

The role of chlorine in high temperature corrosion in waste-to-energy plants

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High temperature corrosion has been a serious problem in municipal solid waste (MSW) incinerators since the emergence of waste-to-energy (WTE) plants in the 1960s. Early researchers conjectured that corrosion was caused by sulfur compounds, but it soon became evident that the dominant corrosive species are chlorides, typically in combination with alkali metals (Na, K) and heavy metals (Pb, Zn). Yet, many uncertainties remain with respect to the complex interactions between metallic materials of construction and their corrosion products with aggressive species in the combustion atmosphere and in fireside deposits. Following a review of historical background, MSW incineration technology and refuse boiler materials/corrosion, this paper will examine the causes and mechanisms of high temperature corrosion in WTE plants, as well as the environmental and alloy-related factors affecting metal wastage. Attention will be called to remaining uncertainties regarding corrosion mechanisms, and to apparent incongruities and conflicting data on materials performance to help identify areas for further R&D.

(Keywords: waste incineration; chloride corrosion; alloy performance)

INTRODUCTION

Over a quarter century ago, British researchers in the field of fossil fuel fired boiler corrosion concluded that there is "a diversity of opinion concerning the role of chlorides in the corrosion process, and at the present time the picture is somewhat confused"¹. Although the state of knowledge has been greatly expanded since then, the role of chlorides in fireside corrosion is by no means fully understood. Several unresolved issues remain and need to be clarified according to a recent overview of British research and experience with burning high-chloride coals².

This situation is mirrored in the incineration of municipal solid waste, often referred to as refuse or garbage, performed in so-called waste-to-energy plants. As with coal-fired combustion, corrosion in refuse boilers has been intensively studied over many decades. Yet, major uncertainties remain as to the complex interactions between gaseous and condensed species with fireside metallic surfaces. There is, however, universal agreement that chlorine compounds are the principal corrosive agents in MSW incineration, in contrast to corrosion in coal-fired power generation where sulfur compounds are the main culprits. This distinction is not surprising, considering that MSW usually contains higher concentrations of chlorine (0.5-2.0%) than sulfur (0.1-0.4%). The principal sources of chlorine in domestic refuse are sodium chloride and polyvinyl chloride (PVC) plastic. As shown in Figure 1, the amount of PVC-derived chlorides is projected to keep on rising, portending that refuse boiler corrosion may become an even greater concern in future years.

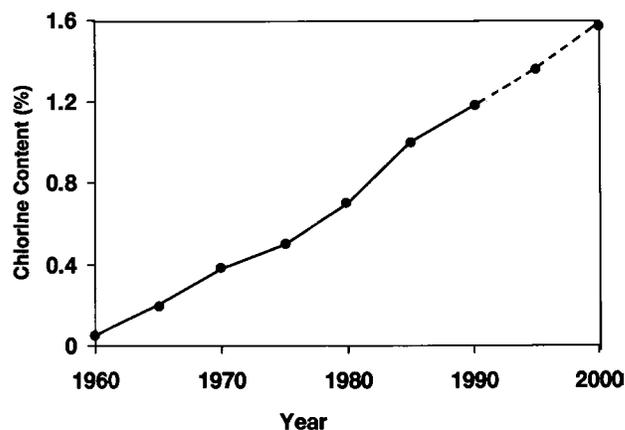


Figure 1 Estimated chlorine content of MSW derived from PVC (ref. 3).

HISTORICAL PERSPECTIVE

European boiler manufacturers who pioneered the development of WTE plants in the 1960s modeled their designs on coal-fired boiler technology. Proceeding on the assumption that comparable thermal efficiencies could be attained, these early units were designed with high steam conditions ranging from 450-540°C (840-1000°F) and 36.2-187.0 kg cm⁻² (500-2650 psig)^{4,6}. In many cases, failures of carbon steel boiler tubes due to corrosion were experienced during the first year of operation. The most severe attack reported occurred in a German incinerator, where a wastage rate of 40.6 mm yr⁻¹ (1.6 in yr⁻¹) was experienced in the superheater⁴.

Numerous corrosion failures in these first-generation WTE plants clearly indicated that corrosion was a far more serious problem than in coal-fired plants operating at comparable conditions. To achieve satisfactory tube life, designers of refuse-fired boilers were forced to accept substantial reductions in steam temperatures/ pressures. The adverse experience in the European plants was not lost on US boiler manufacturers, who accordingly opted for very conservative steam conditions, ranging from 190-323°C (375-613°F) and 13.3-33.4 kg cm⁻² (175-460 psig). Even these modest steam conditions required tube metal temperatures above 260°C (500°F), which was the upper limit recommended by leading researchers of MSW corrosion during these early years.

The large disparity between early European and US plants is illustrated in Figure 2. Between 1960 and 1972, the 11 European WTE plants put into service were designed with steam temperatures averaging 497°C (926°F), as compared to 235°C (456°F) for the six US facilities that started up between 1965 and 1974. Respective differences in average steam pressure were even larger, with the European plants topping US installations more than three-fold.

Several of these early US plants experienced unexpectedly severe corrosion, notwithstanding their low steam conditions. This was attributed to a variety of factors, among them excessive boiler tube metal temperatures and locally reducing atmospheres. Since then, improvements in furnace and boiler design, materials upgrading, and better controlled operation have permitted a progressive increase in steam conditions. This is reflected in the design of 15 large WTE plants, utilizing boilers from 10 different manufacturers, that started up in the US in 1990-1992. Steam conditions in these modern US plants range from 399-463°C (750-865°F) and 46.6-64.3 kg cm⁻² (650-900 psig), which is comparable to modern European facilities.

The historic trend in WTE plant design in Europe and the US differs markedly from the path taken in Japan. During the same 1990-1992 time frame, the 24 WTE

plants that went into operation in Japan had comparatively mild steam conditions ranging Iron, ZU6-300 C, (406-527°F) and 18.6-32.0 kg cm⁻² (250-440 psig)⁹. The greater conservatism reflected by the Japanese plants apparently signals a greater emphasis on plant reliability and availability than on maximizing power production. The thermal efficiency of most Japanese WTE plants is 10-15%, compared to about 20% for US facilities. These figures are far below the typical 33% efficiency attained in coal-fired power stations, which routinely operate at 538°C (1000°F) superheat/reheat cycles, and in supercritical units, up to 245 kg cm⁻² (3500 psig).

The situation in Japan is expected to change markedly with the completion in 1999 of an 8-year program to develop high efficiency waste-fired power generation^{10,11}. This cooperative government/private sector initiative is being conducted under the auspices of the New Energy Development Organization (NEDO), with the objective to design and demonstrate WTE plants having a thermal efficiency of 30%. A key component of this landmark project is development of new corrosion-resistant alloys and composites, notably for superheaters, that can withstand the high temperatures necessary to attain this high efficiency level. This alloy development effort, carried out by major Japanese alloy producers and boiler vendors, is directed by the Japan Research and Development Center for Metals.

MSW INCINERATION TECHNOLOGY

The two competing concepts in common use for MSW incineration are mass-burn and refuse-derived fuel (RDF), described in greater detail elsewhere^{3,12-14}. Massburn incinerators burn as-received unprepared refuse, while in RDF facilities the raw refuse is first separated, classified, and shredded into fist-sized chunks. In recent years, several fluidized bed incinerators have been put into service for combusting and co-combusting MSW.

