

Corrosion and Deposits From Combustion of Solid Waste

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ABSTRACT

Combustion of solid waste in municipal incinerators has resulted in fouling and corrosion on heat transfer surfaces. The nature of these deposits and the extent of the corrosion has been investigated in a combined field and laboratory study. In addition to the elements normally found in boiler deposits, chlorine, lead, and zinc appeared in significant quantities in the incinerator deposits. Twenty specific compounds have been identified in the deposits. The presence of potassium, sulfur, chlorine, lead, and zinc in the corrosion product scale at the metal-deposit interface has been demonstrated. Corrosion resulting from the action of flue gases and accumulated deposits has been measured by means of probes exposed in large municipal incinerators. Mechanisms for the corrosion processes are suggested, and possible remedies are discussed.

INTRODUCTION

The trend toward burning of municipal solid waste in water-wall incinerators with heat recovery and steam generation using standard boiler furnace design has resulted in concern about corrosion and deposits that occur under these circumstances. In addition, there has been interest in the use of solid waste as a low-cost fuel to replace some of the coal or oil now being burned in large power plants. The higher tube metal temperatures in the latter plants make them more vulnerable to corrosion than is the case

with many incinerators. These concerns have led to the investigation of the nature of the deposits and the extent of corrosion that can result from the combustion of municipal solid waste in boiler furnaces. This research has been done under a grant from the Solid Waste Management Office of the Environmental Protection Agency.

FIELD STUDIES

The field studies conducted on this program have included:

(a) Installation of corrosion probes in the municipal incinerator operated by Miami County, Ohio, and in the Salvage Fuel Boiler operated by the Navy at Norfolk, Virginia.

(b) Sampling of flue gas at the Miami County, Ohio, the Oceanside, Long Island, and the Norfolk incinerators.

(c) Analysis of the boiler-tube deposits from the Oceanside incinerator, and those built up on the corrosion probes in the Miami County, Ohio, and the Norfolk, Virginia, incinerators.

PROBE DESIGN AND OPERATION

The probe was designed to provide exposure of 34 specimens of boiler-tube materials. The specimens were machined from 1-in. schedule 40 pipe or equivalent tubing, and were nested together end-to-end on the probe. The probe was inserted into the incinerator through a side wall and was mounted at a 90-deg angle

to the flue gas stream. The section of the probe extending through the wall was water cooled. The specimens exposed within the incinerator were cooled by air flowing inside the tubular specimens. A computer analysis was used to determine the geometry of the internal support tube required to provide the most linear temperature gradient along the probe between 350 and 1100 deg F. Details of the probe design have been published previously [1, 2].

The specimen temperatures were controlled by regulating the amount of cooling air admitted to the probe. The output from a control thermocouple was monitored by a proportional temperature controller. The controller maintained a preset temperature by varying the amount of cooling air bypassing the probe through a motorized butterfly valve located between the blower and the probe. An air pump delivering up to about 34 cfm was used with 5-hp motor as a drive.

The probes were exposed in the refractory-lined municipal incinerator at Miami County, Ohio, and in the water-wall incinerator operated by the Navy Public Works Center at Norfolk, Virginia. Twelve corrosion probe runs have been made at the Miami County site and three at the Norfolk location. Exposure times at temperature ranged from 122 to 1318 hr.

FURNACE-GAS COMPOSITIONS

Understanding of the mechanism by which deposits form and corrosion occurs on the metal surfaces of the incinerator, among other things, requires a knowledge of the furnace-gas composition. Sampling of these gases was done at the Miami County, Ohio, the Oceanside, New York, and the Norfolk, Virginia, sites. The sampling was done at the same location in the incinerator that the probes were placed in the case of of the Miami County and Norfolk sites. At Oceanside the gases were sampled in the area between the flame zone and the first bank of boiler tubes.

As would be expected from the variable nature of the solid waste burned in municipal incinerators, a wide range of values for the different gases was found. The data are summarized in Table 1.

Two gases of primary concern from the corrosion standpoint are SO₂ and HCl. The amounts of these gases found in each of the three incinerators varied greatly. In general, the SO₂ and HCl concentrations at Norfolk were less than those at the other sites. This could have some relationship to the lower corrosion experienced at Norfolk, although factors such as temperature are probably of even greater importance.

It can be noted in Table I that the SO₂ concentrations are relatively low compared with those for

TABLE 1 FURNACE-GAS COMPOSITION

	Concentration Ranges ^(a)		
	Miami County	Oceanside	Norfolk
SO ₂ , ppm	2-303	0-100	0-21
HCl, ppm	5-115	3-330	15-106
HF, ppm	Traces-0.6	Traces-1.1	Traces-6.0
Nitrogen Oxides, ppm	10-138	147 ^(b)	12-15
Organic Acids, ppm	35-136	Not measured	150-340
Oxygen, vol %	15.0-9.5	17.0-8.0	16.5-15.0
CO ₂ , vol %	6.0-12.0	3.5-12	3.9-5.6
Co, vol %	Traces-0.2	0.005 ^(b)	0.1-0.2

(a) Corrected to 12 percent CO₂.

(b) Single measurement.

large coal and oil-fired boilers, which usually range from 2500 to 3000 ppm. On the other hand, such boilers do not contain the HCl found in incinerators. Even at low SO₂ levels, accumulation of sulfates in the incinerator deposits reach the same levels (20 to 30 weight percent) in a few hundred hours as are commonly found in power-station boilers after thousands of hours of service. Although the HCl levels in the incinerator gases are generally of the same magnitude as the SO₂ levels, the amounts of chlorides found in the deposits are smaller than the amounts of sulfates, presumably because of the conversion of chlorides to sulfates and loss of the chlorine.

