

Fireside Metal Wastage in Municipal Incinerators

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ABSTRACT

Presented are the results of a combined field/laboratory study on corrosion in municipal incinerators. The operation of a corrosion probe in an incinerator has been correlated with measurements of flue gas and deposit analyses along with corrosion rates. It was found that accumulation of elements such as sulfur, chlorine, zinc, aluminum, potassium, and occasionally lead and copper occurred at the metal/scale interface as in the deposit. Possible causes of corrosion in incinerators are pointed out and the mechanisms by which chemicals react with construction materials are discussed.

INTRODUCTION

As part of a research program being conducted for the Bureau of Solid Waste Management, U.S. Public Health Service, field and laboratory studies of fireside deposits and corrosion in municipal incinerators are being made by the Battelle-Columbus Laboratories. Incineration has many attractive features, but the traditional approaches to incinerator design are not meeting the demands of our expanding economy. As a result, the trend at present is toward improvements in construction to minimize problems with air pollution, to increase the reliability of incineration, and to increase their throughput.

One important step has been to replace refractory wall of incinerators with water-cooled tubes, much as in modern boiler furnaces, and to provide tube banks to cool the gases leaving the combustion zone. By extracting heat in this way, less excess air is required as a coolant so that the combustion-zone temperature can be higher than that in a refractory furnace. Lower exit-gas temperature also is feasible. Such an incinerator then becomes essentially a boiler furnace burning municipal solid wastes as fuel. With water-cooled walls, there is no spalling and slagging of refractories that would take place at high furnace temperatures as with older types of incinerators built with fire-brick walls. Cooling the products of combustion by passing them through convective heat-transfer surfaces in the form of a bank of boiler tubes decreases the flue-gas temperatures so that electrostatic precipitators and other gas-cleaning systems can be used. This, in turn, can materially reduce air pollution from incineration. Heat recovered as steam from water-cooled incinerators has some value, but this is not likely to be a dominant factor in choosing water-cooled incinerators over ones built from fire-brick.

One problem faced with water-cooled incinerator operation is a possible unpredictably severe loss of metal from convective-heat-transfer tube banks, and even from the furnace-wall tubes. The

cause of this metal loss and the environmental conditions when metal wastage occurred have not been well defined. The need became urgent for carefully planned research to define the conditions under which loss of metals occurs and to establish the mechanism of such metal wastage.

FIELD STUDIES OF INCINERATOR CORROSION

The field studies conducted on this program have included:

- 1) Installation of corrosion probes in the municipal incinerator operated by Miami County, Ohio.
- 2) Sampling of flue gas at the Miami County, Ohio, and the Oceanside, Long Island, incinerators.
- 3) Analysis of the boiler-tube deposits from the Oceanside incinerator, and those builtup on the corrosion probes in the Miami County, Ohio, incinerator.

CORROSION-PROBE CONSTRUCTION AND OPERATION

Corrosion probes have been used successfully in power-plant operations to study metal wastage in boiler furnaces. However, no evidence has been found in the literature that the technique has been employed to investigate corrosion in large incinerators. Because of the difficulty in simulating the complex flue-gas atmosphere encountered in the incinerator, the use of such probes for an incinerator study is particularly important. Although the probe data are more difficult to obtain, they constitute a vital supplement to the laboratory corrosion data. The construction, operation, and corrosion results obtained with the probes installed at the Miami County, Ohio, incinerator are discussed in this section.

Probe Construction

The probe was designed with two specific objectives in view:

- 1) To provide a means for simultaneously exposing a number of specimens for extended periods in an operating incinerator while maintaining the specimens at temperatures in the range 400 to 1100 F.
- 2) To provide a control system to maintain the temperature of the specimen above the dew-point of the gases in the incinerator when the incinerator is not fired.

An air-cooled exposure probe with cylindrical specimens was selected from many conceivable design options. A conceptual design similar to that outlined by Plumley, Lewis, and Tallent [1] in 1965 was used.

Fig. 1 is schematic of the details of the 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.

Specimen temperatures are measured at four stations with Type K thermocouples spot welded to the inner wall of the specimens.

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 Number 3 thermocouple, is monitored by a proportional temperature controller. At the start of a test, the controller setpoint is adjusted to maintain either the lowest temperature at Number 1 thermocouple or the highest temperature at Number 4 thermocouple, depending on the test objective. The controller maintains this temperature by varying the amount of cooling air blown off at a motorized butterfly valve located between the blower and probe.

To protect the blower and probe from deposits, the cooling air to the blow is filtered.

The secondary control system shown in Fig. 1 was installed to meet the second design objective, namely that of maintaining the specimen temperatures above the dewpoint when the incinerator is not fired. This is accomplished by venting the cooling water from the water jacket upstream of the specimens with solenoid valves and by heating the minimum cooling-air flow with a resistance heater.

The corrosion specimen section of the probe comprises 34 specimens made up of four different steels. The low-temperature section of the probe consists of alternate specimens of A106-Grade B and A213-T11 carbon steels. The high-temperature portion has alternate specimens of Type 304 and Type 321 stainless steels.

Operation in the Incinerator

The corrosion probe was installed in the Miami County Incinerator's furnace-outlet sampling port located 15 ft downstream from the incinerator grate.