Mass-burn and RDF plants both employ grates through which primary air is introduced, and which transport the

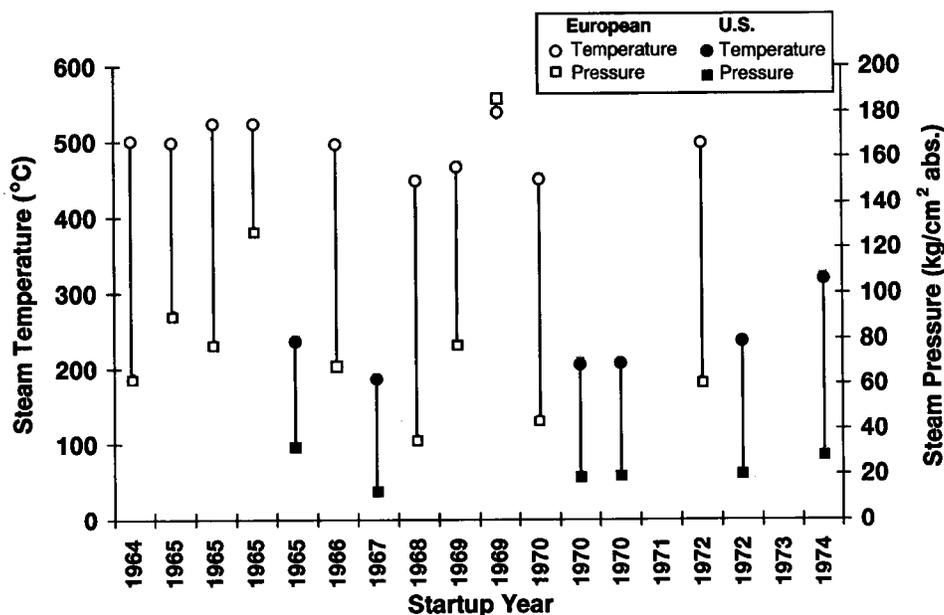


Figure 2 Steam conditions in European and US WTE plants (ref. 8).

burning refuse through the furnace toward an ash dump. Mass-burn grates come in a large variety of proprietary stoker designs, most of which use sloped and stepped metal grates consisting of reciprocating or other moving action grate bars that churn the refuse to facilitate combustion. RDF plants employ traveling grate stokers, with part of the combustion taking place in suspension firing above the grate. All MSW incinerator designs introduce copious amounts of secondary air to complete the combustion process.

A schematic of a typical mass-burn MSW incinerator is shown in Figure 3. Except for the feed system and the lower furnace area, the basic design is similar to that employed in fossil fuel fired power plants. The radiant boiler consists of a membrane waterwall combustion chamber, followed by convective heat extraction in superheaters and economizers. Air pollution control systems in US WTE plants predominantly utilize semi-dry scrubbers (spray dryers) and either fabric filters or electrostatic precipitators. In Europe and Japan, many WTE plants continue to rely on wet scrubbers to control particulate, acid gas emissions and volatile metals.

REFUSE BOILER MATERIALS AND CORROSION CONTROL

Corrosion protection and control is a critical aspect of WTE plant technology and is closely governed by cost considerations. Following the traditional approach taken with fossil fuel fired boilers, designers of WTE plants strive to limit the use of alloy materials by resorting to

favorable design configurations and refractory linings to reduce metal wastage. Such linings, in the form of silicon carbide monolithics¹⁵ and fired shapes¹⁶, are used to good advantage for protecting the lower waterwall in mass-burn units, but have proved unsuitable for RDF installations because of excessive risk of slagging. On the debit side, refractory linings reduce heat transfer and add to the maintenance burden. For added protection against abrasion-corrosion close to the grate, this zone is often fitted with wear-resistant blocks made of cast alloys or ceramics.

An effective method for protecting and restoring carbon steel waterwall tubing is by means of alloy 625 weld overlay¹⁷. An estimated 16,000 m² (170,000 ft²) of alloy 625 weld overlay has been applied in over 100 US refuse boilers. The most corrosion-prone location in mass-burn incinerators is the high heat flux zone directly above the refractory-lined portion, which is often subject to flame impingement. A typical corrosion failure of a steam generation waterwall tube is illustrated in Figure 4. Corrosion of unprotected carbon steel tubing in this vulnerable location has led to numerous in-service failures within the first year of operation in several US WTE plants.

Superheater tubing is customarily made of carbon or low Cr-Mo steel, and fitted with high alloy tube shields for added protection against erosion-corrosion. This approach has met with only limited success in high temperature superheaters because of short shield life and resultant corrosion of the exposed tube. Moreover, shields

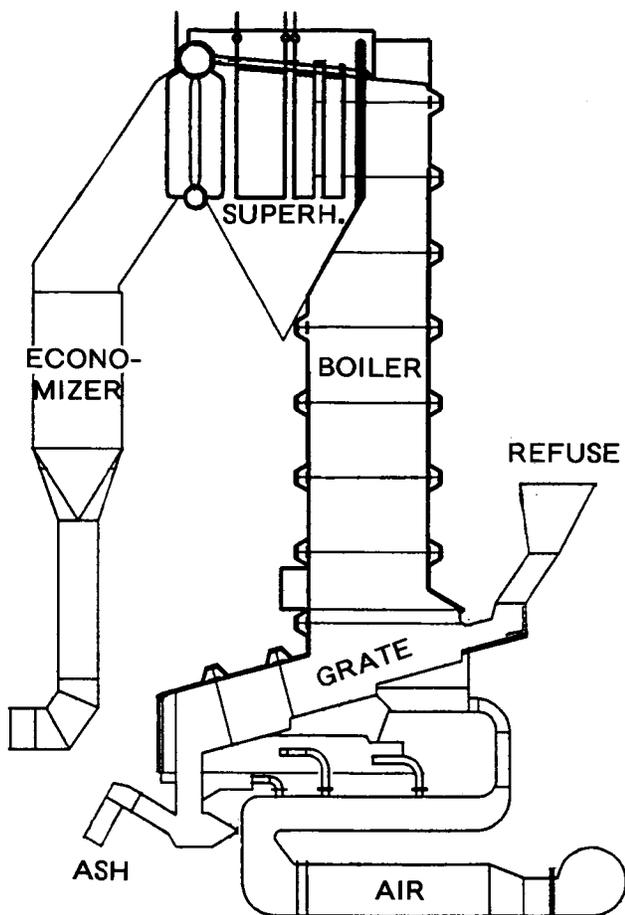


Figure 3 Schematic of mass-burn refuse incinerator.



Figure 4 Waterwall tube failure in MSW incinerator.

may become dislodged, which can lead to corrosion exacerbating flow blockages. Several prominent US refuse boiler vendors routinely specify alloy 825 for hot sections of superheaters. Experience has generally been favorable, as gauged from one plant's reported experience of a 10-year survival rate of 95% of their alloy 825 superheater tubes¹⁸. As another option, some WTE plant operators are now utilizing alloy 625 full-circumference weld overlaid superheater and screen tubes.

An alternative or supplemental approach to alloy upgrading for controlling corrosion/erosion is by means of conservative design features^{4,13,19-23}. This strategy is favored particularly by European boiler vendors, as an outgrowth of the disastrous corrosion experience in their first-generation WTE plants. The primary design-related stratagem for corrosion mitigation is reducing tube metal and gas temperatures. This can be accomplished by accepting lower steam conditions and by decreasing the temperature of the combustion gases entering the convection section. Other beneficial design features include empty and/or water-screened gas passes, parallel-flow finishing superheaters, low gas velocities in convection banks, and mechanical tube rappers (instead of sootblowers). On the debit side, some of these design features reduce energy efficiency and increase furnace size. Boiler vendors and WTE plant operators remain divided as to whether the initial cost premium for alloy construction is compensated by the boiler's more compact configuration and greater energy production.

An important design consideration for reducing corrosion is the use of measures to improve combustion characteristics. High on the list are provisions for a generous supply and good distribution of overfire air, and promotion of strong turbulence in the furnace. In that regard, it should be recognized that controlling and stabilizing combustion conditions in MSW incinerators is inherently much more difficult than in fossil-fueled plants. The difficulty arises from the non-homogeneity and variability of refuse with respect to composition, heat content and moisture.

The use of alkaline additives used by some plants for curbing emissions has not proven effective for corrosion control. To the contrary, addition of calcium compounds (lime) may actually aggravate corrosion^{24,25}. Co-combustion of MSW with sulfur or high-sulfur coal has been reported as a method for suppressing corrosion, as will be discussed later. To the best knowledge, this measure is not being pursued, probably because of concern that introducing large quantities of sulfur would overtax the emission control system.

CAUSES OF CORROSION IN MSW INCINERATORS

Corrosion in refuse boilers has been intensively studied dating back to the emergence of WTE facilities in the 1960s. The largest body of work has been conducted by a Battelle team led by Krause^{7,8,24,26-34}, mostly through grants from the US Environmental Protection Agency (EPA). More recent studies conducted by Battelle researchers were funded by the Electric Power Research Institute (EPRI)^{3,5,35,36} and jointly by the American Society of Mechanical Engineers (ASME) and the US Department of Energy (DOE)¹³.