SO₃ was not believed to be a significant factor. One such measurement at Miami County showed 1 ppm SO₃ and 303 ppm SO₂ in the flue gases at the position where the probe was exposed.

It is concluded that SO₂ and HCl were present in sufficient concentrations in all three incinerators to be of concern from the standpoint of possibilities of corrosive conditions.

The amount of HF found in one of the measurements made at Norfolk (6 ppm) is appreciably greater than the amounts detected at the other two sites. No indications have been found that this gas is of great significance in the tube-metal-wastage process.

PROBE DEPOSITS

After even the shortest exposure periods (100-200 hr), the probes were found to have accumulated deposits and corrosion-product scale. The quantity of deposit was greater at Miami County, Ohio, than at Norfolk for the same length of time. The deposits built up into a V-shaped form of varying depth along



FIG. 1 DEPOSIT ACCUMULATED ON PROBE IN MIAMI COUNTY, OHIO, INCINERATOR AFTER 828 hr

the probe, with the apex of the V pointed into the on-coming gas stream. A photograph of a typical probe deposit is shown in Fig. 1. The deposits were removed from all probes in numbered sequence. Thus the variations in composition could be determined as a function of temperature when the deposits were analyzed.

Emission spectrography and wet-chemical techniques were used to determine the concentration levels of the various elements in the deposits. X-ray diffraction was employed to identify the specific compounds present in the deposit.

MIAMI COUNTY INCINERATOR DEPOSITS

Deposits from the corrosion probes exposed at the Miami County, Ohio, incinerator have given insight into the deposition process and the chemical reactions involved.

The distributions of chemical elements found in significant quantities on the corrosion probe as a function of time are shown in Fig. 2. These exposures cover periods of about 100 to 828 hr and constitute analyses of deposits from seven probe exposures, all made over the bridgewall of the incinerator. Four temperature zones along the length of the probe have been selected for consideration. The changes in sulfur and chlorine concentration have been emphasized by connecting the points in the figure, as these elements are of great significance in the corrosion process. The

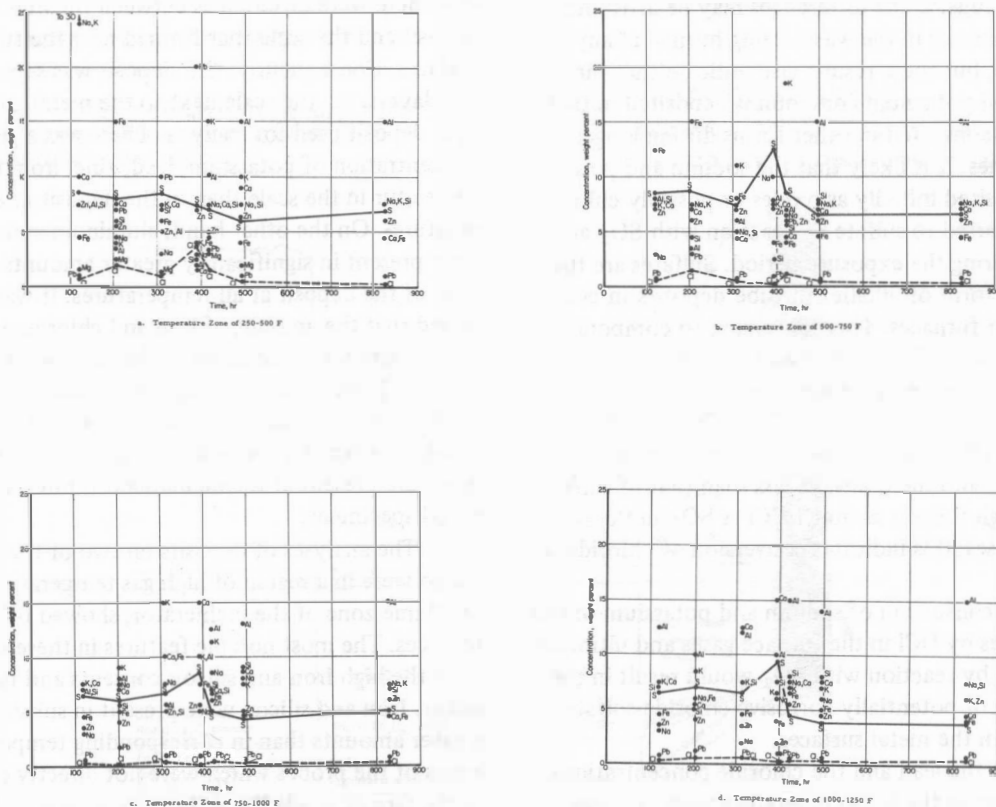


FIG. 2 PROBE DEPOSIT COMPOSITION AS A FUNCTION OF EXPOSURE TIME IN THE MIAMI COUNTY, OHIO, INCINERATOR

sulfur concentration goes through a maximum at about 400 hr in three temperature zones, and the chloride does the same in the lowest temperature zone. However, these peaks represent data obtained from a single probe and may reflect some unusual nature of the waste burned during the period in question. Additional data would be required to establish the sulfur maximum as a fact. Nevertheless, it is important from the aspect of corrosion that the sulfur level builds up rapidly in the deposits and after 100 hr is almost as high as it ever becomes. At the higher temperatures the sulfur level is somewhat reduced, probably because of the volatility of some of its compounds, but it is still present in sufficient quantity to cause corrosion.

The same is true of the chlorine content of the deposits. At low temperatures the chlorine persists in the deposits because of lowered volatility of chlorides and slower rates of conversion to sulfates. However, even the small quantities present in the high-temperature zones can cause serious corrosion.

