JITEE5 16:1–7
DOI: 10.1007/s11666-006-9005-4
1059-9630/$19.00 © ASM International

Peer Reviewed

High-Temperature Corrosion in Waste-to-Energy Boilers

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(Submitted May 20, 2006; in revised form November 16, 2006)

There are 88 waste-to-energy (WTE) plants in the U.S. and over 600 worldwide. In total, they combust close to 143 million metric tons of municipal solid wastes (MSW) and generate about 45 billion kW·h of electricity and an equal amount of thermal energy for district heating and industrial use. The presence of various impurities, especially HCl and chloride salts, in the combustion gases results in much higher corrosion rates of boiler tubes and has led to the development of special alloys and also metal protection techniques, including high velocity oxygen fuel (HVOF) sprayed coatings. This study examines the corrosion mechanisms in WTE boilers and summarizes the findings of a corrosion survey of several WTE facilities in the U.S. The study also examines existing and potential methods for reducing corrosion problems.

Keywords chlorine, corrosion, superheater, thermal spray coating, waste-to-energy, waterwall, boiler

1. Introduction

The per capita generation of municipal solid wastes (MSW) in the U.S. is about 1.2 metric tons. An estimated 7% of this (26 million tons) is used as a fuel in 88 waste-to-energy (WTE) power plants. Worldwide, there are over 600 WTE facilities that process an estimated 143 million tons or 10% of the global MSW (Ref 1). In total, the global WTE industry generates about 45 billion kW·h of electricity and an equal amount of thermal energy for district heating and industrial use. The modern WTE plants have significantly improved and are far superior compared to the older polluting incinerators that have been closed down in all developed nations and are equipped with air pollution control systems that perform much better than most coal-fired power plants in the U.S. However, the variability in the heating value of the MSW feed and its relatively high content of chlorine and various light metals contribute to a highly corrosive atmosphere that shortens the life of the heat exchanger tubes used in the waterwall section, where water is evaporated and, especially, in the steam superheater sections of the WTE, where the tube temperature is at its maximum.

Metal tube corrosion is a major operating problem because it results in downtime and periodic shutdowns in WTE plants and accounts for a significant fraction of the total operating cost of WTE plants. High temperature corrosion has also environmental impacts. Metallic coatings and corrosion resistant alloys such as stainless steels and nickel-base alloys are often used to protect boilers from corrosion and represent a large use of valuable resources. Also, plant shutdowns due to corrosion increase the cost of WTE processing, impede further expansion of this technology, and perpetuate the annual disposal of over 200 million tons of MSW in the U.S. to landfills that contaminate the atmosphere and add considerably to greenhouse gas emissions (Ref 2).

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2. Corrosion Phenomena in Waste-to-Energy Boilers

The advantage of WTE technology over landfills is that it reduces the environmental burden of disposing solid wastes and also recovers the energy contained in MSW. Figure 1 is a schematic diagram of a typical WTE facility that uses the dominant technology of grate combustion. The main sections are: entrance zone with weighing facility and refuse receiving area, refuse holding pit and feeding section, the grate and the combustion chamber, combustion chamber integrated with equipment for heat recovery (boiler with water steam system and steam turbine), flue gas treatment system, residue treatment equipment, electrical installation and control system, and auxiliary equipment and buildings.

As the hot combustion gases flow over the heat transfer surfaces, such as membrane water tubes (waterwall)[1]

[1]Waterwall: The wall of the main combustion chamber is covered by a gas tight membrane consisting of metal tubes joined by means of metal strips welded between the tubes. Water is flowing through the tubes that are heated mostly by radiation and convection from the combustion gases.

