Corrosion Mechanisms and Alloy Performance in Waste-To-Energy Boiler Combustion Environments

George Y. Lai
Consultant to Welding Services Inc.
2110 Pebble Beach Drive, Suite 100
Carmel, Indiana 46032
U. S. A.
Tel: 317-575-0915
Fax: 317-846-7263
Email: g.lai@worldnet.att.net

ABSTRACT
The combustion of municipal solid waste in a boiler for power generation produces a very corrosive environment for the boiler tube materials. The environment contains HCl, SO₂, various metal chlorides and sulfates along with typical combustion products. Due to their low melting points and high vapor pressures, metal chlorides are believed to be primarily responsible for the boiler tube corrosion problems encountered in waste-to-energy (WTE) boilers. Without some sort of corrosion protection method, the standard materials of the construction for the boiler, such as carbon and Cr-Mo steels, are subject to severe high temperature corrosion attack. The present paper discusses the possible modes of high temperature corrosion for waterwalls and boiler tubes in the convection section, and the prevailing protection method for these components as well as the performance of various alloys in these hostile combustion environments.

INTRODUCTION
Municipal solid waste typically contains plastic materials, textile, leathers, batteries, food waste, and other miscellaneous materials. These constituents are the source of chlorine, sulfur, sodium, potassium, zinc, lead, and other heavy metals that form corrosive vapors of various chlorides and sulfates during combustion. These chloride and sulfate vapors, along with fly ash, condense and deposit on the cooler surfaces, such as waterwalls, which surround the combustion zone, and heat exchanger surfaces in the convection path, such as screen tubes, superheater tubes and generating banks. These metallic components are subjected to accelerated wastage rates. Wastage rates of 1.3-2.0 mm/yr (50-80 mpy) or higher have been observed for carbon steel waterwalls, and of 2.5 mm/y (100 mpy) and higher have been observed for carbon or Cr-Mo steel superheater tubes. Corrosion problems in waste incineration are very well documented. [1-8] However, modes of corrosion are not very well understood. This paper attempts to examine the modes of corrosion attack in terms of different corrosion morphologies observed. The paper also discusses the prevailing method of corrosion protection for major components of the boiler.
CORROSION MODES

In order to try to understand the possible corrosion modes that might be responsible for the corrosion reactions, it may be useful to examine the possible corrosive combustion constituents. The deposits and corrosion scales typically are good places for the information. Figure 1 shows the deposits and corrosion scales and the SEM/EDX analysis results for the deposits and corrosion scales. These deposits and corrosion scales were found to be quite complex. Typical elements observed were Fe, Cl, S, Zn, Pb, Na, K, Cd along with Si, Mg and Ca. Significant amount of chlorine was observed throughout the deposit/corrosion scales. In analyses of municipal solid waste at several waste-to-energy plants, chlorine was found to be in the range of 0.33 % to 0.75 % (by weight). [9-11]

It is believed that presence of Zn, Pb, Cd, Na, K along with Cl makes the combustion environment of a WTE boiler much more corrosive than that of a coal-fired boiler. Chlorides of Fe, Zn, Pb, Na, K and Cd as well as eutectic and ternary phases of chlorides involving these elements exhibit very low melting points and high vapor pressures. [12-14] Few of the chlorides along with their melting points in parentheses that can become molten at the waterwall and superheater metal temperatures are listed here: 70% ZnCl2-30% FeCl3 (200° C), 55% ZnCl2-45% KCl (230° C), 70% ZnCl2-30% NaCl (262° C), 58% NaCl-42% FeCl3 (370° C) and 72% PbCl2-28% FeCl2 (421° C). [2] If the tube surface has accumulated adequate chloride salts that become molten, the molten salt deposit can easily dissolve the oxide scale and promote corrosion attack.

Pitting type of corrosion attack was observed on alloy 625 overlay of a superheater tube in a WTE boiler. Examination of the pitting attack by optical microscopy revealed that the morphology of corrosion attack, as shown in Figure 2, was very similar to that by molten salt corrosion. In another case, the corrosion attack was found to follow general wastage, which was then followed by internal penetration along dendritic cores, as shown in Figure 3. The internal penetration along dendritic cores suggests that the internal penetration corrosion was the result of gaseous chlorides.
Figure 3. Optical photomicrograph showing corrosion attack on alloy 625 overlay on an evaporator tube with the corrosion morphology consisting of general wastage followed by preferential attack along dendritic cores.