High percentages of sodium and potassium were found in the low-temperature zone of the shortest probe run, with decreasing amounts in the longer exposure periods. Some differences may be attributed to the variations in the waste being burned at any given time, but these results also indicate that the sodium and potassium compounds deposited initially have been converted to other forms during longer exposure times. It is likely that the sodium and potassium deposited initially as oxides or possibly chlorides were converted to sulfate by reaction with SO_2 and oxygen during the exposure period. Sulfates are the dominant form of alkalis in tube deposits in coal-fired boiler furnaces. This conversion to compounds of higher molecular weight results in lower percentages of sodium and potassium in the deposits. X-ray-diffraction data have shown that NaCl , KCl , Na_2SO_4 , and $(\text{Na},\text{K})\text{SO}_4$ all exist in the deposits, but the amount of chloride is always less than that of sulfate even though there is as much HCl as SO_2 in the furnace gases; this indicates conversion of chloride to sulfate.

The conversion of sodium and potassium oxides to chlorides by HCl in the furnace gases and ultimately to sulfates by reaction with SO_2 would result in the deposition of potentially corrosive chloride-sulfate mixtures on the metal surfaces.

Both the lead and the chloride concentrations were highest in the low-temperature zone of these probes. This result may reflect higher volatility of the compounds containing these elements at high temperatures, as well as more rapid conversion of oxides

and chlorides to sulfates under such conditions. The fact that PbO , $4\text{PbO} \cdot \text{PbSO}_4$, and PbSO_4 have been identified in the deposits by X-ray diffraction shows that there is stepwise conversion of the lead oxide to lead sulfate via the intermediate oxysulfates. The unusually large amount of lead found in the 400-hr deposit probably resulted from the burning of some waste with a high lead content during the exposure period.

As the exposure time was lengthened, aluminum became the predominant element in the deposits, and the amounts of sodium, potassium, calcium, and silicon were significant. This indicates that clay-like materials such as silicates containing sodium, potassium, calcium, and aluminum were formed on long-term exposure. Materials of this type, forming a hard deposit, can build up above the metal surface a protective layer that is chemically inactive and serves as a barrier to diffusion of sulfur oxides, oxygen, and HCl . The decrease in the corrosion rates with time are indicative of such protective action.

The longest exposure (828 hr) resulted in a buildup of deposits up to 4 in. in depth along the probe. Visual examination of the deposits indicated that there were differences between the bulk of the deposit and the scale that formed near the specimen surfaces. Consequently, this deposit was separated into layers: (a) the scale next to the metal and (b) the bulk deposit used for analysis. There was a greater concentration of potassium, lead, zinc, iron, chlorine, and sulfur in the scale than in the deposit at all temperatures. On the other hand, aluminum and silicon were present in significantly greater amounts in the bulk of the deposit at all temperatures. It was observed that the amount of lead and chlorine in both deposit and scale decreased as the temperature increased. These data are in agreement with the results of the electron-microprobe examination of the probes, which revealed that potassium, lead, sulfur, and chlorine were present at the metal-deposit interface on corroded specimens.

The analyses of deposits on two of the probes, which were in a region of high gas temperature near the flame zone of the incinerator, showed other differences. The most notable features in these deposits were the high iron and silicon contents and the low sulfur. Iron and silicon were present in substantially greater amounts than in corresponding temperature zones of the probes which were not directly exposed to the flames, while the sulfur was quite low. The analysis indicated a more highly oxidized condition in these deposits than in those collected further from the flame. Although the metal-specimen temperatures

for three of the zones were the same as those in other probes, the deposit was subjected to higher gas temperatures which could have volatilized some of the compounds formed in the deposits.

A relatively short experiment was run at the Miami County incinerator in which a water-cooled probe was withdrawn at intervals of 2, 8, 24, and 88 hr for removal of deposits. Extremely high concentrations of chlorine (14-27 percent) and of iron (10-22 percent) were found in these deposits, indicating that chloride corrosion begins early in the ex-

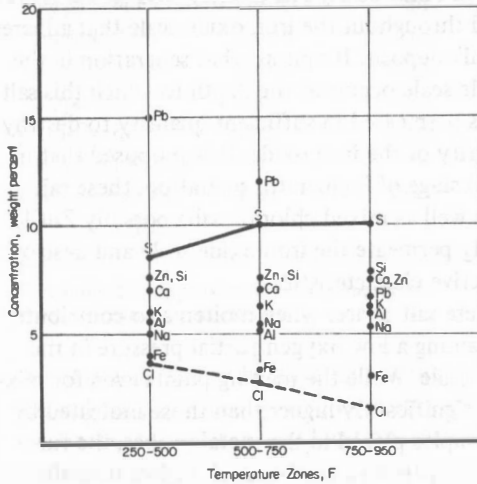


FIG. 3 PROBE DEPOSIT COMPOSITION AS A FUNCTION OF TEMPERATURE FOR EXPOSURES IN THE NORFOLK INCINERATOR

posure. As the chlorides are converted to sulfates and pyrosulfates later in the exposure, corrosion by these compounds adds to the metal wastage. In the early stages of the deposit history, the lead concentration also is high, probably as PbO, and the relative amount of lead decreases as this compound is converted to PbSO₄. The potassium and zinc concentrations remained fairly constant during the time in which these deposits accumulated, while the aluminum and silicon increased slightly.

NORFOLK INCINERATOR DEPOSITS

Three probe exposures were carried out at the Norfolk incinerator. The distribution of elements in the deposits as a function of temperature is shown in Fig. 3. It is significant that lead and sulfur predominated in the deposits. The average chlorine content was higher than that found in the long-term exposures at the Miami County incinerator. These facts show that there was more than enough potentially corrosive material present in the Norfolk incinerator deposits to cause metal wastage, if other conditions were favorable. The factors that minimize corrosion at Norfolk appear to be the relatively low metal temperatures and the small temperature gradient through the deposit.