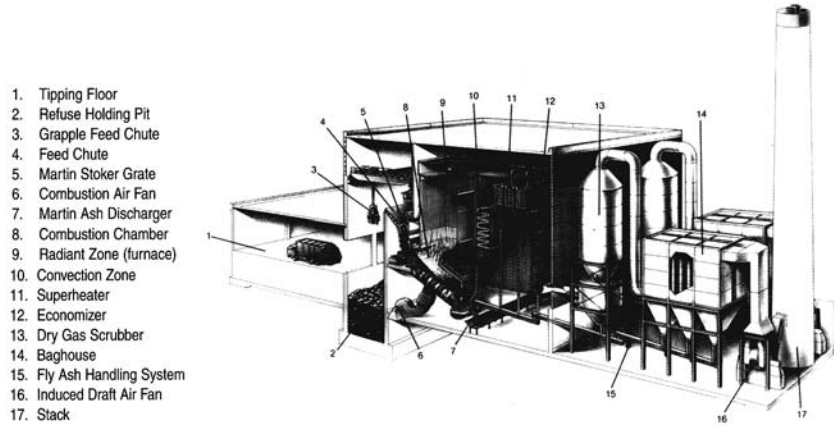

Fig. 1 Schematic of typical waste-to-energy (WTE) facility

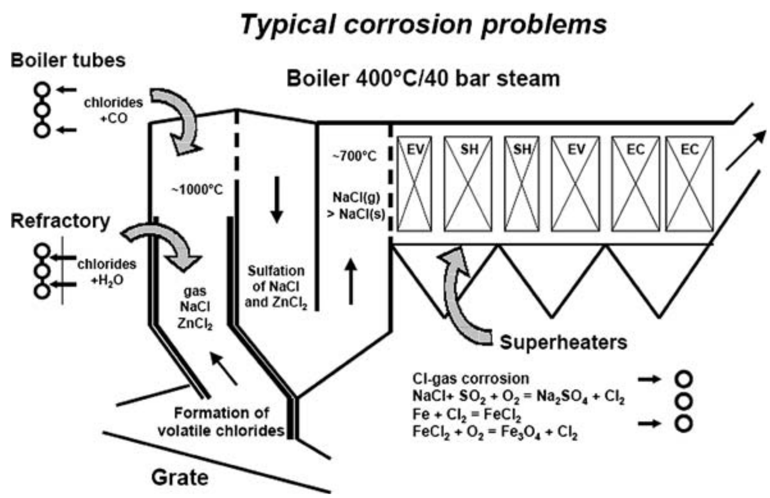

Fig. 2 Corrosion sensitive areas in waste-to-energy (WTE) boilers

superheater tube bundles,[2] evaporator tubes, and economizer tubes, heat is transferred from the gases to the water vapor within the tubes. The superheated steam is then used to rotate the steam turbine generator. The efficiency of conversion of steam energy to electricity increases with higher steam temperatures and pressures. However, with increasing steam temperature, the heat transfer surfaces are subjected to severe high temperature corrosion, caused by both the metal chlorides in the ash particles deposited on the gas tubes and by the high concentration of HCl in the process. Figure 2 shows the corrosion sensitive areas in a WTE facility (Ref 3).

The chlorine concentration in the combustion gas depends entirely on the MSW composition and varies somewhat from region to region. Table 1 shows that the chlorine content in three types of MSW varied from 0.47% to 0.72% (Ref 4). Approximately, one half of the Cl content of MSW is due to natural organics and the other half to chlorinated plastics, mostly PVC. During combustion, nearly all of the chlorine content in the various components of the MSW, both natural organics and chlorinated plastics is volatilized and converted to HCl gas. Assuming that the MSW contains 0.5% Cl, the HCl concentration can be calculated to be about 580 ppmv (Ref 5).

3. Corrosion Mechanisms in Waste-to-Energy Facilities

Metals corrode at high temperatures in the absence of a liquid electrolyte, which is required in the case of low-temperature aqueous corrosion. The mechanism for corrosion is determined by the most abundant deposits observed on the metal after corrosion, i.e. oxidation by metal oxides, sulfidation by metal sulfides, sulfidation/oxidation by mixtures of sulfides and oxides, carburization by metal carbides, and chlorination of metals to metal chlorides. In general there are two principal mechanisms of high temperature corrosion (Ref 4):

[2]Superheater: Steam running through the superheater tubes is heated to temperatures well above the saturation point. Therefore, metal temperatures are much higher than waterwall tubes.

