Corrosion of Carbon and Stainless Steels in Flue Gases from Municipal Incinerators

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ABSTRACT

Both field and laboratory corrosion studies are discussed. The field work involves operation of corrosion probes and/or analyses of gases and deposits in municipal incinerators in Miami County, Ohio, at Oceanside, New York, and in the Navy Salvage Fuel Boiler at Norfolk, Virginia. Examinations of the surfaces of these probes and of the deposits coming from them using X-ray diffraction and the electron micro-probe have shown that compounds containing sulfur, chlorine, lead, zinc, and potassium are contributing to the corrosion reactions.

The results have shown that the corrosion of the carbon and stainless steels used increases as the metal temperature rises from about 350 to 1000 F. The temperature gradient moving from the metal through the deposit to the surrounding gases is also of importance.

The field studies have also included analyses of furnace gases from several incinerators. Average concentrations of corrosive gases such as SO₂ and HCl were found to be about 100 ppm. Laboratory work and field results have provided an explanation of the corrosion reactions. As might be expected, they are complex and interrelated. It is suggested that HCl, Cl₂, K₂S₂O₇, KHSO₄, NaCl, ZnCl₂, and PbCl₂ are involved.

Recommendations have been made that water-wall incinerators be operated at low metal temperatures, near 500 F, to minimize corrosion.

INTRODUCTION

The disposal of solid waste is becoming of increasing importance throughout this country. Incineration has several promising features, but the technology needs further development. Of particular importance are methods for incinerating municipal refuse in such a way that offensive dusts and gases are not emitted to pollute the atmosphere. Air-pollution standards require that solid particulate matter be removed from such flue gas. This cleaning of the gases can be accomplished by mechanical collectors or by electrostatic precipitators, but the volume of gas must be as small as possible and the temperature should not exceed about 600 F. Three basic methods are used for accomplishing this cooling:

1. Spraying water into the flue-gas stream;
2. Diluting flue gas with cool air; and
3. Absorbing heat in flue gas by water-cooled tubes forming the furnace walls and convection surfaces.

Cooling with water sprays results in wastage of large quantities of water, the introduction of the need for disposal of contaminated corrosive water, and the production of an unsightly plume.

Cooling with air requires large fans and the power to run them. Such cooling also requires much larger sizes of pollution-control equipment because of the greatly increased gas volumes.

For large-scale municipal units, it is advantageous to absorb the heat from the flue gas, using the same
basic techniques as in conventional boiler furnaces. In addition to simplifying requirements for pollution-control equipment, a heat-utilization scheme provides a useful outlet for the heat generated by the combustion of the refuse by generating low-pressure steam that can be sent to a turbine. An additional advantage of this procedure is a possible increased throughput because of the rapid heat absorption in the water-cooled furnace.

An attractive design is one in which the refractory walls of the usual incinerator are replaced with water-cooled tubes, much as in modern boiler furnaces, together with tube banks to cool the gases leaving the combustion zone.

One problem faced in water-cooled incinerators is a presently unpredictably severe loss of metal from convective-heat-transfer tube banks, and also from the furnace wall tubes. A number of instances of severe metal wastage in incinerrators have been reported, along with other details of incinerator operation [1-14]. Most experience has been accumulated in Europe, particularly in Germany where many plants with boilers are burning municipal refuse. This experience did not provide a complete explanation as to the cause of the corrosion, but did indicate the possible importance of operating conditions (oxidizing versus reducing) and the effect of chlorine-containing compounds in the refuse. That is, reducing conditions and the presence of the chlorides enhanced corrosion.

Because there is increasing interest in the United States in the construction of large water-wall municipal incinerators, the Solid Waste Management Office of the Public Health Service, Environmental Protection Agency, commissioned Battelle-Columbus to study the fireside wastage that could be anticipated in such units and to devise possible methods of alleviation. This research began on March 1, 1969, under a grant program [15].

As the work progressed, it became apparent that other areas of an incinerator were subject to corrosive attack. Wet scrubbers in particular are quite vulnerable. Accordingly, a companion study has been initiated during the third year of the program on corrosion in wet scrubbers.