X-RAY DIFFRACTION STUDIES

The elemental analysis of the deposits was supplemented by electron microprobe investigation of

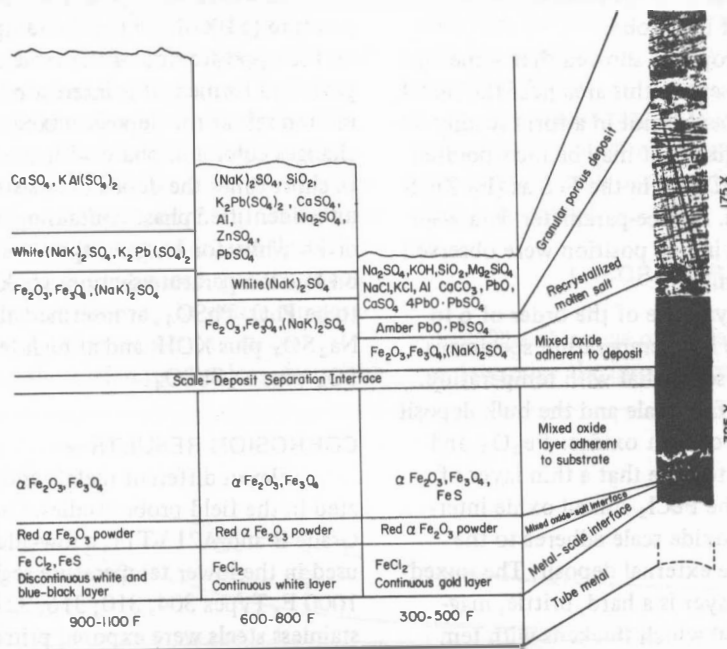


FIG. 4 SCHEMATIC LOCATION OF PHASES IDENTIFIED BY X-RAY DIFFRACTION

corroded probe specimens to determine which of the elements in the deposits predominated near the tube surface. The microprobe results showed that chlorine, sulfur, potassium, zinc, and sometimes lead were present at the corroded tube surfaces [3]. In order to determine what compounds actually were present in the corrosion scale and the bulk deposit, phase studies were conducted by obtaining X-ray diffraction data on the bulk deposit and on the individual layers revealed by microscopic examination. This work revealed the presence of 20 compounds plus some elemental aluminum in the various deposit layers. Fig. 4 presents typical analyses for various probe temperatures and a photomicrograph illustrating the general location and appearance of the scale and deposit as seen under reflected light. The colors indicated in the tabulation were determined under oblique illuminations from an incandescent lamp. It is evident from these results that distinct phase changes occur at various distances from the tube-metal surfaces as well as at different probe temperatures.

It can be seen first, that unlike the normal oxidation of iron which results in a layer sequence Fe-FeO-Fe₃O₄-Fe₂O₃ above 1040 deg F, or Fe-Fe₃O₄-Fe₂O₃ below 1040 deg F, the scale in contact with the substrate metal is found to contain FeCl₂ throughout the entire probe-temperature range 300 to 1200 deg F. At the moderately high temperature end of the probe it was found that the FeCl₂ layer melts and collects into small pools. As can also be seen in Fig. 4, a layer of FeS was also found on specimens from the high-temperature end of the probe.

The electron microprobe showed that some zinc compound was also present in this area near the metal. It appears that this element is not in a form readily detected by X-ray techniques, but may be incorporated in the FeCl₂ as (Fe,Zn)Cl₂ or in the FeS as (Fe,Zn)S with the host structures. Lattice-parameter data were not obtained, but shifts in line position were observed from specimen to specimen.

These interface layers are of the order of 6 to 10 microns thick on the low temperature specimens. The thickness increases somewhat with temperature.

Between the interface scale and the bulk deposit is a multi-layered scale of iron oxides: Fe₂O₃ and Fe₃O₄. It is interesting to note that a thin layer of alpha Fe₂O₃ forms at the FeCl₂-mixed oxide interface. Part of the mixed-oxide scale adheres to the substrate and part to the external deposit. The mixed-oxide (Fe₂O₃-Fe₃O₄) layer is a hard, brittle, magnetic, gray-black material which thickens with temperature and is made up of several layers with loose red Fe₂O₃ between layers. This suggests that reduc-

tion or reaction with other elements occurs in or below this layer. At the higher temperature where FeS forms, the mixed oxide scale is less adherent, and in this area, more of the mixed oxide is removed with the outer deposit. The topography of the corroded metal here changes from relatively smooth to dimpled.

It should be mentioned that the examinations with the microscope indicated that some melting had occurred near the scale. These studies showed the presence of recrystallized continuous phases (Na,K)₂SO₄ and PbO · PbSO₄ on the external surface of the mixed iron oxide scale. The (Na,K)₂SO₄ phase is also dispersed throughout the iron oxide scale that adheres to the bulk deposit. It appears that separation in the iron oxide scale occurs at the depth to which this salt phase has permeated in sufficient quantity to destroy the integrity of the iron oxide. It is proposed that in the initial stage of incinerator operation, these salt phases as well as mixed chloride salts possibly ZnCl₂ and PbCl₂ permeate the iron oxide scale and destroy its protective characteristics.

These salt phases when molten also contribute to maintaining a low oxygen partial pressure in the adherent scale. While the melting points even for mixtures are significantly higher than those indicated by thermocouples placed in the metal probes, the furnace-gas temperature will be much higher than the temperature of the probe because of the thermal gradient in the deposit. This condition is substantiated by the fact that molten pools of FeCl₂ were detected where no deposit had formed on a high-temperature (1100 deg F) probe sample, but did not melt on the opposite side of the same section where the deposit had formed. It is interesting to note that the molten salt at the deposit-mixed oxide interface changes color and phase with time and temperature. In short times the deposit consists of NaCl, KCl, and an unidentified phase containing large quantities of Zn or Pb while for longer exposures the melted deposit on low-temperature sections (~300 deg F) was found to be PbO · PbSO₄, at intermediate temperature Na₂SO₄ plus KOH, and at high temperatures (NaK)₂SO₄ plus K₂PbSO₄.