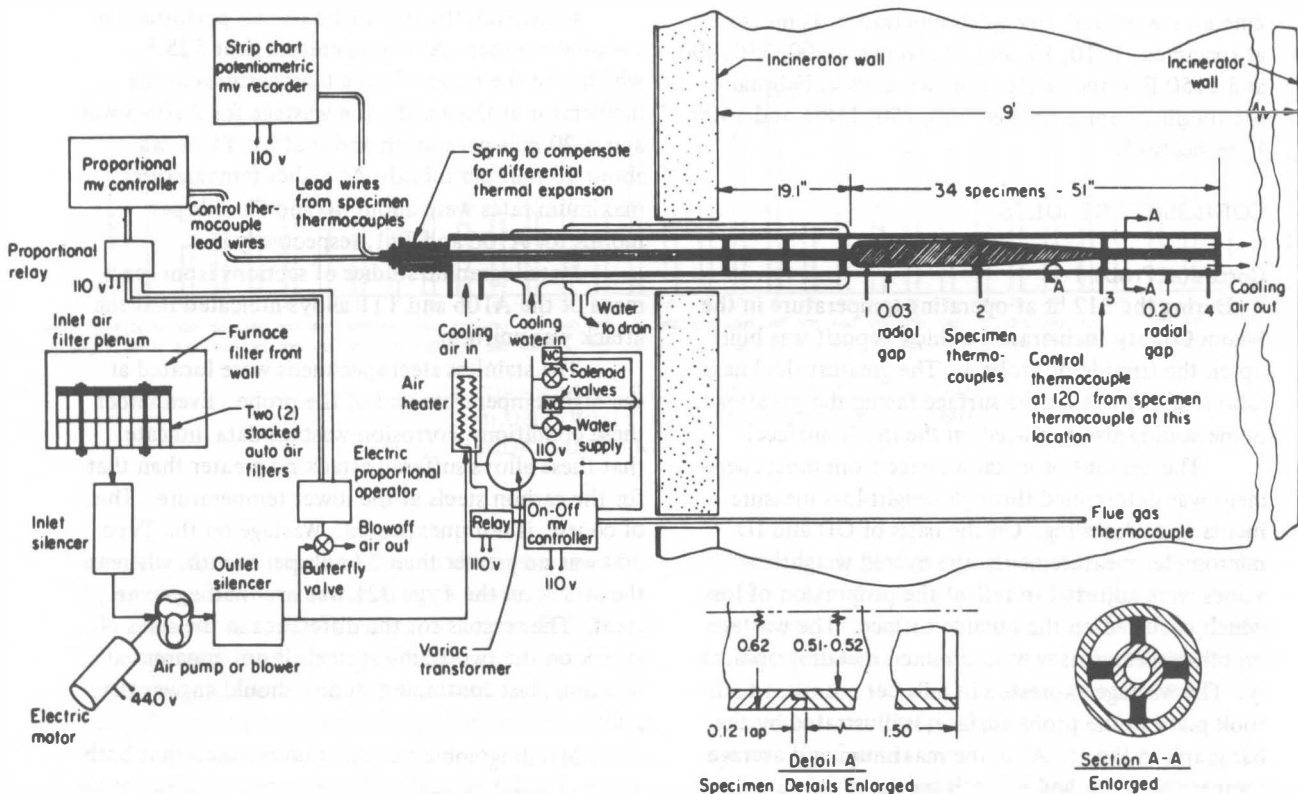


FIG. 1 SCHEMATIC OF SPECIMEN – EXPOSURE PROBE APPARATUS

In this location, the corrosion specimens are exposed both to upstream furnace temperature and to the cooler downstream scrubber temperatures. Seldom, if ever, did flame from burning refuse reach the probe. However, pieces of burning refuse controlled by the flue-gas streams and burning in suspension may deposit on the probe and cause local high temperatures for a short time.

No special firing of the incinerator was done for this study. The 150-ton/24-hr-day incinerator operated around the clock on a five-day week schedule. Burning rates were governed by such factors as the type of refuse received and its moisture content. While the incinerator was being fired, the flue-gas temperature at the location of the corrosion probe normally ranged between 1200 F and 1500 F. During furnace-shutdown periods over weekends of breakdowns, the temperature in the incinerator dropped below 200 F. Because moisture is usually present in the scrubber system, humidity in the incinerator during shutdown could be quite high.

Corrosion Probe 1

Corrosion Probe 1 was exposed in the incinerator from December 2 to 23, 1969. The total ex-

posure time of 506 hr included 312 hr of actual firing. During the 21-day period, the incinerator was down seven times and the specimen thermocouples cooled below 200 F. At times, they actually cooled to near room temperature. During firing, the flue-gas temperatures varied. However, the average temperatures of specimens 1, 10, 19, and 34 were about 350, 800, 1050, and 1250 F, respectively. During the last few days of exposure, a malfunction in the equipment allowed temperatures to reach 1500 at the hot end of the probe.

Corrosion Probe 2

Corrosion Probe 2 was installed in the same location as Probe 1 and was equipped to provide heat to the probe when the incinerator was not fired. The exposure started on January 21, and continued with one unscheduled interruption to March 2, 1970. Total installed time in the incinerator was about 893 hr, 389 hr of which represent actual incinerator firing.

During the entire exposure, the incinerator was shut down a total of 15 times. However, during these periods, the probe was maintained by the air heater at temperatures from 200 to 300 F. When the in-

incinerator was fired, flue-gas temperature, as measured at specimens 1, 10, 19, and 34, averaged 300, 550, 900, and 1150 F, respectively. For two days in February, the thermocouples reached 500, 750, 1180, and 1400 F, respectively.

CORROSION RESULTS

Corrosion Probe 1

During the 312 hr at operating temperature in the Miami County Incinerator, a thick deposit was built up on the fireside of Probe 1. The greatest thickness (about 3/4 in.) was on the surface facing the gas stream. Some scaling also occurred on the inside surface.

The amount of metal wastage from most specimens was determined through weight-loss measurements after descaling. On the basis of OD and ID micrometer measurements, the overall weightloss values were adjusted to reflect the proportion of loss which occurred on the outside surface. The wastage on other specimens was determined metallographically. The wastage expressed in mils per month, which took place in the probe surface, is illustrated by the bar graph in Fig. 2. Also, the maximum and average temperatures reached by each specimen are indicated.

The corrosion is easily measurable, and the attack increased fairly rapidly as a function of temperature (particularly for the A106 Grade B and A213 Grade T11 alloys). However, the results for some specimens vary widely. For example, Specimen 8 appears out of order. This could be the result of highly corrosive conditions in a limited region of the probe. For example, a chloride concentration of 20 wt.-percent was found in one portion of a probe deposit from the Miami County incinerator.

In general, the two carbon steels performed in a similar manner. At a temperature near 525 F, which is in the range of tube temperatures at the incinerator at Oceanside, the wastage for A106-5 was about 20 mils per month and that for T11-6 was about 28 mils per month. At higher temperatures, maximum rates were about 40 and 58 mils per month for A106 and T11, respectively.