Major studies have also been carried out by the

prominent US refuse boiler vendors Babcock & Wilcox³⁷⁻⁴¹, Foster Wheeler^{6,21,42-45} and AB B Combustion Engineering⁴⁶⁻⁴⁹. Important contributions toward advancing the state of knowledge on incinerator corrosion have recently come out of Japan^{9-11,50-56}, most of them associated with the aforementioned NEDO project. Valuable insights into the fundamental aspects of incinerator corrosion have been contributed by researchers in universities and research institutes⁵⁷⁻⁶⁴. Also noteworthy is the strong continuing work effort focused on materials development, testing and performance carried out by major alloy producers, prominently including Haynes, Inco, Krupp VDM, Mitsubishi, Sandvik and Sumitomo.

Recognition that chlorine in the refuse is the primary source of corrosion problems came slowly to the MSW incinerator community⁴. When the pioneer WTE plants ran into severe corrosion problems, these were attributed to the fluxing action of molten sulfates, pyrosulfates and alkali iron trisulfates, the corrosive species responsible for corrosion in high temperature coal combustion environments⁶⁵. This view has been largely discredited as an explanation for refuse boiler corrosion. Although sulfur compounds are still recognized as playing a contributory role, it is now accepted that corrosion in MSW incinerators is strongly chloride dominated. The aggressive species most responsible are chlorides of alkali metals (Na, K) and heavy metals (Zn, Pb, Sn). Chloride-rich ash deposits tend to have far lower melting points than sulfatic deposits, which dictates the lower steam conditions in WTE plants compared to coal-fired power stations.

The influential role of chlorides on corrosion became increasingly evident as study after study detected chlorides at the metal/scale interface, usually at higher concentrations than in the gas-side layer. Chloride corrosion in MSW incinerators proceeds via gas phase attack and, far more importantly, underneath deposits containing solid and/or molten chlorine compounds.

Gaseous corrosion

Essentially all chlorine compounds in MSW are converted to hydrogen chloride in the combustion environment. The amount of HCl in refuse incinerator flue gases ranges from about 400 to 1500 ppm, based on the rule of thumb that each 0.1 % Cl in the waste generates around 80 ppm HCl. Direct gas-phase chloridation of steels to iron chloride is not considered a significant factor. In fact, thermodynamic analysis predicts that this reaction is unlikely to proceed in MSW combustion atmospheres⁶⁶. Experiments with iron- and nickel-base alloys in a synthesized incinerator gas atmosphere showed a sharp increase of attack with progressive amounts of HCl up to 10%⁶⁷. However, the actual corrosion rate was negligible at the low HCl concentrations likely to be encountered in refuse boilers. It can thus be concluded that direct gas-phase chloridation is a minor concern in MSW incineration, except possibly under localized strongly reducing conditions or at exceptionally high temperatures.

It is interesting to note that HCl may actually act as a corrosion inhibitor in some reducing-sulfidizing gas mixtures. In laboratory exposures simulating utility boiler substoichiometric combustion gases containing 500 ppm H₂S, the addition of 350 ppm HCl was found to substantially reduce corrosion rates of carbon and low alloy

steels⁴¹. Similar observations were made with simulated coal gasification atmospheres containing 1% H₂S, where additions of 600 ppm HCl sharply reduced the corrosion rate of low alloy steel⁶⁸. The inhibitive effect was ascribed to chlorine in the sulfide scale acting to slow the outward diffusion of Fe to form the sulfide.

Deposit-induced corrosion

Corrosion in refuse boilers takes place primarily beneath deposits consisting of corrosive salts, usually admixed with a large fraction of ash constituents. In the lower furnace area where local reducing conditions are common, deposits are characteristically rich in chlorides. At higher elevations and in the convection section, deposits contain progressively larger amounts of sulfates, which are more stable than chlorides under oxidizing conditions. Consequently, a sizable fraction of chloride corrosion products is converted to sulfates. Deposition processes are varied, but generally include vapor condensation, physical deposition of flyash, and reaction of gaseous species with previously formed deposits. The cohesion of deposits may be promoted by fusion or sintering of molten or semi-solid alkali, alkaline earth, and heavy metal sulfates, chlorides, phosphates and carbonates^{38,39}.

Corrosion by condensed species is especially severe when these consist of molten salt eutectics, due to their fluxing action on protective scales. Significantly, deposit induced corrosion can be severe even in the absence of molten species. The proposed reaction sequences and mechanisms explaining such "dry" deposit attack will be examined in the section on corrosion mechanisms.

Mechanically-assisted corrosion

The simultaneous action of abrasion and erosion on components exposed in corrosive WTE plant environments synergistically accelerates metal wastage¹³. Rates of attack caused by such conjoint action can easily be an order of magnitude greater than corrosion alone. Abrasion-corrosion is encountered on the waterwall along the grate line in mass-burn plants, caused by the wearing action of the churning refuse. Erosion-corrosion is confined largely to the convection bank, where gas velocities are higher than in the radiant furnace zone. The erosion component results from impingement by flyash particles, and by high-velocity steam blast in sootblower lanes. Mechanically-assisted corrosion is best controlled by appropriate design features and protective barriers, as noted earlier.

CORROSION MECHANISMS

Corrosion in chloride-contaminated combustion environments is governed by competing oxidation-chloridation reactions, which in turn are closely dependent on the type of metal and adjacent micro-environment. The specific factors influencing the relative dominance of oxidation vs chloridation are thermodynamic factors (rates of formation, relative stability of products, vapor pressures, *etc.*) as well as kinetics which, in turn, relate to physico-chemical properties of the product (density, volume, diffusivity, expansion coefficients, *etc.*) and also to the product integrity, *i.e.* its adhesion and cohesion⁶⁰. In oxidizing-chloridizing environments, it is of crucial

importance which attack mode predominates because, unlike oxides, chlorides are ineffective corrosion barriers.

Thermodynamic analysis

Researchers exploring the mechanisms of corrosion in MSW incineration environments rely heavily on thermodynamic analyses, largely by means of thermochemical stability diagrams exemplified in Figure 5. While useful for determining equilibrium phases of metallic elements, such diagrams often fail to accurately predict corrosion products and scales that may actually form in complex multi-component environments because these depend on the specific reaction path and alloy composition. The shortcomings of stability diagrams are of even greater consequence with volatile species because stability diagrams do not take into account the vapor pressure of volatile species that may be in equilibrium with condensed phases⁶³. Thus, in chloride-contaminated combustion environments, chlorides are often found at the metal-scale interface even though oxide corrosion products are thermodynamically stable in the gas phase. Notwithstanding these limitations, thermodynamic analysis is used to good advantage by corrosion researchers. For that purpose, thermodynamics-based computer programs can provide a valuable tool for predicting species in the flue gas and flyash based on fuel chemistry and boiler operating conditions³⁹.

Reaction kinetics

In mechanistic studies of chloride corrosion, it is essential to factor in reaction kinetics, since these determine the rate of transport of gaseous chloride species by diffusion through pores and cracks in otherwise protective oxide scales. Depending on the relative amounts oxides and chlorides formed, corrosion can obey either a parabolic rate law (a combination of weight gain due to oxidation and weight loss due to volatile chloride formation) or a linear law due to chloridation alone⁶⁹. One of the effects of chlorine is that it changes the morphology of the oxide scale to create porosity, leading to more rapid attack even if the amount of chlorides formed is negligible⁶². Such voids at the metal/oxide interface promote scale spallation as well as internal attack by subsurface penetration of chlorides. An astute analysis of reaction kinetics operative in oxidation-chloridation, including schematics describing different cases, has been developed by Grabke⁵⁸.

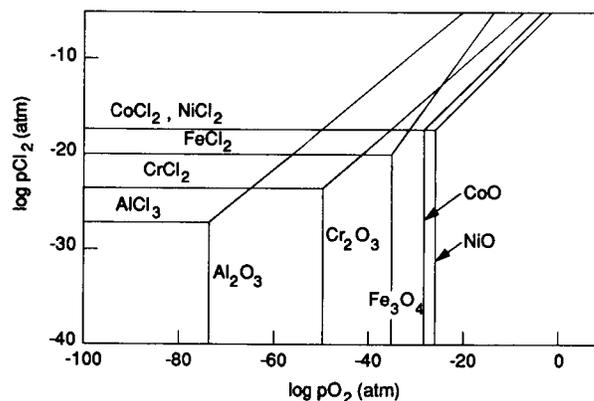
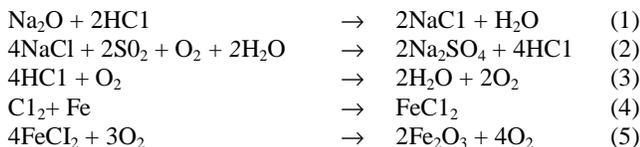


Figure 5 Thermochemical stability diagram for metal-oxygen-chlorine system at 400°C.