One factor that may influence the corrosion mode or morphology of waterwall, superheaters and generating bank is the use of water or steam by boiler operators in removing ash deposits from the heat exchanger surfaces in order to keep the boiler functioning. Some boiler operators shut down the boiler regularly, for example every 6 months, for water washing of the waterwall and tubes in the convection section. For minimizing downtime, the tubes may not be cooled to low enough temperatures before initiating water-washing procedures. Some operators even perform water washing during operation. The effects of water washing at operating temperatures or at temperatures higher than room temperature during shutdown on the corrosion of boiler tube metals is not known. Soot blowers using steam are commonly used to remove ash deposits from heat exchanger surfaces in superheaters. Steam soot blowing is found to significantly increase erosion-corrosion of superheater tubes. [15]

WELD OVERLAY CLADDING

Carbon or Cr-Mo steels have been found to suffer severe corrosion attack with wastage rates of 1.3-2.0 mm/y (50-80 mpy) or higher at furnace waterwalls. In 1984, Welding Services Inc. (WSI) pioneered an innovative, engineering solution for solving this waterwall corrosion problem by performing an overlay of a corrosion-resistant alloy to carbon steel waterwalls on site using automatic gas-metal-arc welding (GMAW) machines in a WTE boiler in Lawrence, Massachusetts. The alloy selected for the overlay was alloy 625 (Ni-21.5Cr-9Mo-3.7Nb). It was an excellent alloy selection. The overlay had proved to be so successful in its performance in the Lawrence boiler that approximately 126,000 kg (280,000 lbs) of alloy 625 weld overlay metal had been applied by WSI from 1985 to 1990 for about 30 boilers. [16]

The general process of weld overlay cladding of the waterwall by automatic gas-metal-arc welding (GMAW) machines has been described in previous publications. [16, 17] The cladding process is briefly described below.

The GMAW overlay machine, which is fully automatic, deposits weld beads in a vertical down mode starting typically from the membrane and then moving to the tube section following a preprogrammed weld bead sequence to achieve a uniform coverage of the waterwall (i.e., membranes and tubes) in a boiler. Each weld bead is overlapped by subsequent weld bead to insure a full coverage with no missing spots. The thickness of the overlay applied to the waterwall in field is typically 1.78 mm (0.070") minimum. Figure 4 shows an overlay machine in the process of applying weld overlay to the waterwall in a boiler.

Figure 4. Photograph showing an automatic GMAW machine in applying an alloy 625 overlay to the waterwall of a boiler.
22.3 m² (180 to 240 ft²) of the waterwall can be overlaid over a 12-hour shift. A waterwall area of about 280 m² (about 3000 ft²) can be routinely overlaid in seven days using a two 12-hour-shift-per-day schedule.

When the waterwall is damaged beyond repair on site, the damaged section can be removed and replaced with shop-fabricated overlay panels. Panels of sizes up to 1.2 m (4 ft) wide and 12 m (40 ft) long can be readily handled in the shop. Construction of an overlay panel consists of fabricating a panel of steel tubes and membranes, which is then followed by overlay welding of the panel on a stand using essentially the same techniques as field overlay.

WSI has also developed a spiral overlay welding process for manufacture of bimetallic tubing using GMAW process to deposit an alloy 625 overlay cladding on a ferritic steel tube, followed by a gas-tungsten-arc welding (GTAW) process to smooth the overlay surface and temper the heat-affected zone (HAZ) in the substrate steel. This dual GMAW/GTAW process has been patented. The process produces bimetallic tubing with very smooth overlay surface and ductile overlaid microstructure. Figure 5 shows typical cross-section of a Unifuse® 625 overlay tube. These overlay clad tubes have been successfully used in the convection section.

Metal wastage rates reported here are based from the available data, and may not be applicable to every boiler. Actual metal wastage rates for some boilers, which are dependent upon the type of the waste constituents being burned, the design of the boiler, design and operating parameters among other factors, can be higher than the values reported here.

**Waterwalls**

The current prevailing method of protection for the furnace waterwalls is alloy 625 overlay cladding by automatic GMAW overlay welding. The performance of alloy 625 overlay has been found to be satisfactory in both mass-burning and refuse-derived fuel (RDF) units. It is generally expected to perform for 10 years or longer [15]. Corrosion attack tends to be of pitting type, as shown in Figure 6. The area that has suffered corrosion attack can be readily repaired by re-overlay welding. This repair-overlay welding is performed by first grinding of corroded, pitted area, then followed by overlay welding.