3.1 Active Oxidation

This mechanism occurs at metal temperatures above 450 °C (840 °F) and comprises several steps:

1. Oxidation of hydrogen chloride in the gas with water vapor or reaction of chlorides such as NaCl with metal oxides form chlorine (Cl_2) at the tube surfaces:

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

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

2. Penetration of chlorine through the metal oxide scale to the oxide/metal interface and reaction with iron or other metal component of the tube to form metal chlorides:

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

$$Fe + 2HCl \rightarrow FCl_2(s) + H_2(g)$$

3. Diffusion of metal chloride vapor outward through the scale covering the tube and reaction of the vapor with oxygen in the gaseous layer surrounding the tube to form metal oxide and chlorine:

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

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

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

In step (3), chlorine is released and diffuses to the bulk gas. However, part of the liberated chlorine may diffuse back to the oxide/metal interface and react with the metal and form volatile metal chlorides again. Therefore, a cycle is formed that provides a continuous transport of metal, in the form of chloride, away from the surface towards the higher oxygen partial pressure.

3.2 Corrosion due to Deposits by Sulfation and by Molten Salts

When volatilized chlorides salts in the combustion gases come into contact with the cooler tube surface they condense and form either liquid or solid deposits that may contain sulfates and alkali chlorides. Deposited metal chlorides react with gaseous SO_2 or SO_3 to form condensed alkali sulfates.

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

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

Table 1 Chlorine concentration in MSW (Ref 4)

	New York City MSW	U.S. typical MSW	UK typical MSW
Total Cl, g/kg	4.71	7.26	4.53
%	0.471	0.726	0.453

The deposits contribute to corrosion in two ways: (a) the chlorinated species in the deposit cause a reaction similar to the gas phase active oxidation described above; (b) the presence of chlorides in the deposits may result in the formation of low melting point eutectics (i.e., salt solutions characterized by the lowest possible melting point) which may dissolve (''flux'') the oxide layer that is protecting the metal surface.

Various factors can affect the rate of corrosion in WTE boilers, such as the concentration of chlorine and sulfur in the MSW, the operating temperature of the combustion chamber, temperature fluctuations at a particular location that may disrupt the protective oxide layer, the method used for periodic cleaning of the process gas side of the tubes, and the design of the boiler that should avoid extremely high temperatures (e.g. horizontal vs. vertical disposition of superheater tube arrays). The influence of some important factors can be summarized as follows:

3.2.1 Metal Surface Temperature. High temperature of the metal surface, due to high radiation fluxes and/or inadequate heat transfer rate to the steam flow inside the tube, results in the melting of deposits and acceleration of the corrosion rate. In general, the metal temperatures of waterwall and superheater tubes are maintained at temperatures below 300 °C (570 °F) and 450 °C (840 °F), respectively (Ref 3). However, as mentioned earlier, operation at higher superheater temperatures increases the thermal efficiency of the steam turbine.

3.2.2 Gas Temperature. The temperature of the combustion gases can affect the deposition rates and also the composition of the deposit and thus accelerate corrosion. The temperature gradient between gas temperature and metal surface temperature is a driving force for the condensation of vaporized species, such as metal chlorides, on the cooled surface (Ref 6). When the temperature gradient is large, the chloride concentration in the deposit is high and the melting point of the salt decreases. Also, thermal stresses induced by the temperature gradient across the deposit and the metal wall can affect the adhesion of oxide scales on the metal surface, thereby resulting in fracture of the protective oxide layer followed by spalling and increase of point defect diffusion within oxide scales (Ref 7, 8).

3.2.3 Temperature Fluctuation. The non-homogeneous physical and chemical composition of the MSW fuel and the corresponding fluctuation in heating value with time result in pronounced fluctuations of the gas temperature within the combustion chamber. Experimental studies have confirmed that the corrosion rate increased several times because of wide temperature fluctuation (Ref 9).

3.2.4 Characteristics of Molten Salt Deposits. As already noted, diffusion of chlorine through the cracks and pores of deposits enhances the rate of corrosion (Ref 4). The presence of chlorides, sulfides, and alkaline and heavy metal components in deposits affects both chemical and physical properties of deposits, such as gas permeability of deposits. Contrary to intuition, the corrosion rate also increases with an increase in thickness of deposits (Ref 6).

A particular reaction that is beneficial in reducing the corrosive effect of chlorine and chloride salts is the sulfation of volatilized alkali salts in the flue gases. This reaction transforms chlorides into sulfate salts and the chlorine released reacts with water vapor to form hydrochloric gas. Sulfate salts are less aggressive since sulfate corrosion occurs at higher temperature (Ref 10). In WTE boilers, the character of deposits is affected by feed composition and the gas-metal temperature gradient.