CORROSION-PROBE STUDIES IN THE FIELD

Procedures

In order to obtain realistic estimates of tube wastage and deposit formation, it was necessary to operate probes in the field over extended periods. These were inserted in a refractory-lined municipal incinerator at Miami County, Ohio, and in a water-wall incinerator operated by the Navy Public Works Center at Norfolk, Virginia [16]. Deposits and gases from an incinerator at Oceanside, New York, were also analyzed. Eleven corrosion probes made up of the following metals were run under controlled-temperature conditions: A106-Grade B and A213-Grade T11 carbon steels, and AISI Types 304, 310, 316, 321, and 446 stainless steels. Metallic coatings of chromium and aluminum were also evaluated.

The probe was designed to include 34 cylindrical specimens nested together end to end and then inserted into the incinerator through a side wall. The section of the probe extending through the wall was water cooled. The specimens exposed within the furnace were cooled by air flowing inside the tubular specimens. A computer analysis was used to ascertain the geometry of the internal support tube required to give the most linear specimen-temperature variation over the range of about 350 to 1100 F for a probe with 34 specimens. Each specimen was about 1.25 in. in OD, 1.00 in. in ID, and 1.5 in. long.

Fig. 1 is a schematic of the final exposure-probe apparatus. The specimens are nested together with lap joints as shown in Detail A, and retained axially at the cooling-air-outlet end by a retainer which is fixed to the internal support tube with webs as shown in Section A-A. The axial restraining force in the internal support tube is obtained by compressing the spring on the air-inlet end of the probe at assembly. The spring compensates for differential thermal expansion between the specimens and the internal support tube.

Specimen temperatures are measured at four stations with Type K thermocouples either welded into the wall of the specimens or inserted into recesses drilled lengthwise into one end of the appropriate specimen.

The thermocouple lead wires are brought out of the probe through the center of the internal support tube, so that temperatures can be recorded continuously on a strip-chart potentiometer recorder. Since the computed results indicated that the temperature variation is linear for regions with a constant gap between the internal support tube and the specimens, the four temperatures accurately define the specimen temperatures.

The specimen temperatures are controlled by regulating the amount of cooling air admitted to the probe. The output from a control thermocouple, which is attached to the specimen at the same axial location as the Thermocouple 3, is monitored by a proportional temperature controller. During a run, the controller maintains this temperature by varying
the amount of cooling air bypassing the probe through a motorized butterfly valve located between the blower and the probe. A Roots-blower air pump delivering up to about 34 cfm was used with a 5-hp motor as a drive.

The corrosion probes as removed from the incinerators are covered with scale and deposits. More of these deposits were found at Miami County than at Norfolk. The deposit built up into a V-shaped layer of varying depth lengthwise along the probe, with the apex or point of the V projected into the oncoming gas stream. These deposits were removed from all probes in a numbered sequence. Thus, the variations in composition as a function of temperature could be determined when the deposits were analyzed.

**Corrosion Measurements and Examinations**

Individual specimens were separated and examined. They were tested first for the presence of sulfide by placing a drop of sodium azide solution on the surface and viewing the reagent under a binocular microscope. Evolution of nitrogen gas bubbles gave a positive identification of sulfide. Another area was checked for pH by placing a moistened strip of Universal pH paper over the surface. Thus, the hydrolytic properties of salts present on the surfaces could be determined.

Selected specimens were retained intact for special examination by X-ray, electron-microprobe, and metallographic procedures.

The other pieces were descaled by methods which prevented attack of the base metal. The carbon steel specimens were stripped cathodically in 10 percent H$_2$SO$_4$ containing 1-ethylquinolinium iodide inhibitor. The stainless steel specimens were descaled in a two-step process: first with 11 percent NaOH and 5 percent KMnO$_4$ at 212 °F, and then with a mixture of 20 percent HNO$_3$ and 2 percent HF at 130 °F.

The amount of metal wastage was determined by weight-loss measurements.

On the basis of OD and ID micrometer measurements, the overall weight loss was adjusted to reflect the proportion of loss which occurred on the outside surface. This was of significance only in the cases where appreciable oxidation had occurred on the inner surfaces. The wastage rates for the specimens were calculated and expressed as “mils per month” penetration. Fig. 2 illustrates data for one of the runs made at Miami County.

Comparison of the results from many probes, when...
arranged according to the time of exposure shows that the initial corrosion rates are high and that they taper off with time, as illustrated in Fig. 3.