Corrosion under solid deposits

To account for the presence of chlorides and sulfates in refuse boiler deposits and associated "dry" deposit attack, Battelle researchers proposed a number of chemical reactions involving chlorine and sulfur species^{7,29}. Those involving principally chlorine compounds are shown below. Similar reactions can take place with sodium and potassium, since Na₂O and K₂O are both refuse combustion products.



The release of HCl and particularly Cl₂ (reaction (5)) was conjectured to take place directly adjacent to the metal surface, and therefore play a critical role in the corrosion mechanism. In that connection, it is noted that Cl₂ is far more corrosive than HCl. As suggested by earlier studies⁷⁰, the chloridation of iron by highly corrosive elemental chlorine (reaction (4)) is self-perpetuating, since fresh Cl₂ continues to be generated by reaction (5). The presence of a FeCl₂ corrosion product layer in contact with the metal is judged to be particularly damaging because it promotes scale disruption or spallation as a consequence of massive growth stresses generated by the six-fold volume expansion relative to the consumed metal².

More recent studies by Battelle³⁴ indicate that a similar chlorine corrosion/regeneration cycle may proceed via FeCl₃ formation. As shown in reactions (6) and (7), it is possible for the ferrous iron corrosion product to be oxidized to the ferric state which, when oxidized, liberates chlorine.



Additional routes for chlorine release during the corrosion process entail direct oxidation of FeCl₂ (reaction (8)) or via ferrite formation (reaction (9))⁵⁷. A further refinement of the self-sustaining chloride corrosion cycle was made by Grabke, who terms this corrosion mechanism "active oxidation"^{57,59}.



Chlorine liberation at the metal surface can similarly take place with alloy and stainless steels, whereby chromia is converted to alkali chromate (reaction (10)).



Chemical interactions between metals, corrosion products, deposits and the combustion atmosphere are, of course, not restricted to chlorine compounds, but also involve other chemical species contained in MSW. Among these, sulfur compounds are the most influential, although they themselves are not primary corrosive agents. As shown in reaction (2), through its chlorine liberating action, SO₂ plays an indirect though important role in promoting corrosion. The limits of this

not permit a closer examination of the sulfur chemistry in refuse combustion. An indication of the complexity of some of these possible interactions between chlorine and sulfur compounds is depicted in Figure 6.

Corrosion by molten species

Attack by molten ash-salt mixtures in MSW combustors is essentially a form of hot corrosion⁷¹, wherein chlorine rather than sulfur compounds are the primary aggressive species. The term 'hot corrosion' was originally restricted largely to sulfidation-oxidation attack of superalloys encountered in gas turbines, but has been broadened in current usage to encompass other manifestations of accelerated oxidation of metal surfaces exposed in a high temperature gaseous environment and coated by a thin fused salt film. As an extension of Rapp's fluxing model of hot corrosion, an 'apparent' acid-base chemistry has been postulated to account for fused chloride attack of austenitic stainless steels and Ni-base alloys in simulated waste incineration environments⁵¹.

The corrosiveness of chlorides stems to a large degree from their low melting points, especially eutectic mixtures of alkali and heavy metal chlorides associated with waste incinerators. A listing of possible molten chloride salt mixtures in MSW incinerator deposits is given in Table 1. While it is unlikely that these exact mixtures will be encountered in practice, the tabulated values give a good indication of the low melting points of fused deposits on corroded refuse boiler tubes.

Compounding the aggressiveness of chlorides is their low vapor pressure. It is generally accepted that high rates of attack can be anticipated at temperatures where the vapor pressure attains or exceeds a value of 10⁻⁴ atmospheres, designated as T₄^{64,73}. A plot of T₄ temperatures of several metal chlorides, together with their melting point (T_M), is shown in Figure 7. Significantly, T₄'s tend to be appreciably lower than T_M's, reinforcing the observation that chlorides can cause high rates of attack even in the absence of fusion. The proposed mechanism whereby this occurs holds that high vapor pressure chloride corrosion products cause volatilization of molecules from the scale to the vapor, while there is simultaneous scale growth by diffusional transport⁶⁴.

Other species that may potentially form in oxidizing-chloridizing environments are metal oxychlorides. These are conjectured to have an even greater corrosion-

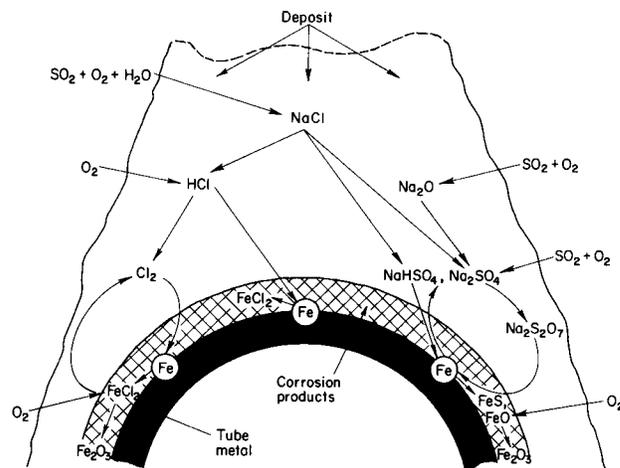


Figure 6 Possible chemical reactions on corroding refuse boiler tube (ref. 7).

Table 1 Possible molten chloride mixtures in MSW incinerator deposits (weight %)

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Salt mixture	Melting point		Ref.
	°C	°F	
27NaCl-73FeCl ₃	156	312	38
66ZnCl ₂ -34 FeCl ₃	200	392	32
15ZnCl ₂ -85SnCl ₂	204	400	32
68ZnCl ₂ -32KCl	230	446	38
56 ZnCl ₂ -30NaCl-14PbCl ₂	238	460	72
51ZnCl ₂ -43KCl-6PbCl ₂	238	460	72
43ZnCl ₂ -49KCl-8PbCl ₂	250	482	72
48ZnCl ₂ -52KCl	250	482	72
82ZnCl ₂ -18KCl	262	504	38
84ZnCl ₂ -16KCl	262	504	38
39ZnCl ₂ -50KCl-11PbCl ₂	275	527	72
73ZnCl ₂ -27PbCl ₂	300	572	38
58ZnCl ₂ -27KCl-15PbCl ₂	320	608	38
35ZnCl ₂ -48NaCl-17PbCl ₂	350	662	72
47KCl-53FeCl ₂	355	671	32
37NaCl-63FeCl ₂	370	698	38
17ZnCl ₂ -59KCl-24PbCl ₂	375	707	72
36NaCl-39KCl-25FeCl ₂	380	716	38
36NaCl-47PbCl ₂ -17CaCl ₂	391	736	72
16NaCl-40KCl-44PbCl ₂	400	752	72
31NaCl-69PbCl ₂	410	770	72
21KCl-79PbCl ₂	411	772	32
17NaCl-83PbCl ₂	415	779	38
15FeCl ₂ -85PbCl ₂	421	790	32
31ZnCl ₂ -69KCl	430	806	72
9CaCl ₂ -91PbCl ₂	475	887	32

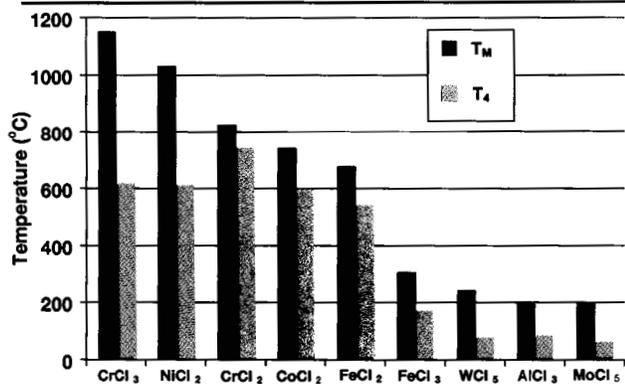


Figure 7 Metal chloride melting points and temperatures where chloride vapor pressure equals 10^{-4} atmospheres (ref. 73).

exacerbating effect than chlorides because oxychlorides are far more unstable and volatile than respective metal chlorides^{60,69}. This applies particularly to refractory metals at elevated temperatures. For example, molybdenum oxychlorides have vapor pressures 10-20 orders of magnitude greater than molybdenum chlorides in equilibrium with oxides and the test environment. This extremely high volatility explains the poor corrosion resistance of alloys having high molybdenum contents exposed in an atmosphere containing 20% O₂ and 2% Cl₂ at 900°C (1652°F)⁶¹. Fortunately such severe conditions are not encountered in MSW incinerators.