CORROSION RESULTS

Eleven different metals and alloys were evaluated in the field probe studies. Carbon steels A106-Grade B and A213-T11, a low-alloy Cr-Mo steel, were used in the lower temperature regions, i.e., not over 1000 F. Types 304, 310, 316, 321, 416, and 446 stainless steels were exposed primarily at the higher temperature regions but some were exposed at lower temperatures to provide a direct comparison with the

TABLE 2 RELATIVE PERFORMANCE OF STEELS USED ON CORROSION PROBES

Alloy	Resistance to Wastage		
	300-600 F	600-1200 F	Moist Deposit
Incoloy 525	Good	Fair	Good
Type 446	Good	Fair	Pits
Type 310	Good	Fair	SCC**
Type 316L	Good	Fair	SCC
Type 304	Good	Fair	SCC
Type 321	Good	Fair	SCC
Inconel 600	Good	Poor	Pits
Inconel 601	Good	Poor	Pits
Type 416	Fair	Fair	Pits
A106-Grade B (Carbon Steel)	Fair	Poor	Fair
A213-Grade T11 (Carbon Steel)	Fair	Poor	Fair

* Arranged in approximate decreasing order.
 ** Stress-corrosion cracking.

carbon-steels. The nickel-base alloys, Inconel 600, Inconel 601, and Incoloy 825 were also used to form specimens for use at several locations over the length of the probe.

Three types of coatings also were evaluated in the corrosion probe work: (a) a hard chromium which has afforded protection to superheater tubes in an oil-fired power station, (b) an aluminized coating which has proven useful in flue gas or exhaust gas atmospheres, and (c) cermets which have protected turbine blades during high-temperature operation.

The relative performance of the steels in resisting corrosion when exposed in the incinerator flue-gas atmospheres is shown in Table 2. As an approximation it can be assumed that "poor" is > 20 mils per month, "fair" is 10-20 mils per month, and "good" is < 10 mils per month. It can be seen that the Incoloy 825 gave encouraging results over the entire temperature range and is much more resistant to stress corrosion cracking than the austenitic stainless steels. The

stainless types, except Type 416, lose less weight than the carbon steels at comparable temperatures, with Types 310 and 446 being superior. The major limitation for these stainless alloys is stress-corrosion cracking or pitting when in contact with moist deposits as during downtime. The Inconel 600 and 601 materials were resistant over the lower temperature region but were severely attacked at high temperatures.

While the aluminum, chromium, and cermet coatings furnished some initial protection to the tube surfaces they do not appear to be sufficiently durable to be considered for long-time boiler operation.

Metal wastage rates were shown to be temperature dependent; for the carbon steels they ranged from about 10 mils per month at 325 deg F to about 35 mils per month at 950 deg F. These values, however, should not be projected to exposure of many months or years since rates decrease with extended exposure. It is estimated that rates for carbon steel tubes at about 500 deg F might be expected to range below about 10 mils per year for extended exposure periods.

Comparison of the results from six probes exposed in the same place in the Miami County incinerator when arranged according to the time of exposure shows that the initial corrosion rates are high and that they are reduced with time. Such a comparison for the A106 carbon steels is illustrated in Fig. 5, where the specimen numbers are plotted as a function of wastage and exposure time. The approximate temperatures are indicated by a lower band near 400 deg F extending to an upper band of 850 deg F. It can be seen that the wastage rates range from about 3 to 12 mils per month at 828 hr to about 30 to 55 mils per month at 120 hr.

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

LABORATORY STUDIES

The objective of the laboratory experiments was to determine the importance of individual factors on

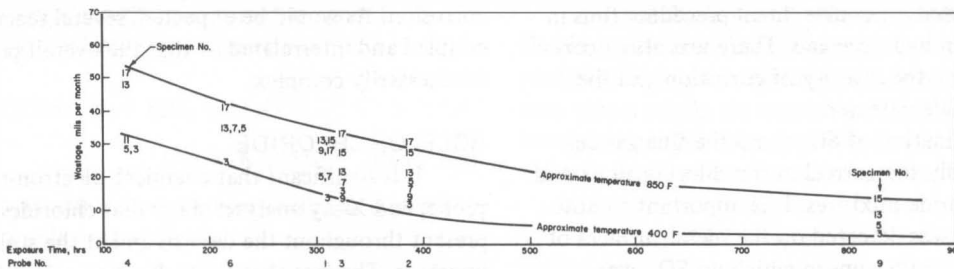


FIG. 5 METAL WASTAGE OF CARBON STEEL AS A FUNCTION OF EXPOSURE TIME

corrosion in incinerators and also to help establish the mechanism by which metal wastage occurs. Since the experiments could be carried out under carefully controlled conditions, it was possible to determine the role of such factors as gaseous components, salts, or deposits, metal composition, and temperatures. The analyses made on the probe deposits by the microprobe, X-ray, and analytical chemistry served to define corrosive salts mixtures to be studied.

EFFECTS OF SYNTHETIC MIXTURES

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

Synthetic furnace gases, consisting of typical mixtures of CO_2 , air, and water as encountered in the incinerator, were used with SO_2 and HCl separately and in combination. The standard composition used was: 80 percent air, 10 percent CO_2 , and 10 percent H_2O with 250 ppm SO_2 . The gas flow was about 0.16 cfm, which corresponds to a linear velocity of 0.2 fps. HCl was added on occasion in amounts of 200 and 2000 ppm. Exposure times were 50 hr for most of the runs.