4. Analysis of Corrosion Cost in Waste-to-Energy Facilities

In 2004, the Waste-To-Energy Research and Technology Council (WTERT) conducted a corrosion survey of several WTE facilities in the u.s. One of the results of the survey showed that the non-scheduled downtime due to corrosion ranged from 0 to 20 days per year (Fig. 3). Another result showed that the yearly maintenance cost per boiler unit due to corrosion ranged from $18,000 to $1,200,000; the maintenance cost due to corrosion ranged from $0.23 to $8.17 per ton of MSW combusted (Fig. 4, 5). The typical cost is in the range of $4 per short ton of MSW combusted.

The percent distribution of revenues and costs of a German WTE facility is shown in Fig. 6. Capital cost and maintenance cost account for approximately 60% and 15% of the yearly cost of a WTE facility, respectively (Ref 11). Therefore, the corrosion problems will cost WTE approximately 5% of its yearly total cost, if the corrosion/total maintenance cost ratio of 1/3 applies. The actual cost will be even higher if the revenue loss due to shutdowns because of corrosion is taken into account.

5. Current Methods of Protection

Over several years of operating experience, the WTE industry has developed general approaches to reduce corrosion that can be classified as primary and secondary measures. Primary measures seek to eliminate corrosion by influencing the process conditions in the boiler. Some of these methods include (Ref 4): (a) improvement of process control, in particular minimizing fluctuations in

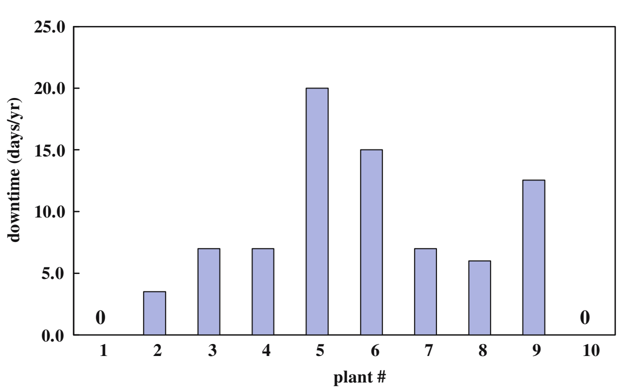

Fig. 3 Non-scheduled downtime due to corrosion of waste-to-energy (WTE) plants (A1, B1, etc. refer to different waste-to-energy (WTE) facilities responding to the WTERT survey)

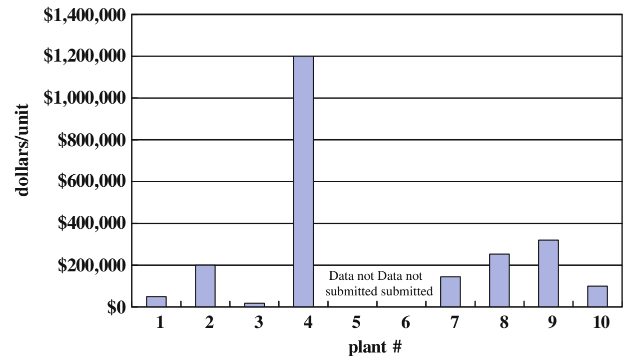

Fig. 4 Yearly maintenance cost per unit due to corrosion (A1, B1, etc. refer to different waste-to-energy (WTE) facilities responding to the WTERT survey)

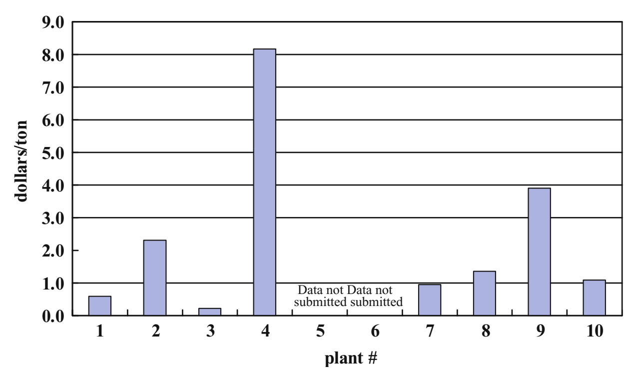

Fig. 5 Cost due to corrosion per ton of MSW combusted (A1, B1, etc. refer to different waste-to-energy (WTE) facilities responding to the WTERT survey)

