt deposits

The chloride, sulfide, alkali metal and heavy metal components which in the deposits affect the physical and chemical properties of the deposits, such as the gas permeability, so chloride can increase the corrosion rate through cracks and pores diffusion of the deposits[4].The consequence is that the thicker of the deposits, the fast the corrosion rate will be.

4. MEASURES OF HIGH TEMPERATURE CORROSION PROTECTION

After several years of continuous innovation and development of the WTE industry, many methods about how to reduce the high temperature corrosion have been established, and some technologies are being developed, such as new materials research and development work, property changes of fuel, promotion of coating technology, design of boiler and so on.

4.1 The use of the alloy steel

Since the composition of steel has a direct effect on its chemical and physical properties, it is important to know how different alloying elements affect steel so that can pick the desire material for practical applications. To solve the phenomenon of high-temperature corrosion of super heater, high-chromium steel is often used as the heating surface of the tube material. On the surface of the high-chromium steel material, a dense oxide membrane Cr_2O_3 is formed, which has a good resistance to molten sulfate corrosion. In addition to this material, Ni-based alloy is also a good material to avoid corrosion. The reason is that the melting point of NiCl2 which from Ni and Cl is 1030℃, it's much higher than of FeCl2 and $FeCl_3$.

Many different steels are commonly used for super heater tubes. The following is a brief discussion of low-alloy ferritic steels, 9-12% Cr ferritic-martensitic steels, austenitic stainless steels, and nickel-based alloys.

4.1.1 Low-alloyed ferritic steels

Ferritic stainless steels have a body-centered cubic (BCC) structure and are ferromagnetic. The maximum temperature of the ferritic stainless steel should not exceed 500℃ due to poor oxidation resistance and limited creep rupture strength. However, they are relatively inexpensive and are usually used as substitutes for other steels at lower temperatures. Therefore, 13CrMo44 (1Cr-0.5Mo-Fe) and 13CrMo910 (2.25Cr-1Mo-Fe) are often used for super heater tubes in waste-to-energy boilers[8].

4.1.2 Ferritic-martensitic steels

Ferritic-martensitic steels have higher creep rupture strength than low-alloyed ferritic alloys. In order to enhance high temperature corrosion resistance, they are usually alloyed with 9-12% Cr[9].Comparedtoausteniticsteels,ferrite-martensitic steels have a faster chromium diffusion rate, which promotes the formation of protective chromium oxide. HCM 12A is a marten site 12% -Cr steel containing about 35% delta ferrite.

4.1.3 Austenitic stainless steels

Austenitic stainless steels have a face-centered cubic (FCC) structure and are non-magnetic. Ni is usually added to austenitic stainless steels to stabilize the austenitic structure, but doing so can lead to higher production costs. The standard 304 is the most common stainless steel with 18% Cr-8% Ni-Fe on the market. Other steels in the AISI 300 series can be considered as standard 304 improvements because they are optimized for high temperature corrosion resistance and higher creep rupture strength.

4.1.4 Nickel-base alloys

Ni-based alloys have a face-centered cubic (FCC) structure. Because of its excellent mechanical properties and good corrosion resistance, it is often used in practical high temperature applications. For example, Inconel 625 with 22% Cr-9% Mo-Ni can be used in waste-to-energy boiler[8]. These alloys are often superior to other candidate alloys, but are very expensive due to the high nickel content.

The selection of super heater material should consider the corrosion characteristics of sulfur, chlorine and the corrosion atmosphere (oxidation or reduction reaction), but economics is also an important factor that cannot neglect.

4.2 Waste and other fuel co-combustion technology

Compared with other fuels, the chlorine content of waste is high. If the waste can be mixed other fuel, like high-quality coal or biomass fuel, it will reduce the chlorine content of flue gas, thereby eliminate or reduce the high-temperature corrosion of super heater.

4.3 Add preservatives in the boiler

This method is based on some chemical reactions between preservatives and compounds which in the boiler to resist the formation of low-melting complex sulfates and complex chlorides and reduce the layers of deposition on the super heater surfaces, thereby reducing molten salt corrosion. For example, the additive can react with the corrosive gases HCl or SO3 and produce ash particles to decrease the concentration of corrosive gas in the flue gas [10]. And CaO and MgO can also be used in waste heaters to remove sulfur and chlorine.

4.4 Reduce temperature fluctuation

The non-uniformity of waste fuel input and the unevenness of time and space caused by the combustion of waste, all lead to the wall temperature fluctuation of the heat transfer. In addition, the different deposition of heat transfer tubes will lead to the overheating situation of superheater tube and further more lead to corrosion.