Metallographic studies of sections from specimens of the A106 and T11 alloys indicated that the attack was uniform.

The stainless steel specimens were located at the high-temperature end of the probe. Even under these conditions, corrosion-wastage data indicate that these alloys suffered attack no greater than that for the carbon steels at the lower temperature. This, of course, is not unexpected. Wastage on the Type 304 was no greater than 22 mils per month, whereas the attack on the Type 321 was over half again as great. The reasons for the difference in the rates of attack on the two stainless steels is not apparent at this time, but continuing studies should answer the point.

Metallographic examination revealed that both types of stainless steel suffered some intergranular attack. The penetration was deepest on the Type 321 material.

Corrosion Probe 2

Probe 2 was in the incinerator for a total time of 893 hr, 389 hr of which represent actual incineration.

The appearance when removed from the incinerator was much the same as that of Probe 1. How-

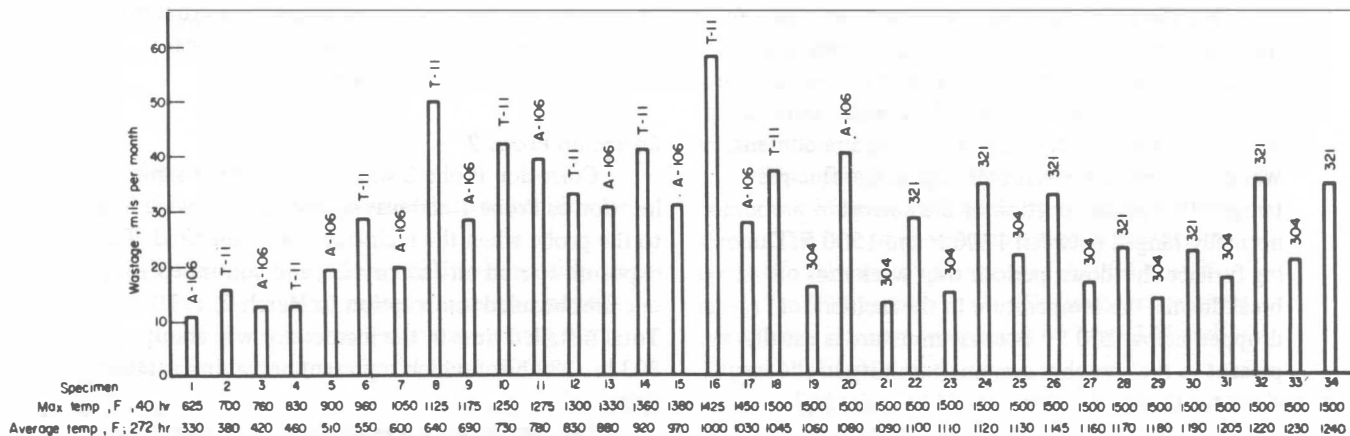


FIG. 2 TUBE-WASTAGE RATE ON PROBE 1 EXPOSED IN MIAMI COUNTY, OHIO, INCINERATOR (ONE MIL EQUALS 0.001 IN.)

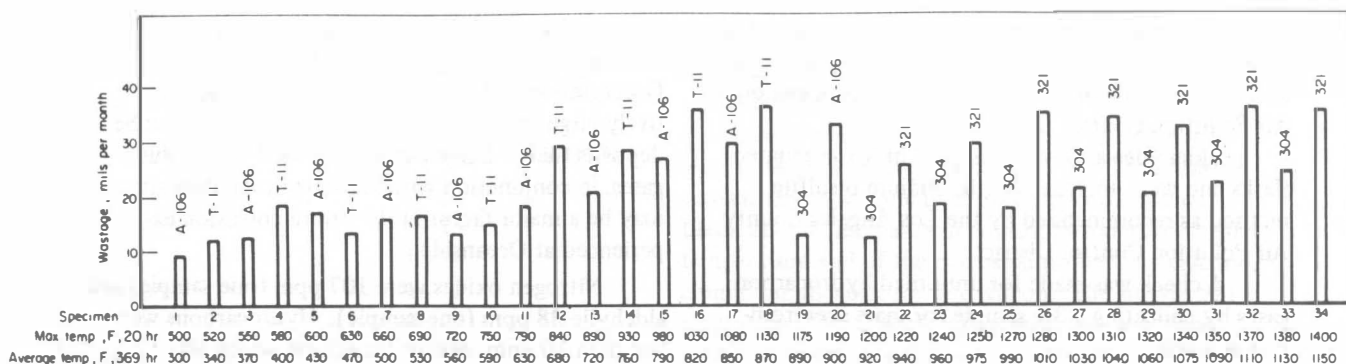


FIG. 3 TUBE WASTAGE RATE ON PROBE 2 EXPOSED IN MIAMI COUNTY, OHIO, INCINERATOR (ONE MIL EQUALS 0.001 IN.)

ever, the thick deposit buildup on the upstream surface was somewhat heavier than on Probe 1.

The results, presented graphically in Fig. 3, are expressed as mils per month. It can be seen that the wastage values for the carbon steel specimens are generally less than those obtained for Probe 1. These results probably reflect the lower operating temperature for Probe 2.

The corrosion of the two types of stainless steel on Probe 2 was quite similar to that for Probe 1. In several instances, the wastage of the stainless steel on the second probe was greater than for the first. The Type 304, again, was somewhat more resistant than Type 321.

The results for the two probes show that easily measurable corrosion occurs in the Miami County incinerator in about 300 hr. It is also of interest that the rates when projected to one year of exposure are great enough to be of the same order of magnitude as these noted on actual tubes at Oceanside.

FLUE-GAS COMPOSITIONS

A study of the mechanism by which deposits form and corrosion occurs on the metal surface of the incinerator, among other things, requires a knowledge of the flue-gas composition. Sampling of these gases has been done at the Miami County, Ohio, and the Oceanside, New York, sites. The samples were taken downstream from the combustion zone and before the gases reached the scrubber or boiler-tube sections of the incinerators.