In general, the tube metal wastage rate for alloy 625 overlay is expected to be 5 mpy or less for majority of the overlaid waterwalls [15]. These 625 overlays in WTE boilers in general exhibited less than 10% dilution (i.e., 10% or less Fe in alloy 625 overlay). It is believed that excessive dilution (i.e., excessive Fe content in the overlay), for example, 15 or 20% dilution, could significantly enhance the wastage rate. High Fe content in the overlay, which results from high dilution, could probably prompt the formation of volatile FeCl₃ and/or FeCl₂, thus higher wastage rates.

---

Figure 5. Typical cross-section of a spirally overlay bimetallic tubing with alloy 625 cladding on a ferritic steel tube.

**TUBE METAL WASTAGE RATES**

The materials issues for different components in the boiler are discussed in the following sections. Particular focuses are on the current alloys that are being used and the metal wastage rates that are generally observed.
Screen Tubes

Screen tubes are installed in some boilers in front of superheater bundles for the purpose of reducing the temperatures and velocities of the flue gas entering into the superheater bundles in order to reduce corrosion and erosion-corrosion for superheaters. Since the tubes are water-cooled, the tube metal temperature at the outer diameter (OD) is similar to that of the waterwall. The screen tubes are expected to experience similar wastage rates as those of the waterwall. Alloy 625 spirally overlaid tubes have been successfully used as screen tubes. In general, the wastage rate for alloy 625 overlay has been observed to be approximately 5 mpy or less. [15]

Superheaters

Some methods of protection are required for carbon or Cr-Mo steel tubes against aggressive corrosion or erosion-corrosion attack. Without protection, steel tubes were found to suffer wastage rates ranging from 67 mpy to 680 mpy. [15]

Spiral 625 overlay tubes offer a viable solution to the superheater corrosion problems. An example is given in Table 1, which summarizes the comparative performance between the bare carbon steel tube and alloy 625 overlay tube in a side-by-side test at a superheater. The superheated steam temperature and pressure for the boiler were 750°F and 750 psi, respectively. Wastage rates were observed to be about 110 mpy (2.8 mm/y) for carbon steel and 18.3 mpy (0.46 mm/y) for alloy 625 overlay. [17] Based on this data, the expected replacement interval for carbon steel tubes and alloy 625 overlay tubes is shown in Table 1. Alloy 625 overlay tubes provide a service life improvement of slightly more than 4 folds.

Another example showing excellent performance of alloy 625 overlay superheater tubes in a WTE boiler in Europe is illustrated in Figure 7. No evidence of corrosion attack after 4-1/2 years of service in a superheater producing 761°F (405°C)/609 psi (42 bars) superheated steam. [15]

Table 1. Expected Replacement Interval for Carbon Steel Tubes and Unifuse 625 Tubes. [17]

<table>
<thead>
<tr>
<th>Carbon Steel Tube</th>
<th>Unifuse 625 Overlay Tube*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4 yr</td>
<td>5.8 yr</td>
</tr>
</tbody>
</table>

* Overlay (0.080" thick) + Steel Tube

Figure 7. Overview (a) and close-up view (b) of alloy 625 overlay tubes after 4-1/2 years of service in a superheater at a WTE boiler. Weld bead ripples were still clearly visible.

However, in some WTE boilers, the environments were so aggressive that alloy 625 overlay did not perform well. This is illustrated in Figure 8, which showed alloy 625 overlay was corroded away in 15 months in a superheater that generated 750°F/650 psi steam.
Alloy 625 overlay was corroded away in 15 months as part of the superheater in a very aggressive WTE boiler. The wastage rates for alloy 625 overlay in superheaters can vary widely from boilers to boilers from less than 10 mpy to 80 mpy. It may be due to the fact that the metal temperatures of the superheater are much higher than those of the waterwall and screen tubes, the wastage rate may become more sensitive to the operating parameters, such as waste constituents, boiler design, temperatures and velocities (also local velocities) of the flue gas stream entering into the superheater bundle, steam temperature and pressure, among other factors. It is believed that the waste constituents, particularly the per cent of chlorine in the fuel, which have been rarely characterized by boiler operators, may be one of the most important factors that influences the severity of the corrosion attack at superheaters.