The results suggest that the scale formed during corrosion is protective to some extent and that the rate of attack will decrease appreciably as the exposure time is increased.

Because of this high initial rate, the penetration rates shown in Fig. 2 should not be used to project anticipated wastage for long-time incinerator operation.

Metallographic studies of sections from specimens of the A106 and T11 carbon-steel alloys indicated that the attack was uniform. Stainless steel specimens, on the other hand, showed some structural changes and varying degrees of intergranular attack.

Some of the stainless steels failed quickly by stress-corrosion cracking when in contact with incinerator deposits under humid conditions at 170°F. Both sensitized and annealed Type 304 specimens cracked after an exposure of one week. Type 310 cracked after 10 weeks. Type 446 did not crack after 22 weeks, but was pitted. Because of stress-corrosion cracking and pitting, these stainless steels do not appear as good choices for boiler construction.

Several trends of importance were found when results of all runs were analyzed.

First, for all materials evaluated,
(1) The temperature gradient through the deposits that separate the tube metal and the hot gases is an important factor. Corrosion rates were greater when larger gradients were present. Thus, direct exposure to the flame could increase the attack.

Second, for the A106-Grade B and A213-Grade T11 carbon steels,
(1) The rate of corrosion increases as the temperature increases and can range from 5 to 15 mils per month at 325°F to about 20 to 50 mils per month at 950°F.
(2) The two steels are comparable in corrosion resistance with the A106-Grade B being slightly superior to the A213-Grade T11 steel.

Third, for the stainless steels,
(1) The corrosion resistance is superior to that for the carbon steels.
(2) The rate of corrosion increases as the temperature increases.
(3) Types 446 and 310 show less weight loss than Types 304, 321, and 316.
(4) Stress corrosion cracking and pitting is a severe limitation, particularly during down-time.

**Studies of Mechanism**

The composition of the deposits removed from the corrosion specimens was carefully determined to provide some idea of possible causes of the corrosion. Significant amounts of chlorine, sulfur, lead, zinc, potassium, and sodium, along with other more inert elements, calcium, silicon, and aluminum, were detected in the deposits from the three incinerators mentioned. The proportions of these constituents depended on the corrosion probe-specimen temperature, and the distributions were consistent with known volatilities of the compounds. A typical distribution of elements in the deposits as a function of temperature is illustrated in Fig. 4 for two of the Norfolk, Virginia, probes.

The electron microprobe is an instrument which permits examination of a surface to determine the location and relative concentration of individual elements. An electron microprobe was used to examine the area at the interface of the base metal and the corrosion scale on sections cut from corroded portions of boiler tubes removed from the incinerator at Oceanside in 1968, 1969, and 1970. Sections from Miami County Corrosion Probes 2 and 3 were also examined, as were sections of Probe 10 from Norfolk, Virginia. None of these specimens was descaled prior to sectioning so that the areas could be viewed with some scale intact. It was found that the elements chlorine, zinc, sulfur, lead, and potassium were concentrated adjacent to the base metal. Table 1 includes the microprobe results for 18 specimens. The column designated “inner layer” represents the interface between metal and adherent scale, while that designated the “outer layer” is in the scale, slightly removed from the metal surface. They both are beneath what is normally considered as deposit, i.e., the massive buildup of material on the tube.

The sodium azide spot test also revealed that sulfide compounds were present near the metal surface on
almost all the probe specimens, particularly on those exhibiting the most severe corrosion.

X-ray diffraction studies identified over 20 compounds in the scale and deposit. Fig. 5 summarizes the data obtained.

Compounds of particular significance are FeCl₂, FeS, KCl, NaCl, ZnSO₄, and mixed PbO·PbSO₄ salts.

Gas Analyses

The compositions of the furnace gases at the three incinerator sites mentioned earlier were measured to assist in determining corrosion mechanisms. The sulfur- and chlorine-containing constituents were of particular interest. While the SO₂ content in incinerators is less than is normally found in fossil-fueled power stations, the HCl content is greater. It was found, for example, that average amounts of these gases in incinerators were in the range of 100 ppm, although HCl concentrations of 300 ppm were measured in one instance. Nitrogen oxides were present in amounts near 100 ppm and organic acids ranged up to 340 ppm. HF was detected in amounts ranging from 1 to 6 ppm.