Methods of Measurement. The incinerator temperatures at the sampling points were measured with both a high velocity shield thermocouple that measures true gas temperatures, and with an unshielded

thermocouple that provides data for radiant heat effects. At the Miami County incinerator, the shielded couple gave average readings of 1220 F, while those of the unshielded couple averaged 1350 F due to radiation from the flame. The situation was reversed at Oceanside incinerator, where the shielded couple showed the flue-gas temperatures to be 30 to 115 F higher than those registered by the unshielded couple. This reversal occurred because of radiation to the nearby boiler tubes. Thus, in this case, the metal surfaces were subjected to higher temperatures than would be recorded by an ordinary thermocouple. As a result of variations in the refuse being burned, there was a wide range of operating temperatures at Oceanside during the sampling period. Temperatures from 1100 to 1900 F were recorded.

Standard Orsat and Fyrite analyzers were used to determine oxygen, carbon dioxide, and carbon monoxide. The water content was measured by condensing the moisture and determining its volume.

Sulfur oxides were sampled by bubbling flue gas through 1 percent hydrogen peroxide solution and analyzing the resulting sulfuric acid by the barium chloranilate method [2]. These solutions were also analyzed for their chloric content and titrated for total acidity.

Fluoride analysis was made with an ion electrode (Orion). Gaseous HF was converted to SiF₄ by reaction with glass and absorbed in a buffered test solution. The chloride content was verified by using a chloride-ion electrode on this same solution.

Total acidity in the flue gases also was monitored using a modified SO₂ analyzer (Instrument Development Company), which is based on the measurement of the electrical conductivity of an absorbing solution of hydrogen peroxide.

Nitrogen oxides were sampled in 3-1 evacuated flasks. Analyses were made by the phenol disulfonic acid method recommended by the Los Angeles County Air Pollution Control District.

Aldehydes also were sampled in 3-1 evacuated flasks and were analyzed by the sodium bisulfite method as recommended by the Los Angeles County Air Pollution Control District.

A check was made for unburned hydrocarbon gases by collecting a 3-1 sample for mass spectrometer analysis.

Results and Discussion. Analyses of the flue gases at the Miami County, Ohio, incinerator show CO₂ concentrations ranging from 6.0 to 10.8 percent by volume, with corresponding oxygen levels from 15.0 to 9.5 volume percent. These values indicate that the incinerator was operating during the sampling periods with excess air levels ranging from 80 to 225 percent, thus providing strongly oxidizing conditions.

Other constituents of the flue gases were:

HC1	90 to 115 ppm
SO ₂	46 to 106 ppm
HF	Traces to 0.6 ppm
Oxides of nitrogen . .	57 to 138 ppm

In combination with deposits of chloride and sulfate, these concentrations of acidic gases could result in serious corrosion problems as evidenced by the effects on the corrosion probes which were exposed in the Miami County, Ohio, incinerator. Total acidities for the flue gases ranged from 10 to 75 percent greater than what could be accounted for by the foregoing gases, and probably were the results of volatile organic acids.

Hydrocarbons, such as methane, ethane, ethylene, propane, and butane, were all less than 10-ppm concentration. Carbon monoxide was usually less than 10 ppm, but once was as high as 2000 ppm. The aldehyde concentrations expressed as formaldehyde ranged from 25 to 58 ppm.

Similar sampling of flue gases carried out at the Oceanside, Long Island, incinerator revealed CO₂ levels from 3.5 to 12.0 percent, with corresponding oxygen concentrations from 17.0 to 8.0 percent. In terms of excess air, these values represent 25 to 350 percent, which is a much wider range of operating conditions than was encountered at the Miami County unit. The corrosive gases also went through wide variations in concentration at Oceanside.

HC1	1 to 330 ppm
SO ₂	0 to 100 ppm
HF	Traces to 1.1 ppm

The relatively high HC1 level noted during one of the sampling periods may occur frequently at Oceanside and, if so, would account for the relatively large amount of chloride found in boiler-tube deposits there. Large amounts of HC1 in the flue gases, in conjunction with chloride in the deposits, may be a major factor in the severe corrosion experienced at Oceanside.

Nitrogen oxides were 107 ppm (one sample) and aldehyde 38 ppm (one sample). Hydrocarbons were less than 10 ppm, except for ethane which was 12 ppm. Carbon monoxide concentration was 45 ppm, showing that practically complete combustion of hydrocarbon gases was occurring.

Analysis of Deposits

In order to determine the causes and mechanisms of incinerator boiler-tube corrosion, analysis of the tube deposits is important. The analysis provides information regarding the distribution of corrosive components in different temperature zones and, as far as possible, identifies specific compounds in the deposits. Samples of deposits obtained from the boiler tubes at the Oceanside incinerator and those built up on the probes inserted in the Miami County, Ohio, incinerator have been analyzed by emission spectrography, wet-chemical methods, X-ray diffraction, and electron probe microanalysis.

Boiler-Tube Deposits

Deposits obtained from boiler tubes at the Oceanside, Long Island, incinerator contained significant quantities of elements not commonly encountered in power station boilers. These components are lead, zinc, and chloride. In the outer layers of the deposit, the lead concentration was as high as 20 wt.-percent in some spots, while in the adherent tube scale, it was present in amounts of 2 to 4 wt.-percent. X-ray diffraction studies of these deposits showed that the lead is present as Pb(SO₄)₂. The chloride present has been identified as NaCl. The high iron content of the scale indicated that it consisted primarily of corrosion products. Zinc was uniformly distributed through deposit and scale in amounts from 5 to 10 wt.-percent. The chloride content was 2 wt.-percent in the deposit as compared to about 1 wt.-percent in the corrosion product scale. A similar distribution of these elements was found in the deposit and the scale from a badly corroded stainless-steel hanger.