The studies were carried out at 600, 800, and 1000 deg F using a variety of salt compositions under the synthetic flue-gas atmosphere. The data indicate that chloride salts added to sulfate salts significantly enhance corrosion, particularly at 800 and 1000 deg F. The SO_2 also is an important constituent in this system. At 600 deg F, the most corrosive salts in decreasing order of activity were KHSO_4 , $\text{K}_2\text{S}_2\text{O}_7$, and ZnCl_2 . At 800 and 1000 deg F, ZnCl_2 and PbCl_2 were very corrosive [4].

It is significant that sodium chloride alone in the presence of flue gas was quite corrosive to the carbon steels. Of even greater significance is the fact that sulfide was found on these specimens. Thus, some reaction involving the SO_2 in the flue gas was of importance since that was the only source of sulfur. Sulfide had been detected, of course, in all preceding runs in which corrosion had occurred. There was also a correlation between the severity of corrosion and the amount of sulfide detected.

The elimination of SO_2 from the flue gas decreased markedly the corrosion for chloride alone and for sulfate-chloride mixtures. It is important to note that no sulfide was detected on the metal surfaces of the specimens for the runs in which no SO_2 was present.

EFFECTS OF INCINERATOR DEPOSITS

Experiments also were carried out in the laboratory using deposits taken directly from the Miami County corrosion probes. For comparison, exposure tests were conducted in synthetic furnace gas only and in Na_2SO_4 containing 1 percent NaCl . Results are summarized in Table 3. The corrosion which occurred is expressed, first, as a weight loss in milligrams; second, as penetration in mils; and third, as a rate in mils per month.

Runs 60 and 61 were conducted for 50 and 250 hr, respectively. The deposit mixture for these runs was a portion taken from the low temperature section of a probe exposed in the Miami County incinerator. It can be seen in Table 3 that the incinerator deposit was much more corrosive than was the Na_2SO_4 - NaCl mixture or the furnace gas alone. It is also evident that the corrosion rate was greater for the 50-hr exposure than for the 250-hr exposure. This corresponds to the observation discussed for the field work in that the corrosion appeared to decrease with increasing times of exposure. The results also show greater attack in the A106 and T11 steels than on the stainless steels, as would be expected. Results, in general, agree fairly well with those obtained in the field.

An oily liquid collected at the cool end of the furnace tube during these experiments. This liquid was quite acidic and analysis showed it to be H_2SO_4 . It is believed that compounds such as pyrosulfates or bisulfates in the deposits are being thermally decomposed during the heating to release SO_3 , which then combines with moisture to form H_2SO_4 . In experiments with bisulfates and pyrosulfates, a similar liquid condensed at the exit by the furnace tube, particularly when bisulfates were heated.

CORROSION MECHANISMS

The results of these studies of the deposits, scale, and corroded surface of fireside tubes and probes in incinerators, combined with the laboratory studies, have provided an explanation of the cause of corrosion. As would be expected, several reactions are coupled and interrelated so that the overall picture is necessarily complex.

ROLE OF CHLORIDE

It is significant that chemical, electron-microprobe, and X-ray analyses show that chlorides are present throughout the deposit and at the scale/metal interface. The fact that FeCl_2 has been identified by X-ray analysis in the scale at the interface layer over

TABLE 3 LABORATORY CORROSION STUDIES WITH INCINERATOR DEPOSITS

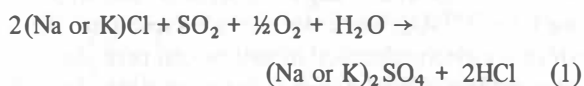
Chemical Environment	Units of Corrosion	Steel Type						
		310	S304	304	446	A106	T11	321
<u>Run 60 – 50 Hours at 1000 F</u>								
Gas only ^(a)	Wt loss, mg	0.4	2.8	3.4	8.2			
Na ₂ SO ₄ + 1 % NaCl in furnace gas	Wt loss, mg	6.3	9.0	39.5	10.6			
	Penetration, mils	0.07	0.1	0.45	0.12			
	Rate, mils/month	1.0	1.5	6.6	1.8			
Deposit from Probe 3 in furnace gas	Wt loss, mg	348	417	411	375			
	Penetration, mils	3.9	4.8	4.7	4.3			
	Rate, mils/month	57	70	70	63			
<u>Run 61 – 250 Hours at 1000 F</u>								
Gas only ^(a)	Wt loss, mg	1.0	8.4	12.7	11.9			
Na ₂ SO ₄ + 1 % NaCl in furnace gas	Wt loss, mg	9.1	24.3	104	34.8			
	Penetration, mils	0.1	0.3	1.2	0.4			
	Rate, mils/month	0.3	0.9	3.6	1.2			
Deposit from Probe 3 in furnace gas	Wt loss, mg	950	953	994	775	1296	1586	
	Penetration, mils	10.8	10.8	11.3	8.8	14.7	18.0	
	Rate, mils/month	31	31	33	26	43	52	
<u>Run 63 – 50 Hours at 1000 F</u>								
Very low temperature deposit from Probe 9 in furnace gas	Wt loss, mg					219	80	14.5
	Penetration, mils					1.0	0.4	0.07
	Rate, mils/month					15	5.9	1.0

(a) 80% air, 10% CO₂, 10% H₂O, 250 ppm SO₂, 2000 ppm HCl.

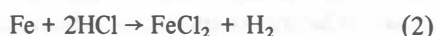
the entire temperature range studied is considered to be important. It is thought that this iron chloride corrosion product is initially formed from the reaction of iron with the hydrogen chloride or elemental chlorine released at the scale/metal interface.

Hazardous corrosive conditions from deposited chlorides have already been pointed out by Cutler and his associates [5], particularly as they apply to burning fossil fuel containing chlorine.