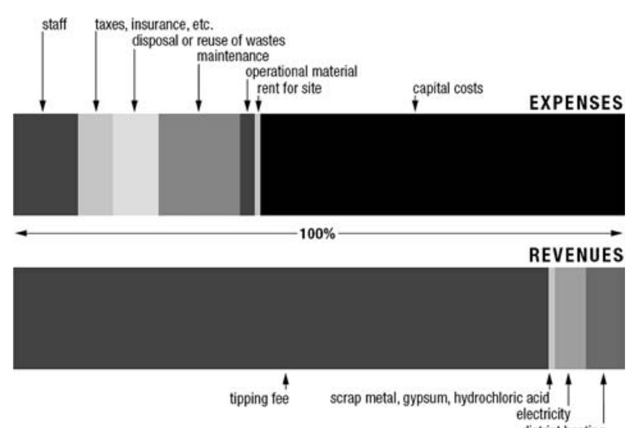

Fig. 6 Expenses and revenues of a German waste-to-energy (WTE) facility

gas temperature; and (b) design modifications, such as process gas recirculation to alter flow dynamics, enhancing mixing of gas through gas recirculation, and design of the boiler system (e.g. horizontal vs. vertical boiler).

Secondary methods of protection are applied to extend the lifespan of the boiler tubes. In the past ten years, many kinds of corrosion-resistant material systems have been tested and applied to actual boilers. For example, high Cr-high Mo nickel-base alloys and high Cr-high Si ferronickel alloy tubing products are used in WTE plants. Furthermore, coating systems such as high velocity oxygen fuel (HVOF) thermal spray and weld overlay have been developed and applied to advanced WTE boilers. Other measures include a new technique named ''Targeted In-Furnace Injection'' (TIFI) (see below) which makes the ash deposits more friable by means of injecting chemicals, such as MgO, directly into the combustion chamber, and the extensive use of high conductivity refractory lining and ceramic tiles in the lower half or the entire height of the combustion chamber.

Some of these methods require either the retrofit of existing WTE boilers or the redesign of boilers of new WTE facilities. In the case of retrofits, the construction time for making equipment changes is a very important parameter since the required shutdown can affect the economic viability of the WTE facility.

Some of the protection methods applied in WTE facilities, or are under investigation, are described in the following section. The actual cost of each method is not shown due to limited information.

6. Adoption of Inconel Alloy 625 Cladding

Waterwall areas that are not protected by a refractory lining and the superheater tubes are the most corrosion prone areas. Cladding consists of overlaying a layer of Inconel 625 (21Cr-9Mo-3.5Nb-Ni base) on tubes to protect them from the attack of HCl/Cl_2. This method has been used successfully in the waterwall tubes and part of the superheater tube bundles in many WTE facilities. The key element regarding the cost is how much Inconel 625 is used and where. Some researchers have shown that Inconel 625 applied on waterwall tubes provides excellent corrosion resistance (Ref 3). Although the price of Inconel 625 is higher than that of a protective refractory lining, the cost of Inconel 625 is partly compensated by avoiding the cost of refractory maintenance. In addition, Inconel 625 has higher thermal conductivity than refractory materials and therefore can reduce gas temperature in the first gas pass.

The application of Inconel 625 on superheater tubes is more complicated because the performance of the cladding depends on the metal temperature reached during operation. One study showed that Inconel 625 does not provide protection above 400-420 °C (750-840 °F) (Ref 12). Another study indicated that at metal temperatures about 540 °C (1000 °F), the wastage rate of Inconel 625 was 0.2 μm/h (0.069 inch/year) (Ref 13). The boilers of some of the existing WTE facilities have been designed to operate at lower temperatures and therefore can apply Inconel 625 on superheater tube bundles. However, problems still arise because the lifetime of Inconel 625 cladding is unpredictable. It may last as much as two years, or as little as three months. According to data that the authors obtained from a WTE facility, the cost of replacing the superheater tube bundle with Inconel 625 cladding is $350,000/unit; and only $250,000/unit without Inconel 625 cladding. The labor cost of installation is $75,000/unit. If the lifetime of the superheater tube bundle with Inconel 625 cladding is sufficiently longer, the additional cost of this cladding can be compensated by the avoided costs of shutdown and replacement of tubes. For new WTE facilities, where boilers are designed to operate over 420 °C, cladding of superheater tubes with Inconel 625 cladding is not recommended.

