Combating Corrosion in WTE Facilities – Theory and Experience

Shang-Hsiu Lee, Nickolas J. Themelis, and Marco J. Castaldi
Department of Earth & Environmental Engineering
Henry Krumb School of Mines, Columbia University
New York, NY 10027

Abstract

In boilers that use municipal solid wastes as fuel, metal wastage due to corrosion and erosion and tube fouling due to the buildup of deposits present serious problems to the system designer and operator. This study examines the corrosion mechanisms in Waste-To-Energy (WTE) boilers and summarizes the findings of a corrosion survey of several WTE facilities and of interviews with senior engineers in the WTE industry. In addition, this study examines the existing methods of reducing corrosion that are adopted in WTE plants. Finally, the study proposes experimental research on corrosion resistant materials to be carried in the near future.

Introduction

Waste-To-Energy (WTE) technologies produce clean, renewable energy by means of the combustion of Municipal Solid Wastes (MSW). In well designed and operated WTE plants, MSW is combusted and converted to thermal energy that is transferred to steam that generates electricity in a steam turbine. The environmental benefits of WTE technologies include: conserving fossil fuels by generating heat and electricity, reducing the emission of green house gases, recovering ferrous and non-ferrous metals, and reducing the space required by landfills.

A major problem of operating WTE plants is the relatively high rate of corrosion in WTE boilers. High temperature corrosion results in downtime and periodic shutdowns in WTE plants and accounts for a significant fraction of the total operating cost of WTE plants. Aside from the economic aspect, high temperature corrosion also has environmental impacts. Metallic coatings and corrosion resistant alloys such as stainless steels, nickel-base alloys, and titanium alloys are often used to protect boilers from corrosion, and these result in unnecessary use of valuable resources (metals) and energy. Also, corrosion issues hinder further expansion of WTE technology and perpetuate the annual disposal of over 200 million tons of MSW in the U.S. in landfills that contaminate the atmosphere and may affect water resources in the future [1].

Corrosion phenomena in Waste-To-Energy facilities

The advantage of WTE technologies over landfills is that it reduces the environmental burden of disposing solid wastes and also recovers the energy contained in MSW. Over 130 million tons of wastes are combusted annually in over 600 WTE facilities worldwide and the recovered energy is converted to electricity and steam [2]. Figure 1 shows a schematic of a conventional modern WTE facility. 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 pass over heat transfer surfaces, such as membrane water tubes (waterwall), superheater tube bundles, evaporator tubes, and economizer tubes, heat is recovered to provide steam for electricity generation. To increase the efficiency of power generation, an increase in the boiler steam temperature and pressure is required. However, with increasing steam temperature, the heat transfer surfaces are subjected to severe high temperature corrosion, caused both by the metal chlorides (ash) deposited and the flue gas that contains a substantial amount of chlorides. Figure 2 shows the corrosion sensitive areas in a WTE facility [3].

The concentration of chlorine/HCl in the flue gas is determined by the MSW composition and varies somewhat from location to location. Table 1 shows that the chlorine content in three types of MSW varied from 0.47 to 0.72% [4].

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 [5].

*Waterwall: The tubes are welded together normally forming in a gas tight membrane wall. The tubes in this position are heated from the outside by radiation heat and cooled by water inside.

**Superheater: Steam temperatures inside the superheater tubes exceed saturation temperature, thereby generating higher metal temperature than in the water-wall tubes.

<table>
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<tr>
<th>Table 1. Chlorine concentration in MSW [4]</th>
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<td>New York City MSW</td>
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<td>Total Cl, g/kg</td>
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Corrosion mechanisms in Waste-To-Energy facilities

High temperature corrosion is a form of corrosion that does not require the presence of a liquid electrolyte, as in the case of aqueous corrosion. The corrosion mechanism is indicated by the most abundant corrosion 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, and carburization by metal carbides. In general, there are two major corrosion mechanisms in WTE facilities [4]:

1. Active oxidation: This mechanism occurs at metal temperatures above 450 °C (840 °F) and comprises several steps: (a) the formation of chlorine at the scale surface; (b) penetration of chlorine into the scale to the oxide/metal interface; (c) formation of chlorides on the metal surface components; (d) diffusion of metal chloride vapors outwards; (e) reaction of the metal chloride with available oxygen in the atmosphere to give metal oxide and chlorine.

2. Corrosion due to deposits by sulfation and by molten salts: Gases containing Cl₂, HCl, and gaseous alkali chlorides, e.g. NaCl and KCl, can accelerate the active oxidation mentioned above. Also, volatilized salt chlorides carried in the sulfide gases are deposited on the boiler tubes during cooling and contribute to corrosion in two ways: (1) the chlorinated species in the deposit cause a reaction similar to gas phase/active oxidation; (2) the presence of chlorides in the deposits may result in the formation of low-temperature melting eutectics (salt solution characterized by the lowest possible melting point) which may flux (dissolve) the oxide layer that is protecting the metal surface.