It is suggested that the corrosive agent hydrogen chloride is released by the reaction



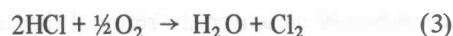
The hydrogen chloride then reacts with the iron surfaces to form ferrous chloride



As indicated by the laboratory studies at Battelle and supported by the work of Brown, DeLong, and Auld [6], the corrosive effects from HCl would not be expected to be severe below temperatures of about 600 deg F.

Since FeCl₂ has been detected on corrosion-probe samples exposed at temperatures well below 600 deg F, it is believed that some other mechanism is operating in this temperature range.

Although elemental chlorine has not been identified in incinerator furnace gases and would not be expected at high gas temperatures, it is believed that it may play a role in the corrosion reaction. It is postulated that metal oxides, possibly Fe₂O₃ or PbO, on the tube surfaces catalyze the reaction.



The chlorine, which is formed only near the catalytic

surface, then combines directly with the iron



It has been shown that once a layer of FeCl_2 has formed on the iron surface, reactions forming iron oxides (Fe_2O_3 and Fe_3O_4) and sometimes sulfides take place. Microscopic examination of the scales has shown that a molten salt phase has been present at points within the scale and as an interface layer between the scale and the deposit. This, of course, would act as a barrier to the motion of gases in and out of the layer adjacent to the metal surfaces. Under oxidizing conditions, it would be expected that FeCl_2 (and also FeS) would react with oxygen to form Fe_2O_3 . Under reducing conditions, on the other hand, it would be expected that this oxide would be reduced to Fe_3O_4 . It is suggested that once a thin scale has formed on the metal tubes, such a cycling takes place. The mixed-oxide and molten-salt layers limit the availability of oxygen and retain chlorine and sulfur within the adherent scale.

It has been shown by Fassler [7] that the reaction involved could be



The chlorine retained within the scale deposit then reacts further with the iron according to Reaction [4].

Three observations suggest that chlorine is involved. First, as was just mentioned, ferrous chloride is found next to the corroded tube wall even at the low-temperature end of the corrosion probe. Second, the reaction of chlorine with carbon steel is extremely rapid at temperatures of 400 deg F and higher. The work of Brown, et al., [6] shows the high corrosion rate of carbon steel in dry chlorine at low temperatures. Third, the Deacon Process (Reaction 3) is favored at temperatures near 500 to 700 deg F in the presence of catalysts. Thus, it is suggested that chlorine reactions with steel are important at the low temperatures, and that HCl and Cl_2 reactions take place at the high temperatures.

The release of Cl_2 and HCl directly adjacent to the tube wall is an important part of the mechanism just proposed. It is, of course, necessary to explain how the chlorides reach the tube surfaces. It is suggested that the relatively short residence time in an incinerator would favor the deposition of any chloride originally present in the refuse. It has been well demonstrated that solid-phase chlorides can be volatilized during burning processes [7, 8].

The observation that measurable amounts of chlorides are found in incinerator deposits agrees quite well with the work reported by Bishop [9] on the combustion of coal containing 0.9 percent chlorine. He showed that initial deposits could contain up to almost 40 percent sodium chloride at temperatures near 900 deg F.

Other chlorides in the deposits come via HCl which is released when chlorinated plastics such as polyvinyl chloride are burned. This HCl then combines with the K_2O and Na_2O , which are also refuse combustion products, to form KCl and NaCl .

It is proposed further that some of the chloride found on the corrosion probes has been transferred as PbCl_2 or ZnCl_2 . Several lead and zinc compounds are added to polyvinyl chloride as thermal stabilizers. They act in this capacity because of their ability to react with the HCl liberated from the polymer as it is thermally decomposed. This can account at least in part for the presence of lead and zinc salts on the corrosion probes. Additional lead and zinc compounds of course could come from the volatilization of metal scrap in the refuse. They are probably first released as oxides in the flame and then are converted to sulfates and chlorides on the tubes.

Part of the deleterious function of the lead and zinc salts, particularly chlorides, could be the formation of molten-salt layers, since their melting points are low and since when mixed with other chlorides (NaCl , KCl) they form eutectic compositions which melt at even lower temperatures. These low-melting materials permeate and destroy the initial oxide scale so that the substrate metal becomes exposed to chlorine as it is released from the chlorides in subsequent reaction with furnace gases.

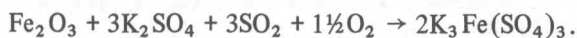
ROLE OF SULFUR COMPOUNDS

It is believed that sulfur-bearing compounds play an important role with regard to corrosion at both low and high temperatures. For example, the most corrosive salts studied in the laboratory at 600 deg F were the pyrosulfates and the bisulfates. It is suggested that this high corrosivity is related to the fact that these materials have relatively low melting points, i.e., about 575 deg F for $\text{K}_2\text{S}_2\text{O}_7$ and 415 deg F for KHSO_4 . Since the corrosion reactions, which are electrochemical in nature, can take place more readily in liquids than in solids or gases, the presence of a liquid phase is of great importance. It is possible that the melting points of these salts are lowered in the deposits by the zinc and lead salts also shown to be present on the corroded samples.

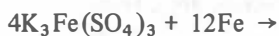
The presence of bisulfates, pyrosulfates, or alkali trisulfates in the incinerator deposits has not been proved by X-ray diffraction. This, of course, does not mean that they are not present, since previous studies at Battelle and elsewhere have shown that these materials are difficult to detect in small amounts. The bisulfate and pyrosulfate salts can react directly with the tube metal to form iron sulfide, which was identified in the corrosion probe scale by X-ray diffraction. In addition, qualitative tests showed the presence of sulfide on almost all of the probe specimens, and sulfur was found adjacent to the metal surface on specimens examined with the electron microprobe. The following reaction would account for sulfide formation.