ENVIRONMENTAL FACTORS INFLUENCING CHLORIDE ATTACK

The principal environmental factors influencing the severity of chloride corrosion are chloride concentration,

gas and metal temperatures, and the presence of oxidants in the atmosphere.

Chloride concentration

Battelle was the first to conduct a systematic study on the corrosion effects of chlorine content in MSW⁸. Probe tests with PVC-spiked refuse at temperatures from 204°C (400°F) to 538°C (1000°F) showed that additions of 2% PVC increased corrosion rates of carbon steel by 40-150% and that there was also a steep rise in chloride concentration of probe deposits. Other researchers have observed a positive correlation between corrosion and the chloride content in deposits^{10,53,56}, as exemplified in Figure 8.

Gas and metal

Both metal and flue gas temperatures are important parameters affecting corrosion in waste-fired boilers. Flue gas temperatures determine the types of volatile species that can be transported in the gas, as well as the maximum temperature of any deposits. Tube metal temperatures determine the location and minimum temperature of such deposits, and thus have a decisive influence on corrosion^{3,35}. As shown in Figure 9, gas temperatures may exert a stronger corrosion-accelerating influence than metal temperatures. A similar trend was discerned from more recent test data from three MSW incinerators, plotted in Figure 10. Generally speaking, a corrosion accelerating influence with increasing temperatures has been discerned in nearly all refuse boiler corrosion studies^{10,11,38,45,55,74}. A notable exception was revealed by

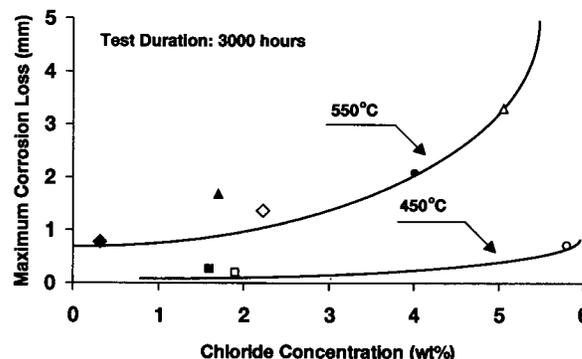


Figure 8 Effect of chloride content in deposits on corrosion of carbon steel in MSW incinerators (ref. 10).

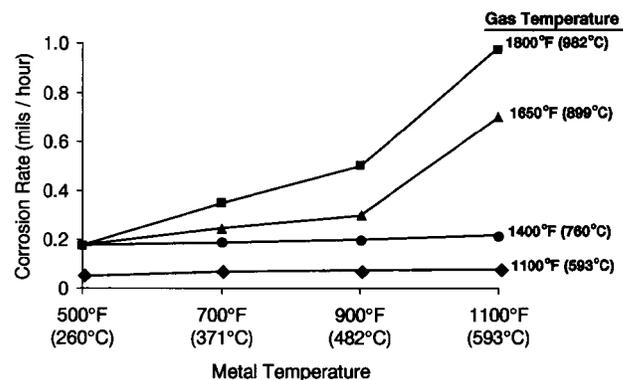


Figure 9 Effect of temperature on corrosion of carbon steel in MSW incinerator (ref. 31).

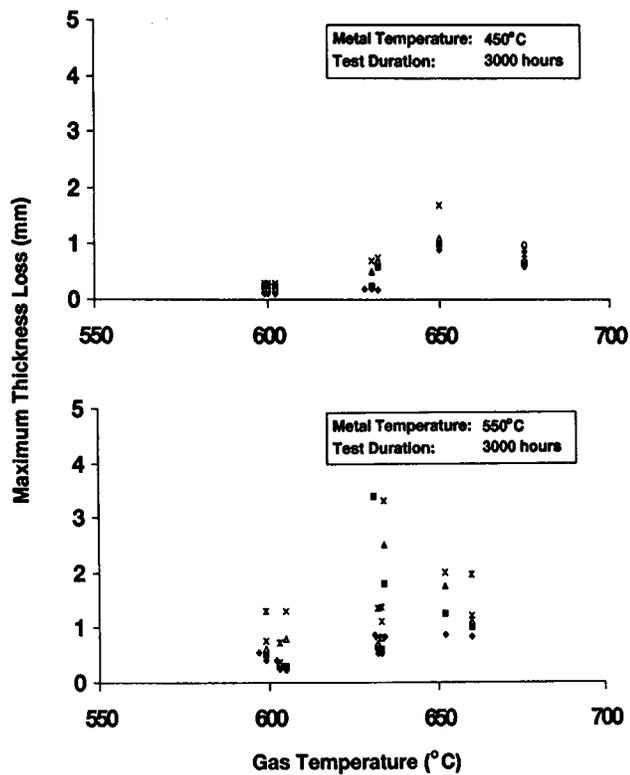


Figure 10 Effect of temperature on corrosion of Fe-base and Ni-base alloys (ref. 11).

a laboratory study using chloride-rich ash, in which generally higher weight losses of steels and alloys were observed at 450°C (842°F) than at 550°C (1022°F)⁵⁴. This was especially surprising considering that 550°C is above the ash melting point. This reverse temperature effect was rationalized on the basis that lead oxide in the ash may have catalyzed the release of chlorine from the dry ash via the Deacon reaction (reaction (3)).

Another temperature-related variable influencing boiler tube corrosion is heat flux. The importance of this factor was revealed by a field study investigating a serious waterwall failure in a RDF boiler⁴⁷. Maximum tube wastage occurred in the overfire air region where heat fluxes calculated from thermocouple readings ranged from 46,000 to 67,000 Btu/h⁻¹ ft⁻², about 2-3 higher than in other furnace zones. In mass-burn units, the highest heat flux and also the most corrosion vulnerable area is the bare waterwall zone just above the refractory-lined area.

Oxidants in furnace atmosphere

Accelerated waterwall tube wastage in coal-fired boilers has long been closely associated with the presence of carbon monoxide in localized reducing zones, brought on by incomplete combustion due to an inadequate supply or poor mixing of combustion air. When WTE plants first ran into severe corrosion problems, it was naturally assumed that MSW incinerator corrosion would be similarly governed, and that substoichiometric CO-containing atmospheres are detrimental. While this remains the consensus to this day, the picture is clouded by some seemingly contradictory findings, as explained below. However, in general, oxidizing conditions characterized by ample excess oxygen tend to suppress corrosion. The positive effect of oxygen in retarding corrosion

has been demonstrated in simulated incineration atmospheres^{55,75}. Water vapor content in the combustion atmosphere can exert a similar corrosion-suppressing effect, as shown in Figure 11.

In several laboratory studies, the unexpected discovery was made that corrosion of steels coated with or immersed in chloride-containing salt deposits was greater under oxidizing than under reducing conditions^{40,53,66}. The results from two laboratory tests, presented in Figures 12 and 13, appear to negate the long-held position that reducing conditions are more damaging. This paradox can be explained by the fact that reducing conditions raise the vapor pressure of alkali chlorides and thus enhance their formation and deposition but, that once formed, these deposits are more corrosive under oxidizing conditions. This finding suggests that alternating

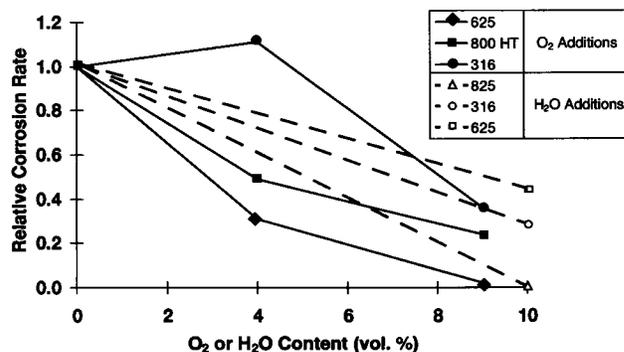


Figure 11 Effect of O₂ or H₂O on corrosion in MSW incineration environments (ref. 75).