There are different kinds of factors that can affect corrosion in WTE boilers, such as the concentration of chlorine in the MSW, the operating temperature of the combustion chamber, the presence of molten salts deposits, and so forth. The influence of different corrosion factors can be summarized as follows:

1. Metal surface temperature: High temperature of metal surfaces due to high radiation fluxes accelerates the melting of deposits and activates the corrosion rate. In general, the metal temperatures of waterwall and superheater tubes are maintained at temperatures of about 300 °C (570 °F) and 450 °C (840 °F), respectively [3].

2. Gas temperature: The temperature of the combustion gases can affect both deposition rates and deposit compositions and thus accelerate the corrosion rate. 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 [6]. At a large temperature gradient, 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 metal tubes (thereby resulting in cracks of the protective oxide layer and increase point defect diffusion within oxide scales, thereby affecting the oxidation kinetics) [7, 8].

3. Temperature fluctuation: The non-homogeneous composition of the waste
fuel and the uneven temperature profile of combustion gas flow cause sharp fluctuations in gas temperature. Experimental studies have confirmed that the corrosion rate increased several times because of temperature fluctuation [9].

4. Characteristics of molten salt deposits: The diffusion rate of corrosive gases through the cracks and pores of deposits is an essential factor for increasing corrosion [4]. The presence of HCl, SO₂, and alkaline and heavy metal components in deposits can affect both chemical and physical properties of deposits such as gas permeability of deposits [10]. The corrosion rate also increases with an increase in thickness of deposits [11].

One particular reaction that is beneficial for corrosion reduction is the sulfation of volatilized alkali salts in the flue gases. This reaction can transform chlorine salts into sulfate salts and the released chlorine then reacts with water vapor to form hydrochloric gas. Sulfate salts are less aggressive since sulfate corrosion occurs at higher temperature [12]. In WTE facilities, the character of deposits is mostly affected by feed composition and gas/metal temperature. The heterogeneous nature of the fuel increases the variation in the composition of deposits, and makes it more difficult for operators to forecast the corrosion.

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 (Figure 3). Another result showed that the yearly maintenance cost per unit (i.e. an individual combustion chamber and boiler system) due to corrosion ranged from $18,000 to $1,200,000; the maintenance cost due to corrosion per ton of MSW combusted (Figures 4 and 5).

![Figure 3. Non-scheduled downtime due to corrosion of WTE plants (A1, B1, etc. refer to different WTE facilities responding to the WTERT survey)](image-url)
In an interview between the authors and engineers of a major WTE company, the maintenance cost of a WTE facility was reported to be $10-20 per ton of MSW, one-third of which was due to either replacing corroded materials or applying corrosion resistant coatings. If it is assumed that the maintenance cost of a WTE facility is $15 per ton of MSW, the corresponding cost of corrosion will be $5 per ton of MSW. This number is close to the average number of $4.2
per ton of MSW that WTERT obtained from the results of WTERT corrosion survey.

The percent distribution of revenues and costs of a German WTE facility is shown in Figure 6. Capital cost and maintenance cost account for approximately 60% and 15% of the yearly cost of a WTE facility respectively.

Therefore, the corrosion problems will cost a WTE plant approximately 3% of its yearly total cost, if the corrosion/total maintenance cost ratio of 1/3 applies. The actual cost may be even higher if the revenue lost of shutdown due to corrosion is taken into account.

Current methods of protection

Accumulated operating experience has resulted in reducing corrosion in the boiler tubes. Over the years, the industry has adopted general approaches to reduce corrosion which can be classified as primary and secondary measures. Primary measures seek to eliminate corrosion by influencing the process conditions in the boiler. Some of the methods include [4]: (a) improvement of process control, in particular minimizing fluctuations in gas temperature; and (b) design modifications, such as process gas recirculation to alter flow dynamics, enhancing gas mixing through the use of process 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 being 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 secondary measures include the injection of chemicals to remove deposits and use of refractory lining and ceramic tiles in the lower half or the entire height of the combustion chamber.

As discussed above, there are several methods that can be used to combat corrosion problems at WTE facilities. However, some of them may require either the retrofit of existing WTE facilities or different designs of new WTE facilities. The design and construction of WTE facilities comprise many parameters, and complex analysis is required to optimize the final design. In either case of existing or new WTE
facilities, it is essential to identify expensive/inexpensive design details of the project as well as conditions that influence the thermal process within the combustion unit. In addition, the construction time for making equipment changes in existing facilities is a very important parameter since the shutdown decreases the revenues of the WTE facility.

Below are details of some protection methods that have been applied in WTE facilities or are still under investigation. The advantages and disadvantages of these methods are described, including the concern of their cost. However, the actual cost of each method is not shown due to the limited available information.