Other components that are commonly found in deposits from power station boilers were present in various amounts:

Component	Concentration Range, wt.-percent
Sodium	5 - 10
Potassium	5 - 15
Calcium	1 - 4
Aluminum	1 - 3
Iron	1 - 20
Silicon	1 - 3
Sulfate, as SO ₃	21 - 29

The data show that not much iron is in the bulk of the deposit. This is an indication that little iron is volatilized from the waste, whereas the fly ash in most power stations contains a significant amount of iron. The corrosion product scale contained iron in amounts up to 20 wt.-percent. The relatively high potassium content and rather low calcium, aluminum, and silicon contents also are different from those found in power station experience. The sulfate concentration is typical of deposits on superheaters of coal-fired boilers.

Corrosion Probe 1

Analysis of the deposits built up on the first corrosion probe exposed in the Miami County, Ohio, incinerator revealed that significant changes in the distribution of components of the deposit occurred

along the length of the probe. However, these differences were not unexpected. For example, at the cooler end of the probe, lead and zinc contents were the highest, and sodium, potassium, and iron also were present in greater concentrations. The chloride concentration was the highest in the cooler zone. Elements that increased in concentration at the higher temperature end of the corrosion probe were calcium, aluminum, magnesium, and silicon. The sulfate concentration did not show any segregation with temperature, and was fairly uniform along the length of the probe. Changes in concentration of the various metal components with temperature are shown in Fig. 4. Chloride values ranged from 1.3 to 0.3 wt.-percent from the cooler to the hotter zone. Sulfur was present in amounts from 6.5 to 8 wt.-percent.

X-ray diffraction studies were made of the deposit samples to identify specific components. The following compounds have been identified in the deposit: PbO, Na₂SO₄, CaSO₄, Fe₂O₃, and Fe₃O₄. The distribution of these compounds in the various temperature zones of the deposit is shown in Table 1.

Corrosion Probe 2

The average elemental analyses of the deposits built up on the second corrosion probe exposed in the Miami County, Ohio, incinerator also are included in Fig. 4. In the lower temperature region, the lead content of the deposit was significantly

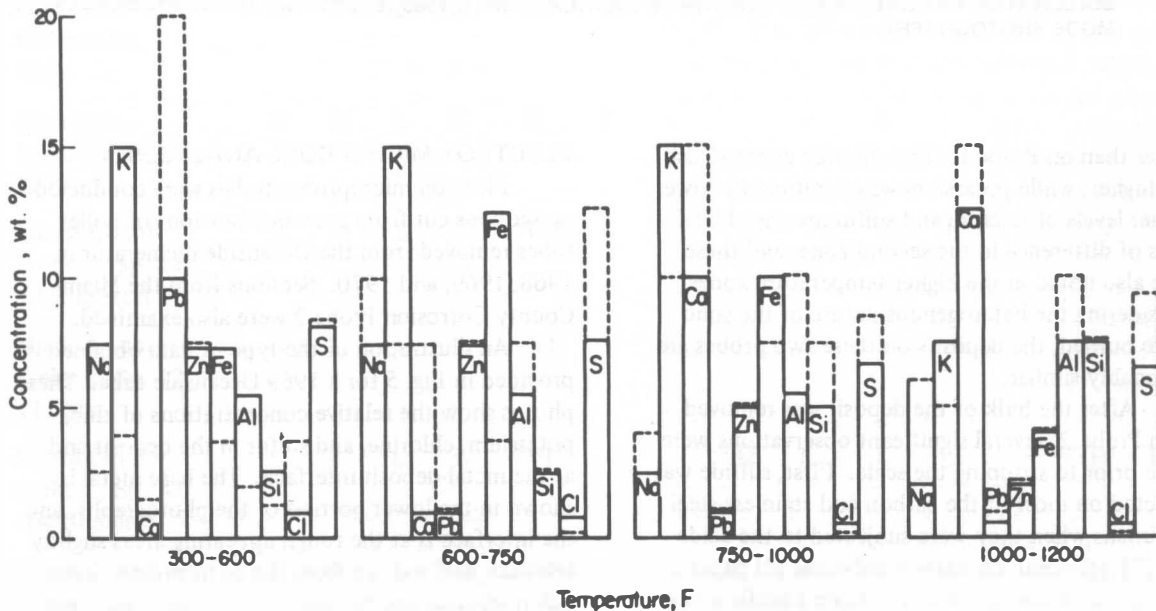


FIG. 4 ELEMENTAL ANALYSIS OF DEPOSITS FROM DIFFERENT ZONES OF CORROSION PROBES 1 AND 2 (SOLID LINES - PROBE 1, BROKEN LINES - PROBE 2)

TABLE 1 X-RAY DIFFRACTION RESULTS ON CORROSION PROBE 1

Average Temp, F.	Compounds Observed				
	Fe ₂ O ₃	Na ₂ SO ₄	Fe ₃ O ₄	CaSO ₄	PbO
330	x	x			x
460	x	x	x	x	
600	x	x	x		
730	x	x	x		
985	x	x		x	
1060	x	x			
1110	x			x	
1220	x			x	

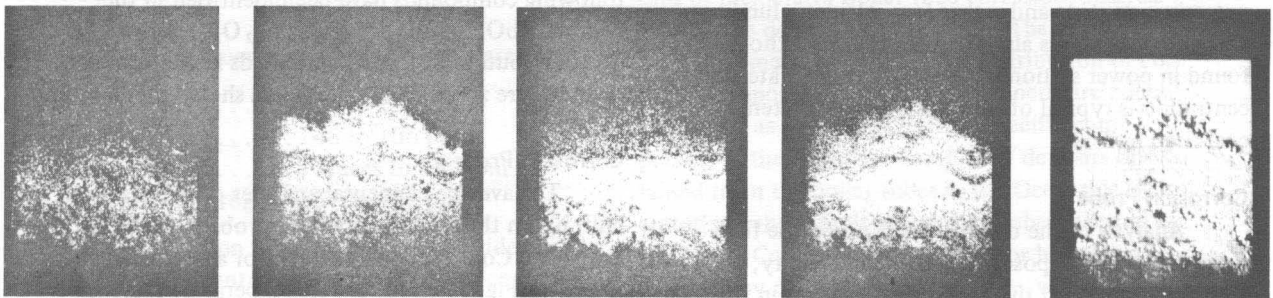


FIG. 5 RELATIVE CONCENTRATIONS OF SELECTED ELEMENTS IN METAL-DEPOSIT INTERFACE OF CORRODED BOILER TUBE REMOVED FROM OCEANSIDE INCINERATOR IN 1969 (ELECTRON MICROPROBE PULSE MODE PHOTOGRAPH)

higher than on Probe 1. The chloride content also was higher, while potassium was significantly lower. Higher levels of calcium and sulfur are the chief features of difference in the second zone, and these were also noted in the higher temperature zones. Considering the heterogenous nature of the solid waste burned, the deposits on these two probes are reasonably similar.