7. HVOF and Thermal Sprayed Coatings

Apart from the selection of corrosion resistant metals for cladding, the technologies used to apply these materials on metal tubes also affect the lifetime of protection layers. Technologies such as weld overlay and thermal spray processes that consist of HVOF and thermal plasma sprayed coatings have been used in WTE boilers. Weld overlay is mostly applied in severe corrosive environment, but one major concern regarding weld overlay is that repeated applications at the same area may cause embrittlement of the old overlay and lead to cracks that will propagate into the overlaid tube (Ref 14).

Thermal spray processes can provide hard, dense, sufficiently thick, and tight coatings for long term protection of erosion (Ref 15). The porosity of HVOF coatings has been reduced to less than 1%, which is much lower than the typical range of 3% to 5% encountered in flame or arc spraying overlays (Ref 16). Experimental tests have indicated that both HVOF and plasma coatings have good erosion resistance because they produce homogeneous and low microstructure coatings (Ref 15). The application of corrosion resistant materials like Inconel 625 by means of the HVOF or plasma coating processes has shown to be the best combination of erosion-corrosion resistance among all other thermal spray processes (Ref 15, 17). In practical applications, NiCrSiB alloy HVOF coatings and Inconel 625 plasma sprayed coatings have been used successfully on waterwall tubes while TiO_2-Al_2O_3/625 cement HVOF coatings applied on superheater tubes show long-term durability of more than 3 years (Ref 18).

8. Design of Flue Gas Pass of Boilers

In general, there are two major flow-pass designs of boilers: vertical and horizontal (Fig. 7). With regard to the erosion-corrosion issue, the design objectives are to obtain a uniform gas flow pattern, minimize impact velocity on the tubes, and provide smooth transition from