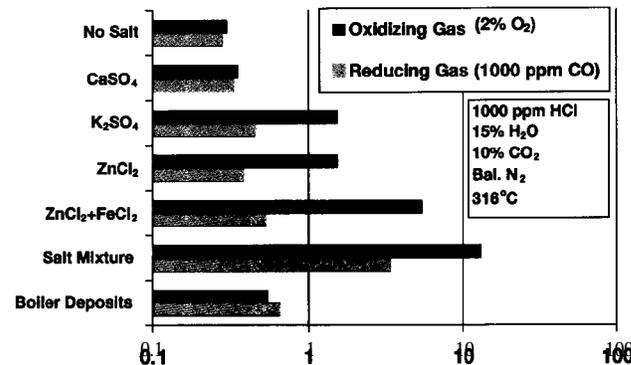


Figure 12 Corrosion of salt-coated carbon steel coupons in simulated MSW incinerator flue gases (ref. 66).

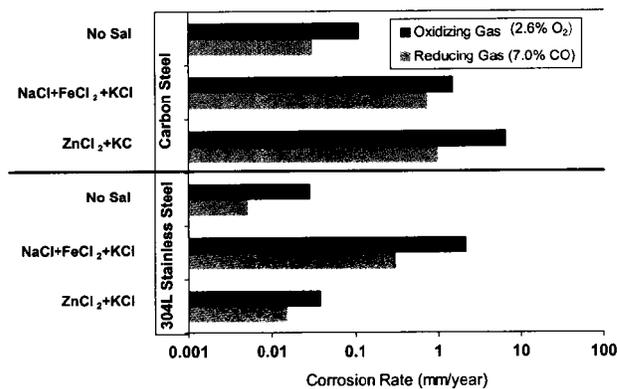


Figure 13 Corrosion of salt-embedded steel coupons in simulated MSW incinerator flue gas at 316°C (ref. 40).

oxidizing/reducing conditions characteristic of unstable combustion conditions in the lower furnace area may promote especially rapid attack.

Heavy metals in waste stream

Intensive laboratory studies of refuse boiler deposit chemistries, conducted by Foster Wheeler during the early days of MSW incineration, concluded that Pb and Zn were important contributors to corrosion^{42,43,44}. Since then, many other researchers have confirmed the detrimental effect of Pb, Zn and Sri in exacerbating corrosion by chloride-containing deposits^{10,11,37,38,53,55}. Heavy metal chlorides significantly depress the melting point of ash deposits; for example, raising the PbO + ZnO content from 2% to 8% has been shown to lower the melting point by 50°C (90°F)¹¹. Some studies suggest that Zn is more detrimental than Pb, while others find the opposite. Lead appears to be particularly harmful to stainless steels; in one series of tests, Type 304 S.S. corroded more rapidly than carbon steel³⁸. Indicative of the detrimental role of zinc is the close resemblance between the corrosion responses of a wide range of alloys tested in condensing ZnCl₂ vapor and in an incinerator burning refuse containing significant amounts of zinc^{14,76}.

It has recently been discovered that copper may yet be another corrosion-aggravating heavy metal contained in MSW Laboratory studies with mixtures of alkali chlorides and heavy metal oxides in oxidizing-chloridizing atmospheres have revealed that CuO may actually be more harmful than ZnO⁷⁷. To account for the corrosion-stimulating role of CuO, it was postulated that it may catalyze the formation of elemental chlorine via the Deacon reaction. The detrimental effect of CuO in deposits leads to the speculation that copper alloying additions might similarly impair corrosion resistance. If this speculation is substantiated by further studies, it may help explain the variable performance of alloy 825 (2.3% Cu), discussed later.

Corrosion inhibition by sulfur

During Battelle's test program to discern the effects of chlorine and sulfur compounds on MSW incinerator corrosion, the discovery was made that additions of elemental sulfur unexpectedly caused a substantial reduction of corrosions. This finding gave rise to a comprehensive series of tests to investigate this inhibitive effect further, first by controlled additions of sulfur²⁶ and later by co-firing with sulfur-containing coals^{27,28}. The positive results achieved with sulfur additions to MSW plotted as a function of SO₂/HCl ratios, are presented in Figure 14. These studies led to the conclusion that corrosion in refuse boilers can be effectively reduced by providing sufficient sulfur to exceed an approximate S/Cl ratio of 4³⁰.

The explanation for the corrosion-inhibiting effect of sulfur postulates that the most serious corrosion-promoting reactions are caused to occur harmlessly in the gas stream rather than inside or underneath deposits. Specifically, in the presence of sufficient SO₂ in the furnace atmosphere, metal chlorides (MCl) in the combustion products are converted to sulfates in the gas stream, according to the reaction (11), which is a generalized version of reaction (2).

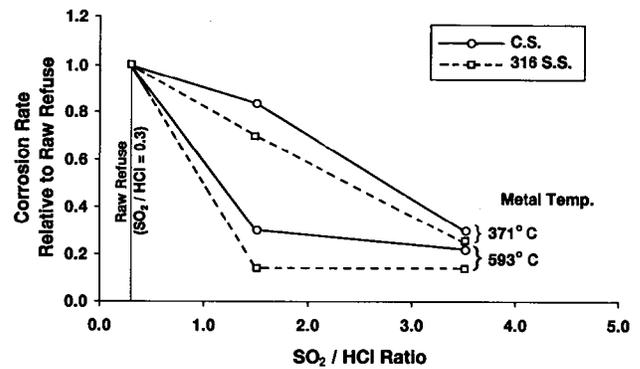
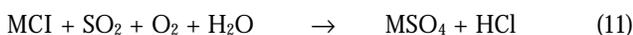


Figure 14 Effect of sulfur additions to raw refuse on corrosion of steels (ref. 31).

Because the HCl is released in the gas stream rather than within deposits, it does not have the opportunity to react with the tube metal and participate in the cyclic corrosion sequence described earlier.

The encouraging results from these series of tests led to a longer-term test program utilizing probes and integral tube sections located in the furnace and superheater areas of a coal-fired boiler. The objective was to determine whether co-firing with up to 22% RDF could be achieved without any negative corrosion consequences³³. The high sulfur coal in these tests produced a S/Cl ratio of about 11, which was expected to be ample for vapor phase conversion of chlorides to sulfates and hence suppression of chloride attack.

While co-firing MSW did not affect corrosion in the furnace area, a 6-10 fold increase in corrosion of low alloy steels was experienced in the superheater area. This increased corrosion was attributed to sulfide attack, on the rationale that the deposits had a higher sulfur content during the co-firing period than during coal firing alone. This explanation appears flawed since superheater deposits in refuse boilers typically are fairly high in sulfur because chlorides tend to convert to more stable sulfates. Consequently, the presence of sulfur-rich corrosion products per se does not disprove that the corrosion was chloride dominated. To the contrary, one would expect to see less, not more, sulfur in deposits during cofiring, since the MSW/coal mix had a 20% lower sulfur content than the coal. On these considerations, the results from this field test are judged inconclusive for assessing the efficacy of sulfur in curbing chloride attack.

CORROSION-RESISTANT ALLOYS

The relatively high chlorine content of MSW profoundly influences materials selection for refuse boilers because carbon and low alloy steels, the workhorses in regular utility boilers, possess inadequate resistance to chloride attack at elevated temperatures. As will be shown, this applies also to a large measure to conventional austenitic stainless steels. The materials of choice are high nickel-containing austenitics and especially nickel-base alloys. Some common Fe-base and Ni-base alloys employed in waste incinerators are listed in Table 2.