After the bulk of the deposit was removed from Probe 2, several significant observations were made prior to stripping the scale. First, sulfide was detected on most of the carbon and stainless-steel specimens when they were subjected to the azide test [3]. Second, moistened universal pH paper placed over these specimens indicated acidic areas with a pH of about 2. The low pH indicates the presence of acidic salts such as alkali pyrosulfates, alkali iron trisulfates, or zinc and iron chlorides.

ELECTRON MICROPROBE ANALYSES

Electron microprobe studies were conducted on sections cut from corroded portions of boiler tubes removed from the Oceanside incinerator in 1968, 1969, and 1970. Sections from the Miami County Corrosion Probe 2 were also examined.

An illustration of the type of data obtained is provided in Fig. 5 for a 1969 Oceanside tube. These photos show the relative concentrations of zinc, potassium, chlorine, and sulfur in the deposit and at the metal-deposit interface. The base metal is shown in the lower portion of the photographs, and the interface is at the rough appearing areas slightly less than half way up from the bottom line. The chlorine, zinc, and potassium are directly adjacent to the metal surface. In fact, some selective penetration of zinc and chlorine into corroded areas of the metal is indicated at the pitted appearing center

area. The sulfur in this instance as in most others is found in the deposit somewhat removed from the metal deposit interface.

Data on other elements, which were present in the metal-deposit interface of the three Oceanside boiler tubes, are presented in Table 2. For purposes of comparison, the zinc, potassium, and chlorine of Fig. 5 are rated high and sulfur is rated low. The tube removed in 1968 shows much the same situation as depicted in Fig. 5, except that potassium was present only in moderate concentration, and copper appeared in high concentration. The 1970 Oceanside tube showed somewhat more sulfur than the 1969 tube. Lead was relatively low at the interface in all three Oceanside tubes, but it appeared in greater amounts further out in the deposit.

Electron microprobe data on four selected specimens from Probe 2, exposed in the Miami County, Ohio, incinerator also are included in Table 2. It will be noted that, in general, the deposits were of similar composition to those at Oceanside. However, high chloride levels were noted in only one sample of the deposit. Sulfur was present in a moderate amount as was zinc. In general, the iron was more in evidence as a corrosion product at the interface of the Probe 2 specimens than it was for the Oceanside tubes.

LABORATORY CORROSION STUDIES

The objective of the laboratory experiments is to determine the importance of individual factors on corrosion in incinerators. Since the experiments can

TABLE 2 ELECTRON PROBE MICROANALYSIS OF THE METAL-DEPOSIT INTERFACE OF CORRODED SPECIMENS

Sample	Relative Concentrations of Elements													
	Cl	S	Pb	Zn	Fe	Cu	Na	K	Ca	Al	Si	Sn	Ni	Cr
Oceanside boiler tube, 1968	H	M	L	H	H	H	—	M	VL	—	—	L	—	—
Oceanside boiler tube, 1969	H	L	L	H	H	M	VL	H	VL	L	—	VL	—	—
Oceanside boiler tube, 1970	H	M	L	H	H	L	—	—	—	L	—	—	—	—
Miami County Probe 2, Sp. 11, A106B Steel	L	M	L	VL	VH	—	VL	L	VL	L	L	L	—	—
Miami County Probe 2, Sp. 12 T11 Steel	H	L	L	L	VH	—	L	L	L	M	VL	—	—	M
Miami County Probe 2, Sp. 33 304 Stainless	L	L	L	L	VH	—	—	M	L	L	L	—	H	H
Miami County Probe 2, Sp. 34 321 Stainless	L	L	L	M	VH	—	—	L	VL	L	M	—	H	VH

VH = very high, H = high, M = moderate, L = low, VL = very low
Dash indicates no analysis made