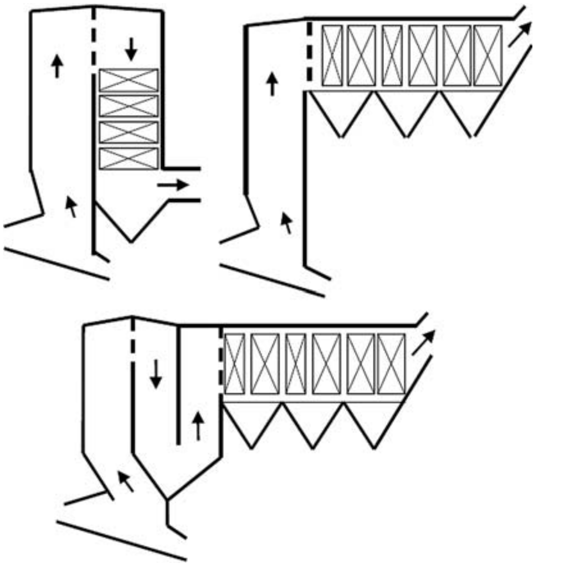

Fig. 7 Schematic diagram of vertical and horizontal boilers

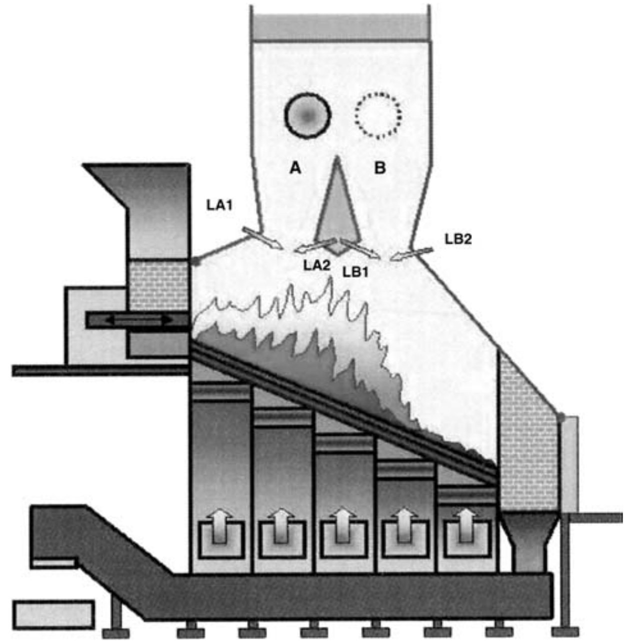

Fig. 8 Schematic diagram of the Seghers Boiler Prism

the 1st pass (combustion chamber) to the 2nd pass[3] of the boiler. Under the same operating conditions, superheater tube bundles in a vertical design boiler, which has fewer gas passes (upper left in Fig. 7) will have more critical corrosion problems than the tubes in a horizontal design boiler (bottom in Fig. 7), because the former are subjected to higher metal temperatures and flow velocities of flue gas. The disadvantage of the horizontal design is that it needs more floor space than the vertical design. In practical terms, the determination of vertical vs. horizontal set-up and the number of gas passes also depend on other factors, such as space, past operating experience, and cost.

9. The Seghers Prism

The Seghers Prism (Ref 10) is a prism-shaped tubular structure equipped with several tuyeres through which secondary air is injected into the combustion gases as they rise above the combustion grate. It is inserted horizontally through the center of the combustion chamber at the lower end of the first radiant boiler pass (Fig. 8). It is water-cooled and refractory lined. Corrosion phenomena can be reduced since the function of the prism is to mix the combustion gases, increase turbulence and decrease temperature fluctuation, thus minimizing hot spots. The advantage of the prism is that it can be implemented in existing plants as a retrofit. However, the retrofit requires a long plant shutdown (Ref 10).

[3]Passes in the boiler industry denote the interconnected heat transfer vessels, e.g., first pass is the waterwall surfaces in the combustion chamber.

10. Recirculation of Flue Gas

In some of the most recent WTE facilities, e.g. the Brescia plant in Italy, part of the flue gas is recirculated through secondary tuyeres in the combustion chamber. This has similar beneficial effects (better mixing, increased turbulence, fewer hot spots) as those claimed for the Seghers Boiler Prism.

11. Injection of Chemicals into Combustion Chambers

The objectives of injection of chemicals such as $Ca(OH)_2$ or $Mg(OH)_2$ into combustion chambers are to (a) decrease HCl concentration in the flue gas; (b) facilitate the removal of deposits and decrease their corrosion potential. This method is still under investigation, but preliminary results have shown it to be effective (Ref 19). The disadvantage is that continued injection of chemicals is required, which increases the cost of operation and also the amount of fly ash.

12. Improvement of Cleaning Method

On-line methods for cleaning heat exchanger tubes, such as high-pressure water washing and explosive cleaning have been developed in order to limit the build-up of deposits and shorten plant downtime. These cleaning methods are effective in removing the ash deposits; however they also may cause increased erosion-corrosion at

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some locations of the superheater tubes. Furthermore, some cleaning methods require WTE plants to come off-line for complete cleaning. Therefore, development of cleaning methods that are less harmful to tube life without reducing cleaning efficiency is needed. A new technology named TIFI has been invented by Fuel Tech Inc. (Ref 20) and applied to some WTE facilities for deposit removal and fouling control. This technique injects the deposit control agent such as MgO directly to the problem area to react with ash deposits and makes them more friable and easy to remove; by doing so, the performance and cost effectiveness of the tube cleaning process are improved (Ref 20).

13. Conclusions

Many WTE facilities experience severe corrosion problems. The difficulty of combating corrosion is that there are many contributing factors and their effects may be overlapping effects. Also, the effects of these factors vary widely among WTE facilities, given the heterogeneous nature of MSW and differences in grate and boiler designs of WTE plants. The prevailing methods of protection from high temperature corrosion were described in this paper. Primary measures of protection seek to minimize the adverse effects of these corrosion factors while secondary methods seek to increase the lifespan of tubes. Most of these methods have been applied to actual WTE facilities and shown different levels of effectiveness.

Ongoing experimental studies at Columbia University aim at providing more information as to the effect of these factors and their interaction on corrosion phenomena. The experimental team is also interested in testing better tube alloys and tube coatings produced by advanced metal spraying techniques.

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