More recently developed alloys targeted primarily at the incineration sector, listed in Table 3, are alloys HR160⁷⁸, AC 66⁷⁹, 45 TM⁸⁰, HR11N⁵², HR30M¹¹ and JHN24¹¹. All of these contain major fractions of nickel for providing primary resistance, together with

Table 2 Wrought alloys for high temperature applications in MSW incinerators

Alloy designation	UNS number	Nominal chemical composition (wt. %)				
		Fe	Cr	Ni	Mo	Other (>1%)
304 S.S.	S30400	Bal.	19	9.3		
309 S.S.	S30900	Bal.	23	13.5		
310 S.S.	S31000	Bal.	25	20.5		
253 MA ^a	S30815	Bal.	21	11		1.7Si
800H	N08810	39.5 ^d	21	32.5		
RA85H ^b	S30615	Bal.	18.5	14.5		3.6Si, 1.1Al
825	N08825	22.0 ^d	21.5	42	3	2.3Cu
556 ^c	R30556	Bal.	22	20.8	3.3	18.5Co, 2.8W
601	N06601	Bal.	23	60.5		1.4Al
625	N06625	5.0 ^e	21	58.0 ^e	9	3.8[Nb+Ta]

^aAvesta Sheffield AB; ^bRolled Alloys, Inc; ^cHaynes International, Inc.; ^dMinimum; ^eMaximum.

Table 3 Recently developed alloys for high temperature applications in MSW incinerators

Alloy designation	UNS number	Nominal chemical composition (wt. %)						
		Fe	Cr	Ni	Mo	Co	Si	Other
HR-160 ^a	N12160	2	28	37		30	2.8	Ti
AC 66 ^b		Bal.	27	32				Nb, Ce
45 TM ^c	N06045	23	28	46			2.8	N, Ce
HR11N ^d		29	29	40	1		0.2	N
HR30M ^d		40	28	30	1		0.2	N
JHN24 ^e		3	20	59	18			Nb
65 ^f		8	21	Bal.	8		0.4	
625M ^g		7	21	Bal.	8.5	2.3	0.3	

^aHaynes International, Inc. ^bMannesmann Edelstahlrohr GmbH. ^cKrupp VDM GmbH; ^dSumitomo Metal Industries, Ltd. ^eMitsubishi Materials Corp. ^fSandvik AB. ^gDaido Steel Company, Ltd.

substantial chromium content for protective scale formation. Alloy 65⁸¹ and look-alike alloy 625M¹¹ are modified versions of alloy 625 (minus refractory metal additions) optimized for weld overlay applications.

Effect of alloy composition

The well-established role of nickel for providing outstanding corrosion resistance in reducing-chloridizing environments applies equally to oxidation-chloridation. The beneficial effect of Ni and Cr in retarding corrosion in incineration environments was quantified in recent Japanese studies^{10,11,52,54}. Correlations from these investigations are shown in Figures 15, 16 and 17. The results plotted in Figure 17 are of special interest because they are based on long-term, *in situ* exposures in three MSW

incinerators. Chromium is important for the formation of protective oxides on iron- and nickel-base alloys, which requires a minimum content of about 20% Cr. Although higher Cr levels may further enhance corrosion resistance, 30% Cr is a judged to be a practical maximum for engineering alloys to assure good ductility and weldability.

Molybdenum appears to be highly beneficial in improving corrosion resistance in MSW incineration environments. The strongest evidence is the outstanding performance of alloy 625 weld overlay in refuse boiler waterwall applications. Alloy 625 (9% Mo) was found to be even more resistant than 55Ni-14Cr-1Mo alloy in long-term field exposures¹⁰, lending strong support for the corrosion-suppressing effect of Mo. The beneficial role of Mo has been further verified by other field and laboratory data^{11,51,54,82-84}. However, high Mo contents

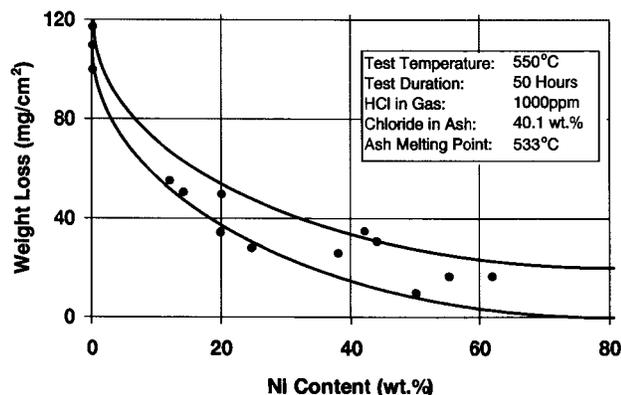


Figure 15 Effect of Ni content on corrosion in simulated MSW incineration environment (ref. 5-1).

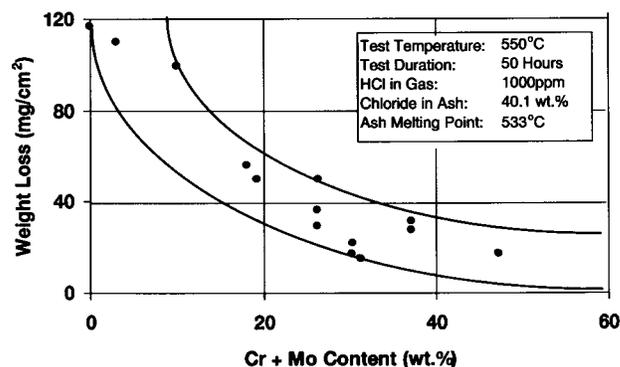


Figure 16 Effect of Cr + Mo content on corrosion in simulated MSW incineration environment (ref. 54).

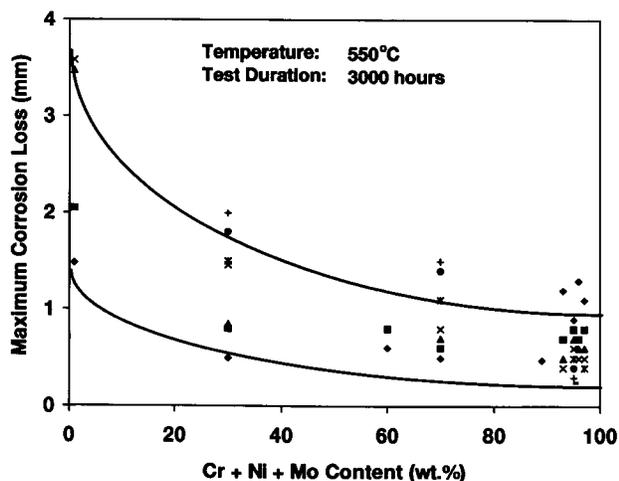


Figure 17 Effect of alloy composition on corrosion in operating MSW incinerators (ref. 11).

(over about 15%) can be counterproductive in oxidizing-chloridizing environments, especially at elevated temperatures^{60,61}. The concern is formation of molybdenum chlorides or oxychlorides and consequent risk of forming molten corrosion products.

An interesting and unexplained Mo effect was discovered during the development of alloy HR11N⁵². It was found that developmental alloys with Mo contents of 3% or higher suffered from a newly discovered form of high temperature 'stress corrosion cracking', while compositions with very small or no Mo content sustained intergranular attack. These findings account for Sumitomo optimizing the Mo content of alloys HR11N and HR30M at 1% Mo^{11,52}. Effective suppression of intergranular attack in both of these alloys is achieved by additions of about 0.15% nitrogen.

The effect of silicon appears to be variable. While Si additions enhance the protectiveness of oxide scales and decrease the formation of volatile metal chlorides⁸⁵, Si is reported to be detrimental in reducing-chloridizing environments⁸⁴. Cobalt is considered beneficial for improving chloridation resistance, but to a far lesser extent than Ni. Cobalt may possibly be detrimental at temperatures above 740°C (1364°F) which is the melting point of CoCl_2 ⁷³. Aluminum, similar to silicon, enhances the effectiveness of protective oxides, and has been shown to improve corrosion resistance in reducing chloridizing environments⁶¹.

High-nickel alloys

Based on extensive test data and service experience, alloys containing large fractions of nickel have demonstrated outstanding corrosion resistance in MSW incineration environments. Among these, Ni-Cr-Mo alloy 625 has established itself by far as the most widely used material for effective corrosion protection in refuse boilers, primarily in the form of weld overlay on waterwalls. There is broad consensus that wastage rate of alloy 625 is less than 0.25 mm yr^{-1} (10 mpy) and that it outperforms carbon and low alloy steels by at least a factor of 10. For instance, in an exceptionally severe RDF boiler exposure where the carbon steel corrosion rate was 180 mpy, alloy 625 corroded at less than 3 mpy⁴⁷. The outstanding performance of alloy 625 was verified in an extensive field evaluation encompassing several

operating MSW incinerators¹⁰. Alloy 625 excels not only for refuse boiler waterwall protection but also for superheater tubing. For that application, the corrosion rate of alloy 625 was estimated to be 10 to 20 times lower than for carbon steel⁸⁶. A comparable improvement factor over a low alloy steel (T-22) is shown in Figure 18.