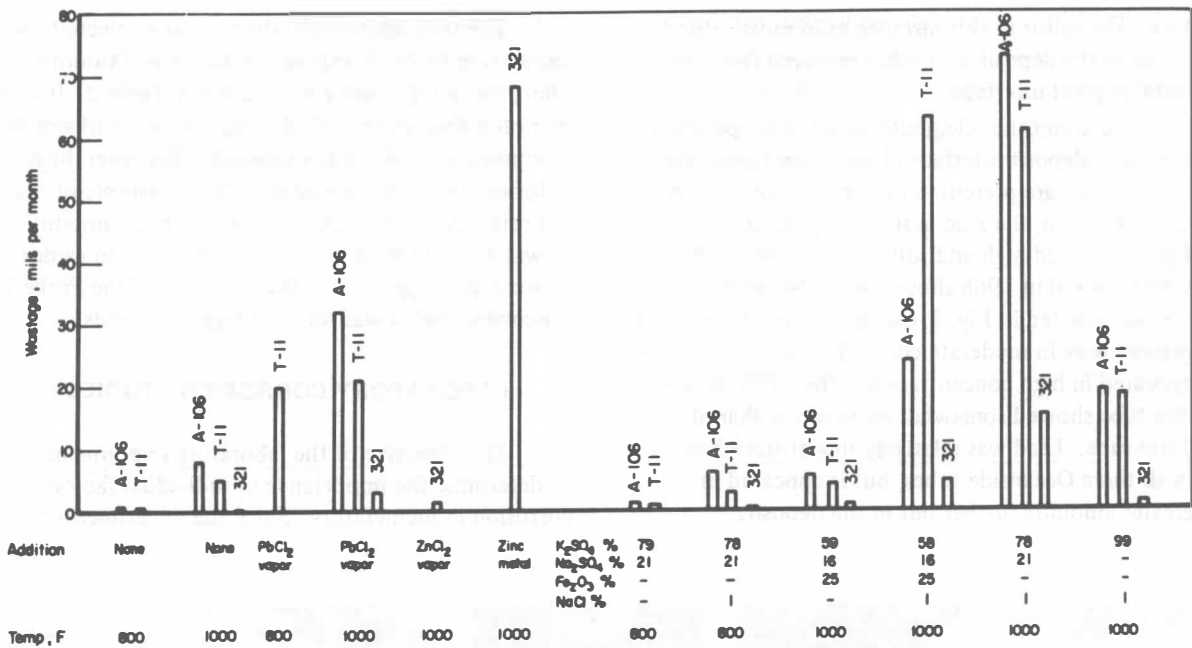


FIG. 6 METAL-WASTAGE RATE FOR LABORATORY SPECIMENS. GAS COMPOSITION: 80 PERCENT AIR, 10 PERCENT CO₂, 10 PERCENT H₂O, 250 PPM SO₂. (ONE MIL EQUALS 0.001 IN.)

be carried out under carefully controlled conditions, it is possible to determine the role of such factors as gaseous components, salts or deposits, metal composition, and temperature.

APPARATUS AND PROCEDURES

Metal specimens are placed in porcelain boats or crucibles located within quartz or Vycor tubes passing through resistance-heated tube furnaces. Gases are preheated in a section which is packed with quartz wool to enhance heat transfer.

Synthetic flue gases consisting of typical mixtures of CO₂, air, and water as encountered in the incinerator were used with SO₂ and HCl, separately, and in combination. The standard composition used was: 80 percent air, 10 percent CO₂, and 10 percent H₂O with 250 ppm SO₂. HCl in amounts of 200 ppm was added in some experiments. The gas flow was about 4.6 lpm which corresponds to a linear velocity of 0.5 fps.

The equipment upstream of the reactor consists of flowmeters for metering carbon dioxide and air to the reactor, manometers to regulate the pressure of these two gases at 19.7 psia, and a manometer for determining pressure drop through the system and exit portion of the setup. The controlled and small amount of SO₂ and HCl was brought into the

stream of carbon dioxide through capillary tubes. The flow of sulfur dioxide was determined and checked periodically by the hydrogen peroxide method. The flow of HCl was followed with a flowmeter. By sparging air through heated water, water vapor was introduced into the system and was controlled by the flow of air and the temperature of the water reservoir.

Corrosion specimens about 0.75 x 2 x 0.125 in. were cut lengthwise from the same A106, T11, and Type 321 stainless-steel tube materials used for preparing the probe specimens. The extent of corrosion was evaluated by weight-change measurements and by metallographic examinations.

In addition to the synthetic flue gases, the specimens were exposed to fly ash from Miami County, to mixtures of sulfates and iron oxide with and without sodium chloride, and to lead chloride, zinc chloride, and zinc. These latter materials were included because of the observations here and elsewhere, that 10 percent each of lead and zinc expressed as oxides or chlorides have been found in the deposits on fireside-wall tubes of incinerators. The sulfate-chloride mixtures were studied because of the known corrosiveness of high chlorine containing coals and because of the HCl found in incinerator gases. In addition, the microprobe exam-

inations had revealed concentrations of sulfur and chlorine, as well as zinc and lead at the corroded metal surfaces on samples obtained in the field studies.

Exposure times varied from 25 to 150 hr.

RESULTS

Typical results, usually the average of the weight loss for at least two specimens, are summarized in Fig. 6. Flue gas containing 250 ppm SO_2 was passed through the furnaces during these experiments. The other operating conditions, such as temperature or the presence of solid or vapor additions, are shown in the figure.

Gas-Phase Reactions. As might be expected, the attack of metals by gas-phase reactions was relatively mild at normal operating temperatures. For example, as can be seen in Fig. 6, the corrosion was 0.5 and 0.6 mil per month at 800 F for T11 and A106, respectively, when SO_2 was present in the flue gas. The addition of HCl increased the attack only slightly, i.e., from 0.7 to 0.9 mil per month.

The wastage as a result of oxidation was increased about tenfold for the two steels just mentioned when the temperature was raised to 1000 F. Again SO_2 and HCl had a negligible effect. Extremely mild attack occurred on the Type 321 steel at 1000 F in these gases.

Experiments in which the specimens were embedded in fly ash contained in porcelain boats showed that essentially no acceleration of corrosion occurred for A106 and T11 at 800 F or of Type 321 at 1000 F.

Effect of Lead Chloride, Zinc Chloride, and Zinc Metal

Studies with lead chloride were made by vaporizing the salt at 1000 F in a preheater section prior to contacting the metal specimen. As indicated in Fig. 6, the carbon steels and the Type 321 stainless steel suffered accelerated attack. In other experiments, not included in the figure, the stainless steel was placed directly on a porcelain boat containing lead chloride in stagnant air at 800, 900, and 1000 F. The attack was extremely severe at 1000 F with rates up to 183 mils per month (based on weight loss) being experienced in a 100-hr exposure. At 800 and 900 F, an intergranular penetration up to 6 to 9 mils deep occurred particularly on specimens touching the lead salt.

The experiment with Type 321 stainless steel and zinc chloride was conducted with the zinc chloride in the preheater at 500 F and the coupon

at 1000 F. Under these conditions, the stainless steel was attacked less severely than by the lead chloride. When the 321 stainless-steel specimens were immersed in granular zinc at 1000 F, the weight loss was also very great; i.e., a corrosion rate of 69 mils per month was noted.

Effect of Sulfate and Chloride Salts

Several corrosion mixtures, combinations of K_2SO_4 , Na_2SO_4 , Fe_2O_3 , and NaCl, were studied since these compounds have been identified as constituents of various incinerator deposits. The potassium salt was in preponderance, since both chemical analyses and microprobe analyses show that potassium is present on an incinerator tube surface in greater concentration than sodium.