At higher temperatures, where the bisulfates and pyrosulfates are not stable, the corrosion by sulfur proceeds through formation of the well-known alkali iron trisulfates



The source of the Fe_2O_3 can be either the bulk deposit or the protective oxide scale on the tube metal. The latter situation would be a more serious condition, because the tube metal would then be exposed to oxidation or to attack by the trisulfate if it becomes molten.



CONCLUSIONS

These field and laboratory studies have demonstrated that the wastage in water-wall refuse boilers can be more severe than that normally encountered in fossil-fuel-fired boilers. The complex nature of the refuse used as the fuel and the relatively poorer control of burning in an incinerator combine to increase the possibility for corrosion. The contributors to the attack are corrosive gases and low-melting chloride and sulfur-containing salts which exert a fluxing action on the protective films on the metal surface. These low-melting salts probably contain compounds such as zinc and lead chlorides along with potassium

bisulfate and potassium pyrosulfate. The data developed reveal that the gases SO_2 , HCl , and Cl_2 are also playing a major role in the wastage processes.

Analyses of tube deposits and furnace gases confirm the belief that sufficient quantities of the deleterious salts and gases are present in all municipal incinerators to warrant careful consideration from a corrosion standpoint.

The work carried out with the corrosion probes inserted in the incinerators has demonstrated that the wastage rates of boiler-tube metals are directly related to the operating metal temperatures. Some attack will be experienced in the 300 to 600 deg F range and greatly increased rates can be anticipated as temperatures are raised to 1000 deg F. The temperature gradient between the metal surface and the furnace atmosphere is also important. Thus relatively low metal temperatures are to be preferred in flame areas.

While the stainless steels, particularly Types 310 and 446, furnish good resistance to fireside corrosion, their use is limited because of the deleterious effects which can take place during downtime under humid conditions. The Type 310 can fail because of stress-corrosion cracking and the Type 446 can be severely pitted. The other austenitic stainless steels evaluated—Types 304, 316, and 321—also were more resistant than the carbon steels but are subject to stress-corrosion cracking. The type 416 stainless steel did not perform well enough to be seriously considered. The Inconel 600 and 601 materials were quite resistant over the lower temperature region 300 to 500 deg F but were severely attacked at higher temperatures and thus are not good choices.

Incoloy 825 gave encouraging results over the entire temperature range and is much more resistant to stress-corrosion cracking than the austenitic stainless steels so it could be considered for use in high-temperature areas where the carbon steels would not be recommended.

While the aluminum, chromium, and inorganic coatings furnished some initial protection to the tube surfaces they do not appear to be sufficiently durable to be considered for long-time boiler operation.

It is concluded that water-wall incinerators should be operated at relatively low metal temperatures, near 500 deg F, to minimize tube wastage. If high-temperature superheated steam is desired for more efficient power production, it appears that there is merit in using the refuse to heat the water in a separate furnace and do the additional heating in another furnace with fossil fuel as the heat source. Thus, corrosive deposits and gases will be kept away from tubes operating at high metal temperatures.

Another important consideration is that downtime could be a critical corrosion period for a refuse-fired boiler in that hygroscopic salts on the tubes could become wet and cause acid attack. Furthermore, metal temperatures in the effluent gas stream should be kept high enough to avoid either H_2SO_4 condensation or HCl/H_2O dew point condensation.

It should be pointed out that many years of research were required to develop the best techniques for burning fossil fuels with a minimum of fouling and corrosion. Fuel preparation and combustion control are an important part of that technology. If refuse is to be considered as a fuel, it should be treated as such.

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REFERENCES

- [1] Miller, P. D., and Krause, H. H., "Fireside Metal Wastage in Municipal Incinerators," ASME Winter Annual Meeting, Dec. 1970, Paper No. 70-WA/Inc-2.
- [2] Miller, P. D., and Krause, H. H., "Factors Influencing the Corrosion of Boiler Steels in Municipal Incinerators," *Corrosion*, Vol. 27, 1971, pp. 31-45.
- [3] Miller, P. D., and Krause, H. H., "Corrosion of Carbon and Stainless Steels in Flue Gases from Municipal Incinerators," *Proceedings of the 1972 National Incinerator Conference*, ASME, New York, N.Y., pp. 300-309.
- [4] Miller, P. D., Krause, H. H., Zupan, J., and Boyd, W. K., "Corrosive Effects of Various Salt Mixtures Under Combustion Gas Atmospheres," *Corrosion*, Vol. 28, 1972, pp. 222-225.
- [5] Cutler, A. J. B., Halstead, W. D., Laxton, J. W., and Stevens, C. G., "The Role of Chloride in the Corrosion Caused by Flue Gases and Their Deposits," ASME Winter Annual Meeting, Dec. 1970, Paper No. 70-WA/CD-1.
- [6] Brown, M. H., DeLong, W. B., and Auld, J. R., "Corrosion by Chlorine and by Hydrogen Chloride at High Temperatures," *J. Ind. Eng. Chem.*, Vol. 39, 1947, pp. 839-844.
- [7] Halstead, W. D., and Raask, E., "The Behavior of Sulfur and Chlorine Compounds in Pulverized Coal Fired Boilers," *J. Inst. Fuel*, Vol. 42, 1969, pp. 344-349.
- [8] Bishop, R. J., and Cliff, K. R., "Condensation of Sodium Chloride Vapor from a Moving Gas Stream," *J. Inst. Fuel*, Vol. 42, 1969, pp. 283-285.
- [9] Bishop, R. J., and Samms, J. A. C., "The Corrosion of Austenitic Superheater Steels by Alkali Sulfate/Chloride Mixtures in Air and in a Flue Gas Atmosphere," *Arbeitsgemeinschaft Korrosion*, Frankfurt, April, 1965.