Seemingly at variance with the excellent performance of alloy 625 is the reported metal loss of 0.35 mm (14 mils) on a test section of alloy 625 overlaid screen tubing after a 15 month exposure in a US WTE plant⁸⁶. Notwithstanding these mediocre test results, the plant went ahead with weld overlaying the entire screen section. Significantly, after 30 months' service, the alloy 625 overlay showed no discernible attack. The marked disparity between the earlier test results and the follow-on full-scale installation probably stems from uncertainties regarding metal loss determinations on the original test section. These were based on ultrasonic thickness measurements, which are very difficult to perform accurately on rippled weld deposit surfaces.

Alloy 825 is another long-established alloy in US WTE plants, used primarily for high temperature superheater tubing, as noted earlier¹⁸. This Mo-enhanced Ni-Fe-Cr alloy has generally performed well, but there are scattered instances where it failed to provide satisfactory life. Most noteworthy is the unfavorable corrosion experience with alloy 825/carbon steel composite waterwall tubing in a RDF incinerator²⁰. After as little as two years, corrosion of the alloy 825 O.D. necessitated progressive repairs by piecemeal weld overlaying with alloy 625. The restored waterwall has now been in service for up to six years and shows no signs of corrosion⁸⁷. As would be expected from its lower Ni and higher Fe content, alloy 825 is less resistant than alloy 625, as exemplified in Figure 18. Another example of the superiority of alloy 625 was provided by side-by-side tube shield installations of these materials in a MSW incinerator, which showed substantially shorter life of the alloy 825 shields²¹.

Austenitic stainless steels

Austenitic stainless steels gave fairly good service in early WTE plants, many of which operated with relatively mild conditions. With accumulating plant experience, it became increasingly clear that the performance of stainless steels proved unreliable, and that stainlesses may offer only little, if any, improvement over ordinary boiler tube steels^{14,20,38,45,51,88,89}. In several instances, Type 304 S.S. composite tube test panels had to be taken

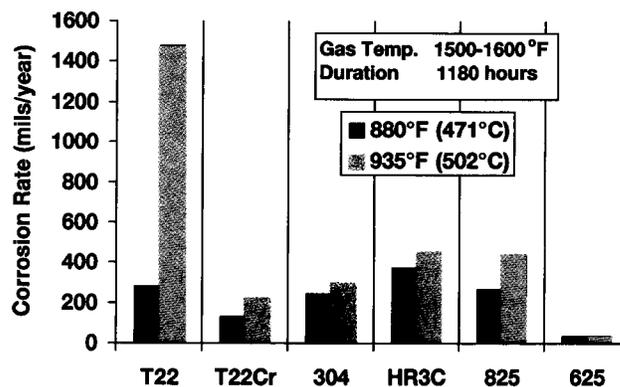


Figure 18 Corrosion of test tubes in an RDF incinerator (ref 45).

out of service due to excessive corrosion. Even more highly alloyed stainless grades may fare badly. In one instance, a niobium-enhanced version of 25Cr-20Ni S.S. (HR-3C) corroded faster than Type 304 S.S., as shown in Figure 18. It is conjectured that the poor showing of the HR-3C may possibly be related to the very high volatility of niobium chloride.

The presence of FeCl₂ appears to be especially detrimental to stainless steels. In laboratory tests with chloride-rich salt mixtures, compositions containing FeCl₂ or PbCl₂ proved to be extremely aggressive³⁸. Salt mixtures containing either one of these metal chlorides attacked Type 304L S.S. more severely than carbon steel. These experiments led to the conclusion that mixtures of NaCl + KCl, previously thought to be noncorrosive to refuse boiler steam generating tubes, can become highly corrosive when mixed with FeCl₂ present as a corrosion product. The aggressiveness of FeCl₂ is apparent also from Figure 13, which similarly shows higher corrosion rates of Type 304L S.S. than for carbon steel in iron chloride containing salt mixtures.

An additional shortcoming of 300 Series stainless steels is their susceptibility to chloride-induced pitting and stress corrosion cracking during downtime. The risk of such attack by moist tube deposits was identified as a potential problem area when WTE plants first came onto the scene. The WTE sector is slow in accepting that the performance of stainless steels in refuse boilers varies widely and therefore are a questionable choice for dependable corrosion resistance. Nonetheless, many MSW incinerator operators continue to employ stainless steels, partly on the basis that they do perform fairly well in some plants, and partly on reluctance to upgrade to costlier corrosion-resistant alloys.

Composites and coatings

Co-extruded composite Type 304 S.S./C.S. waterwall tubing performed well in several Swedish WTE plants⁸⁶, but these operated with quite mild steam conditions unrepresentative of modern higher temperature units. In the US, the single large-scale commercial application of composite tubing was in the aforementioned RDF plant where co-extruded alloy 825/C.S. waterwall tubing failed to provide adequate life⁸⁷. The superior performance of Alloy 625 prompted several attempts to produce coextruded Alloy 625/C.S. composite tubing on a commercial scale, but this effort proved unsuccessful due to the large strength differential. Difficulties in manufacturing alloy 625 composite tubing by co-extrusion have fostered the development of novel techniques for producing Ni-Cr-Mo alloy composites that offer alternatives to conventional overlay deposition by Gas Metal Arc Welding (GMAW). Recent developments aimed largely at the WTE sector include liquid atomized metal deposition of alloy 65⁸¹, plasma powder weld deposition of alloys C-276 and alloy 625M¹¹, and helical rolling of alloy C-22¹¹.

Boiler vendor and plant operators have experimented with a wide range of metallic coatings in the hope of finding a cost-effective method for extending the life of refuse boiler tubing, primarily for waterwall panels^{45,47,49,55,82,91,92}. The success of these test installations has varied greatly. Some field trials indicated unsatisfactory coating performance and life, while others produced fair to good results. In general, coatings need to be renewed on an

annual basis because they spall off or are consumed¹³. Good results are reported with a heavy-body fused coating consisting of tungsten carbide in a high-nickel braze matrix⁴⁹. A highly promising development is a thermal spray applied dual-layer Al/80Ni20Cr coating, reported to have maintained excellent durability for over three years⁵⁵. The outer aluminum layer is claimed to function in a sacrificial manner to provide cathodic protection for the underlying alloy layer during downtime. This coating system has now been applied at seven Japanese WTE plants, most recently by high velocity oxygen fuel (HVOF) spraying⁹³.

AREAS FOR FURTHER R&D

There are several areas where further R&D could be productively focused to attain a fuller understanding of chloride-induced corrosion in MSW incineration, and to advance the development of corrosion-resistant materials. Corrosion-related issues meriting further elucidation are listed below.

- Mechanism by which chlorides permeate protective oxide scales.
- Characterization of the corrosive environment and ash deposits.
- Corrosion inhibitive effect of sulfur species.
- Mechanism of high temperature stress corrosion cracking and intergranular attack.
- Effect alloying additions of molybdenum and copper on corrosion behavior.
- Synergism between corrosion and abrasive/erosive wear.

To gain further insights into corrosion mechanisms and manifestations, various novel approaches are being exploited. Among these are electrochemical techniques based on A.C. impedance^{94,95} and potentiodynamic polarization⁹⁶, electron microscopy²⁵ and calorimetry⁵⁶.

Continuing work effort should additionally be directed at developing new and improved corrosion-resistant materials. This includes not only alloys optimized for refuse boiler applications, but also cost-effective composites and coatings. To support the corrosion research and materials development effort, more intensive monitoring and data collection/dissemination is needed to precisely characterize the corrosive environments and to evaluate materials performance. All of these endeavors are being systematically pursued in the aforementioned NEDO Program on developing high-efficiency WTE technology^{10,11}. Further progress toward that objective could be achieved if a similar collaborative development program would be instituted in the Western hemisphere.

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