A noticeable increase in corrosion was experienced at 800 F, particularly for the carbon steels when sodium chloride was added. At 1000 F, an extremely high corrosion rate was noted for the carbon steels and an appreciable one for the Type 321 stainless steel. The attack on the stainless was usually localized.

It is significant that azide tests showed sulfide present on the metal surfaces after exposure to the more corrosive mixed sulfate-chloride salts. This indicates that the metals reduce the sulfates under the conditions used. These findings are in good agreement with those from the Miami County probes where sulfide is usually detected on the corroded metal surfaces.

DISCUSSION AND CONCLUSIONS

Several factors of importance have been established during the present research. Chemical and X-ray analyses of deposits, spot tests, and microprobe studies at metal/scale interfaces indicate that a variety of potentially corrosive compounds are present to react or have reacted with the tube metals. It is quite significant that the microprobe analysis of sections at the metal/scale interface show concentrations of sulfur, chlorine, zinc, and occasionally lead and copper. It is believed that compounds containing these elements are major contributors to the corrosion. The concentrations of aluminum, potassium, sodium, and calcium also noted in the scale probably serve as the cation portion of the sulfur and chlorine containing compounds.

The fact that chlorine has been identified as being adjacent to the metal in corroded tubes is of particular significance. It is interpreted to mean that chlorine or some chlorine containing compound,

probably a chloride salt, has reacted with the metal. Although the mechanism by which chloride salts accelerate the wastage of carbon steels has not been established, it is believed to be related to the ability of chlorides to penetrate protective oxide film and allow oxygen to react with a fresh metal surface. In the case of stainless steels, a mechanism has already been proposed by Pickering and Associates [4]. According to these workers, dry sodium chloride and oxygen in the temperature range of 1100 to 1400 F form a nonprotective sodium chromate containing scale in a process which causes wastage of surface layer in addition to intergranular penetration. The laboratory studies reported in this paper have demonstrated that severe corrosion results from the presence of PbCl₂, ZnCl₂, and NaCl, in the presence of typical incinerator flue gases. Other information related to corrosion from chloride-containing fossil fuels shows that the presence of chloride can accelerate corrosion markedly [5-8]. Thus, there is a good possibility that chloride has participated in a

major way in the wastage process in operating incinerators.

The presence of sulfur (determined by the microprobe) in the corrosion scale near the metal surfaces, coupled with the observation that sulfide, as shown by the azide test, is usually found on corroded specimens from the incinerator, leads to the conclusion that sulfur compounds are also contributing to tube wastage processes. It is suggested that the participating corrosion reaction is one involving the reduction of the sulfur-containing compound by iron in the case of carbon steel and can be expressed by the equation:



It should also be pointed out that a reducing condition of the gas atmosphere is not required for the formation of sulfide on these metals. For example, sulfide was always detected on those laboratory specimens involving mixed sulfates and sodium chloride where noticeable corrosion had occurred.

TABLE 3 ANALYSES OF DEPOSITS FROM VARIOUS INCINERATORS

	German*	Norfolk*	Oceanside*	Miami Co., Ohio Probe 1	Miami Co., Ohio Probe 2
SiO ₂	15.0	36.5	6.00	5.3	3.2
Al ₂ O ₃	7.0	17.5	4.0	9.4	3.8
Fe ₂ O ₃	7.0	12.0	18.0	10.7	4.3
CaO	8.0	10.0	1.80	1.4	2.1
SO ₃	31.7	8.40	26.1	20.6	20.9
K ₂ O	7.68	3.00	13.0	18.1	4.8
TiO ₂	0.65	2.00	0.50	—	—
Na ₂ O	2.40	3.51	5.12	10.1	4.0
ZnO	5.61	7.44	9.65	9.3	9.4
P ₂ O ₅	1.31	1.71	0.60	—	—
MnO ₂	0.10	1.00	Nil	—	—
CuO	0.12	0.31	Nil	—	—
NiO	0.18	0.25	0.13	—	—
V ₂ O ₅	Nil	0.75	Nil	—	—
Cr ₂ O ₃	0.20	0.60	Nil	—	—
MoO ₃	0.15	0.10	Nil	—	—
MgO	4.1	0.90	Nil	—	—
Cl	0.40	0.02	1.58	1.0	3.8
PbO	8.0	0.67	5.12	10.8	21.6
SnO ₂	1.02	0.40	1.12	—	—
Ag ₂ O	Nil	0.15	0.08	—	—

*From Data of Bryers and Kerekes, Ref. 9.

This work was carried out in synthetic flue gas consisting of a mixture of CO₂, air, water vapor, and SO₂.

The roles of lead, zinc, copper, and potassium, which are also detected adjacent to the metal surface, have not yet been established, but they are very likely of significance as indicated by the laboratory experiment already conducted.

Consideration has been given to the supposed anomaly of the presence of severe tube corrosion at the Oceanside incinerator and its absence at Norfolk, Merrick, Atlanta, etc. The present work suggests a twofold explanation. First, the operating conditions at Oceanside include a substantially higher metal temperature than at the other locations, and this elevated temperature, according to the corrosion probe results, would accelerate tube wastage. Second, the chemical analyses of deposits taken from the convection passes at sites where corrosion is severe, i.e., Oceanside and Miami, Co., Ohio, show considerable amounts of corrosive constituents, whereas those at Norfolk do not.

Data from analyses of deposits by Bryers and Kerekes [9] have been combined with those obtained on the Miami County, Ohio, corrosion probes and are presented in Table 3. There are significant differences in the deposits that could account for the lack of corrosion at Norfolk; namely (a) low concentrations of SO₃, chlorine, and lead; and (b) high concentrations of SiO₂ and Al₂O₃ (54 percent of the deposit) which are inert components and might provide protection to the tube surface.

Many fundamental aspects of incinerator corrosion remain to be investigated. The form in which the metallic ingredients are transported from the combustion zone has not been identified. Chemical reactions within the deposit that lead to formation of corrosive compounds need to be elucidated. Until such time as answers have been provided to these important points, only stop-gap measures against fire-side corrosion, such as operating at low metal temperatures, can be offered as a remedy.

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