WSI has been performing field testing to determine a superheater overlay alloy that can handle most, if not all, of the WTE boilers. So far, the tests have shown that alloy 622 (Ni-21Cr-14Mo-3W), C276 (Ni-16Cr-16Mo-4W), 52 (Ni-30Cr-10Fe) and 72 (Ni-44Cr) were not as good as alloy 625 in performance. These test results suggest that increases in Mo would not improve the alloy’s performance. Also, high Cr, Ni alloys containing 30% Cr and 44% Cr did not seem to improve the alloy’s performance. A systematic field test program is now underway to test several new overlay alloys. A test tube containing a new overlay alloy being tested as part of a superheater in a very aggressive WTE boiler is shown in Figure 9. The tube had been in service for 6 months when the photo was taken, revealing the weld bead ripples. Exposure testing of this test tube is continuing.

Figure 8. Alloy 625 overlay was corroded away in 15 months as part of the superheater in a very aggressive WTE boiler.

Figure 9. Testing of a new overlay alloy in the superheater of a very aggressive WTE boiler.

Generating Bank

The generating bank is typically located behind the superheaters. Thus, the temperature of the flue gas stream is significantly lower after passing through superheaters before entering into the generating bank. Carbon steel tubes can still suffer erosion/corrosion attack from the flue gas stream in the generating bank, even though the flue gas temperature is much lower. Furthermore, the soot-blower erosion can pose another serious problem to carbon steel tubes. Typically, stainless steel tube shields are used to protect the tubes from soot-blower erosion. The stainless steel tube shields often suffer high-temperature corrosion, erosion/corrosion, and distortion, particularly at the attachment straps. As a result, shields drop off from the tubes with many being caught in the tube bundle impeding flue gas flow and adversely affecting heat transfer. Figure 10 shows a failed tube shield on a carbon steel tube. The tube shield provided protection from the back against soot-blower erosion. The straps used for holding the shield to the tube were badly corroded and distorted. Figure 11 shows that the stainless steel tube shield had suffered severe chloride corrosion attack after three years of service. The windward side of the tube, which was unprotected, suffered erosion/corrosion attack from the flue gas stream, causing tube wall thinning at about 50° angles on both sides. The shields and the tube bundle had been in service for three years, and required tube replacement.
Alloy 625 overlay has been used successfully in protecting carbon steel tubes in the generating bank. Due to much lower temperatures, the wastage rates for alloy 625 overlay are believed to be less than 5 mpy. [15] The 625 overlay should also resist soot-blower erosion attack.

Figure 10. A generating bank carbon steel tube with a stainless steel tube shield failed after three years of service.

Figure 11. Type 309 SS tube shield suffered severe chloride corrosion attack after three years of service in a generating bank.

SUMMARY

1. Corrosion modes in WTE combustion environments are believed to be of high-temperature chloride corrosion. Chloride corrosion can involve in either molten chloride salt corrosion or gaseous chloride corrosion. Per cent of chlorine in the fuel may be the most critical factor influencing the severity of the corrosion in the WTE combustion environments. Unfortunately, this information has rarely been determined by boiler operators.

2. Automatic GMAW overlay cladding using alloy 625 has become an industry “standard” solution to waterwall corrosion problems in WTE boilers. Wastage rates of alloy 625 overlay, in most cases, have been found to be in the range of less than 5 mpy.

3. A spiral overlay tube manufacturing process for producing alloy 625 overlay tubes involving both GMAW and GTAW, which was developed and patented by WSI, has played a significant role in solving severe corrosion and erosion/corrosion problems in screen tubes, superheater tubes and generating bank tubes.

4. Wastage rates for alloy 625 overlay for both screen tubes and generating bank tubes are estimated to be less than 5 mpy.

5. GMAW/GTAW spiral 625 overlay tubes have provided a viable solution to severe superheater corrosion problems. The wastage rates of alloy 625 overlay have been found to exhibit less than 20 mpy for many boilers.

6. However, in some aggressive boilers, alloy 625 overlay tubes have been found to be less than adequate in performance. This may be due to boilers burning more plastic materials (i.e., higher concentration of chlorine), combined with higher operating temperatures, higher flue gas velocities and soot-blower erosion, among other factors. Field testing to find a better overlay alloy has been underway. The test results so far have indicated that Ni-Cr-Mo alloys containing more Mo, or high Cr nickel alloys provided no improvements in performance over alloy 625. A systematic field testing program is being set up to test several new overlay alloys in a number of aggressive boilers.

7. The performance of alloy 625 overlay discussed in this paper was associated with the overlay exhibiting less than 10% dilution. Excessive dilution (e.g., 15% or more) in the overlay may result in higher wastage rates than those values cited in the present paper.

REFERENCES