LABORATORY STUDIES

Laboratory studies were carried out to determine the importance of individual factors on corrosion in incinerators and also to help establish the mechanism by which metal wastage occurs. Since the experiments can be carried out under carefully controlled conditions, it is possible to determine the role of such factors as gaseous components, salts or deposits, and temperature.

Experiments were carried out at 600, 800, and 1000 F using a variety of salt compositions and under a simulated flue-gas atmosphere containing SO₂, HCl, and, on occasion, HCOOH (formic acid). The data in Fig. 6 indicate that chloride salts added to sulfate salts significantly enhance corrosion, particularly at 800 and 1000 F. For example, at 1000 F, the corrosion rate of carbon steel T11 is about 7 mils per month in a mixed Na₂SO₄-K₂SO₄ salt. When 1 percent NaCl was added, the corrosion increased about 10 times. It was also shown that SO₂ was a necessary constituent in the gas atmosphere to provide the increased corrosion. At 800 and 1000 F, ZnCl₂ and
PbCl₂ were also very corrosive. At 600 F, the most corrosive salts in decreasing order of activity were KHSO₄, K₂S₂O₇, and ZnCl₂.

**DISCUSSION**

The corrosion probe results reported herein agree fairly well with those observed in practice. For example, Fassler [9] and his associates suggest that high-temperature corrosion begins near 600 F. Hilsheimer [2] has reported accelerated corrosion in high-temperature areas of water-wall incinerators in Germany. Tube life of less than a year has been reported on occasion.

Maikranz [17] cited experience with the Munich refuse-burning power plant in which metal wastage of wall tubes amounted to 1.4 mm in 3500 h of operation. This rate of corrosion is 11.3 mils per month, which is comparable to the wastage found on many of our probe specimens.

Comparison of these results with experience in U. S. power plants is difficult, because few data of this type are available. Barnhart [18] stated that the corrosion rate in superheaters and reheaters is typically about 20 mils per year. In extreme cases, austenitic tube hangers have shown wastage rates of 250 mils per year.

Correlation of the results of the different studies
made on the deposits and corroded surfaces combined with the laboratory results provided at least a possible explanation of the corrosion mechanism.

It is proposed that HCl and Cl₂ released adjacent to the tube surfaces are important factors. In addition, SO₂ and SO₃ gases, along with sulfur-containing compounds, cause additional corrosion. The roles played by the sulfur- and chlorine-containing compounds in the refuse are of great importance and are closely inter-related. The sequence of chemical reactions that are involved in the corrosion mechanism is depicted in Fig. 7. Chlorides and oxides reach the tube surface by direct volatilization in the flames and by reaction of the HCl formed during burning with the K₂O and Na₂O volatilized. Sodium salts are shown in Fig. 7 by way of example, but similar reactions occur with potassium salts. Chloride salts deposited on the metal surface react with SO₂ and oxygen near the tube to evolve high concentrations of HCl directly adjacent to the metal. Some of this HCl reacts directly with the iron to form FeCl₂. However, a more serious condition may involve catalytic oxidation of the HCl to Cl₂. The Cl₂ is much more reactive with the tube metal and can take part in a closed cycle of reactions in which the product FeCl₂ is converted to Fe₂O₃, and Cl₂ is regenerated, as shown on the left side of the diagram.

The additional role played by sulfur is that of forming low-melting pyrosulfates or bisulfates by reaction of sulfates in the deposit with additional sulfur oxides. This action is shown on the right side of the diagram, where another closed loop is possible. In this case, pyrosulfates or bisulfates react with the iron to form FeS and FeO and regenerate Na₂SO₄.

The corrosion process is further complicated by the presence of zinc and lead salts which serve to lower the melting points of the mixtures on the metal surface. It is concluded that water-wall incinerators using the metals evaluated should not be designed to generate superheated steam, but should be operated at relatively low metal temperatures, near 500 F, to minimize corrosion. The down-time of an incinerator can be important from the corrosion standpoint since acidic salts can become wet by absorption of water when the surfaces become cool.

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Fig. 7 Sequence of chemical reactions explaining corrosion on steel tube.

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REFERENCES