4.5 Thermal sprayed metal coating

The metal coating used for corrosion protection can form a barrier between the pipe and the corrosive medium, and providing protection, however, the metal coating itself will be corrosive slower. To achieve the purpose of anti-corrosion, the chemical composition of the coating needs to be guaranteed. There are four main thermal spraying technologies:

flame spray, supersonic flame spray, plasma spray and arc spray.

Flame spraying is the first spray technology, this technology has a low efficiency and high cost. There are some new flame spray technology like supersonic flame spraying (HVOF) and plasma spray; they have high-quality protective coatings with low porosity, high density, and good bond strength to substrates, but the equipment of these technologies are expensive [11].

Arc spraying is another technology that can prevent corrosion. It has excellent coating performance, high spraying efficiency, high energy efficiency and low cost of equipment, so the cost is much lower than other spraying methods. At present, the arc spray has been applied to protect the power plant boilers in many developed countries, it has huge economy benefits. It can be used in super heater tube, economizer tube and other materials which need avoid corrosion. The coating can get rid of the chlorine and sulfur corrosion. by changing the chemical composition of the arc spray coating [11].

5. CONCLUSION

Superheater corrosion mainly comes from chlorine, sulfur and its compounds in the incinerator for complex, variable, cyclic chemical reaction, resulting in hydrogen chloride, sulfate and other highly corrosive substances are generated. Therefore, more serious corrosion will be produced in such a vicious cycle. Factors affecting the high temperature corrosion also include the concentration of chlorine and sulfur in the MSW, the operating temperature of the combustion chamber, the temperature fluctuations of the metal pipe sections, the design of the boiler, and the characteristics of molten salt deposits and so on.

The economical methods which proposed in this paper to prevent high-temperature corrosion are: low-alloyed ferritic steels (at lower temperature), arc spraying, and adding preservatives in the furnace.

In the future, with the large application of alloy steelinchlorine-containing high-temperature environment, the strengthening of the basic research on the corrosion mechanism of chlorination, the accumulation of comprehensive chlorination corrosion, and the laboratory research conditions as close as possible to the actual working environment will contribute to the chemical analysis and the assessment of life reliability of the materials, and also have an important application background in the design and development of new chlorine-resistant materials and protective coatings.

ACKNOWLEDGEMENTS

The authors would like to thank Shanghai Natural Science Foundation (16ZR1423200) for financial support for this research.

REFERENCES

[1].High temperature corrosion in a 65 MW waste to energy plant. Kristoffer Persson, Markus Broström,Jörgen Carlsson,Rainer Backman. 2007, Fuel Processing Technology, Vol. 88, pp. 11-12.

[2].P. Rademakers, W. Hesseling,J. van de Wetering. Review on corrosion in waste incinerators,and possible effect of bromine. s.l.: TNO industrial Technology, 2002.

[3].Alkali and zinc chlorides in waterwall tube corrosion:Effects of pure salts and mixtures. SLOMIAN, ANDREAS. Gothenburg : s.n., 2013.

[4].Albina, Dionel O. Theory and Experience on Corrosion of Waterwall and Superheater Tubes of Waste-To-Energy Facilities. master thesis : Columbia University, 2005.

[5].Reducing high temperature corrosion when burning waste by adding digested sewage sludge . Sofia Karlsson1, Lars-Erik Åmand,Jesper Pettersson. 2006, Corrosion Science, pp. 1368-1378.

[6].High temperature corrosion mechanisms and effect of alloying elements for materials used in waste incineration environment. Kawahara, Yuuzou. 2, s.l: Corrosion Science, 2002, Corrosion Science, Vol. 44, pp. 223-245.

[7].Hot corrosion in a temperature gradient. G.R.holcomb. 8, 2000, Materials and Corrosion, Vol. 51, pp. 564-569.

[8].Superheater corrosion in biomass and waste fired boilers. Viklund, Peter. Stockholm: Chemical Science and Engineering , 2013.

[9].Cr heat resistant steels: alloy design, TEM characterisation of microstructure evolution and creep response at 650℃. Jara, David Rojas. Bochum : s.n., 2011.

[10].Broström, Markus. Aspects of alkali chloride chemistry on deposit formation and high temperature corrosion in biomass and waste fired boilers. Umeå: s.n., 2010.

[11]. ZUO Jun, CHEN En-jian, LIN Bo-chuan , Y AN Chang-feng, Y ANG Wei-bin. Research Status Of Corrosion and Protection in superheter. BOILER TECHNOLOGY.2002, Vol. 33