1. Adoption of Inconel Alloy 625 cladding and composite tubes: Waterwall and superheater tubes are the most corrosion sensitive areas. This technique consists of overlaying a layer of Alloy 625 (21Cr-9Mo-3.5Nb-Ni base) on these tubes to protect them from the attack of HCl/Cl₂. 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 Alloy 625 should be used and where. Some researchers have shown that Alloy 625 applied on waterwall tubes provides excellent corrosion resistance [3]. Although the price of Alloy 625 is higher than that of a protective refractory lining, the cost of Alloy 625 can be partly compensated by avoiding the cost of refractory maintenance.

The application of Alloy 625 on the superheater tubes is more complicated since its performance on superheater tubes depends on the metal temperature. One study showed that Alloy 625 does not provide protection above 400 – 420 °C (750-840 °F) [14]. Another indicated that at metal temperature of about 540 °C (1000 °F), the wastage rate of Alloy 625 is 0.2μm/h (0.069 inch/year) [15]. Some boilers of existing WTE facilities are designed to operate at lower temperatures and therefore can apply Alloy 625 on superheater tube bundles. However, problems still arise in these WTE facilities because the lifetime of Alloy 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 Alloy 625 cladding is $350,000/unit; and $250,000/unit without Alloy 625 cladding. The labor cost of installation is $75,000/unit. If the lifetime of the superheater tube bundle with Alloy 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 at higher temperatures, the Alloy 625 cladding on superheater tube bundles is not recommended.

2. Different designs of flue gas pass of boilers: In general, there are two major flow-pass designs of boilers: vertical and horizontal (Figure 7). Regarding the erosion-corrosion issue, the object of protection is to minimize impact velocity, create a uniform flow pattern, and smooth transition from the 1ˢᵗ to the 2ⁿᵈ pass **. Under the same operating conditions, superheater tube bundles in a vertical design, which has fewer gas passes (upper left in Figure 7) will have more critical corrosion problems than that in a horizontal design (bottom in Figure 7) since 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 depend also on other factors, such as space, past operating experience, and cost.

*** Passes in the boiler industry denote the interconnected heat transfer vessels, e.g., first pass is the waterwall surfaces in the combustion chamber.
3. **The Seghers Prism**: The Seghers Prism [12] is a prism-shaped tube 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 (Figure 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 new designs as well as in existing plants as a retrofit. For an existing plant, the retrofit project of installing prism was stated to require a rather long plant shutdown [12]. The installation cost of the prism was not provided in the paper.
4. Recirculation of flue gas: In some of the most recent WTEs, 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 Seghere Boiler Prism.

5. 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 the preliminary result has shown to be effective [16]. The disadvantage is that continuing injection of chemicals is required and this increases the cost of operation and also the amount of fly ash.

6. Improvement of cleaning method: Some 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. These cleaning methods are effective in removing the slag and ash deposits; however they also cause the erosion-corrosion on some area of the superheater tubes. Furthermore, some cleaning methods require WTE plants to come off-line for complete cleaning. Therefore, improvement of cleaning methods which can be less harmful to the tube life without reducing the cleaning efficiency is needed. A new technology named Targeted In-Furnace Injection (TIFI) has been invented by Fuel Tech, Inc. [17] and applied to some WTE facilities for slag and fouling control. This technology is able to inject the slag control agent directly to the problem area, and by doing so the performance and cost effectiveness are significantly improved.

Ongoing experimental research

As discussed above, high temperature corrosion occurs in regions of the furnace where the fireside tube metal temperature is higher than 200 °C (392 °F), a variety of mechanisms for chemical attack of the metal tube surfaces then become pervasive. The chemicals that need to be considered are not only the oxidized halogen and metals but also the complex salts and eutectics that form as slag on the surfaces of waterwall or superheater tubes [18].

Planned laboratory tests at Columbia

There have been many laboratory tests seeking to clarify the effects of corrosion factors mentioned above on corrosion rates of waterwall and superheater tubes in WTE plants. However, most of the tests were performed under conditions that gas (environment) temperature and metal surface temperature were the same. As we have discussed above, the temperature gradient between gas temperature and metal surface temperature is a driving force for the condensation of vaporized species such as chlorides on the cooled surface. Therefore, creating a temperature gradient to simulate the actual environment in WTE plants has become critical in laboratory tests.

The objectives of planned laboratory experiments at Columbia University are to (a) test the corrosion resistance of different commercial tubes and coating materials under different corrosive environments; (b) find better operating conditions for WTE plants to reduce corrosion problems; and (c) develop processes for reducing concentration of active chlorine in combustion gases. The control variables will include temperature gradient, SO$_2$/HCl ratio, oxidizing/reducing atmospheres, and molten salts deposits. These tests have been planned in collaboration with senior engineers of the WTE industry with long experience in WTE corrosion problems.

The experimental system (Figure 9) is designed to test multiple samples simultaneously under well controlled environments. It is capable of maintaining a pre-set desired atmosphere simulating various conditions in the combustor. In addition, a very well controlled thermal gradient across the test sample can be maintained for the duration of the experiments. Finally, actual slag samples are applied to the test coupons in order to ensure the real chemical make-up of the slag is used and not a synthesized slag.
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 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.

References:

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