

High Temperature Corrosion Problems in Waste Incineration Systems

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Corrosion of high temperature metal surfaces in waste incineration systems results primarily from compounds of chlorine, sulfur, and metals such as lead, zinc, and tin. The presence of such compounds in municipal refuse and chemical wastes can result in severe metal wastage in energy recovery systems. The corrosion mechanism involves interaction of sulfur oxides with chlorides in deposits to generate HCl and chlorine at the metal surface. Metal chlorides also can contribute by forming low melting eutectics. Reducing atmospheres, particularly carbon monoxide, in the combustion gases also appear to be a factor in corrosion. Corrosion rates of carbon and low alloy steels increase significantly with both metal temperature and gas temperature. The rates for stainless steels initially decrease as the metal temperature increases, and are less sensitive to gas temperature. Corrosion by chlorine can be inhibited by maintaining a sufficiently high concentration of sulfur or silica in the fuel. The results of corrosion probe exposures in waste-fueled boilers are presented to illustrate these mechanisms.

INTRODUCTION

There has been increasing incentive in recent years for disposal of wastes by incineration. The need to recover energy from waste material, coupled with the difficulty in obtaining adequate landfill sites, has created a great deal of interest in this approach. In addition, municipal refuse is being considered as a supplementary fuel for existing fossil-fuel power-generating stations and for industrial needs for process steam. However, the corrosion of heat recovery surfaces exposed to combustion products from the burning of industrial and municipal wastes has been a major problem in utilizing these materials as a source of heat energy. Corrosion probe exposures conducted by Battelle's Columbus Laboratories in recent years demonstrated that chlorine in the refuse is the most important contributor to corrosion of boiler tubes.¹⁻⁸ The sulfur in the refuse definitely plays a

part in promoting corrosion by chlorine, and other components which are not present in fossil fuels such as zinc and lead may contribute to the unusual amount of corrosion which can occur during incineration. Experiments were conducted to investigate the inhibition of chloride corrosion by the introduction of relatively large amounts of sulfur into the fuel. One of the most convenient ways of achieving this result has been to utilize high-sulfur coal in co-firing with shredded refuse in a stoker-fired boiler. Inhibition by silica was investigated in an incinerator where sewage sludge was burned with refuse.

CORROSION IN FIRING OF BULK REFUSE

Corrosion rates from burning of bulk municipal refuse were obtained by exposing specially designed probes to the combustion gas environment at the Miami County, Ohio incinerator. The design of the corrosion probe is shown in Figure 1. The specimens were machined from 1-inch (2.54 cm) schedule 40 pipe or equivalent tubing and were nested together with lap joints, as shown in detail A. The probe was inserted into the incinerator through a side wall and was mounted at a 90 deg angle to the flue gas stream.

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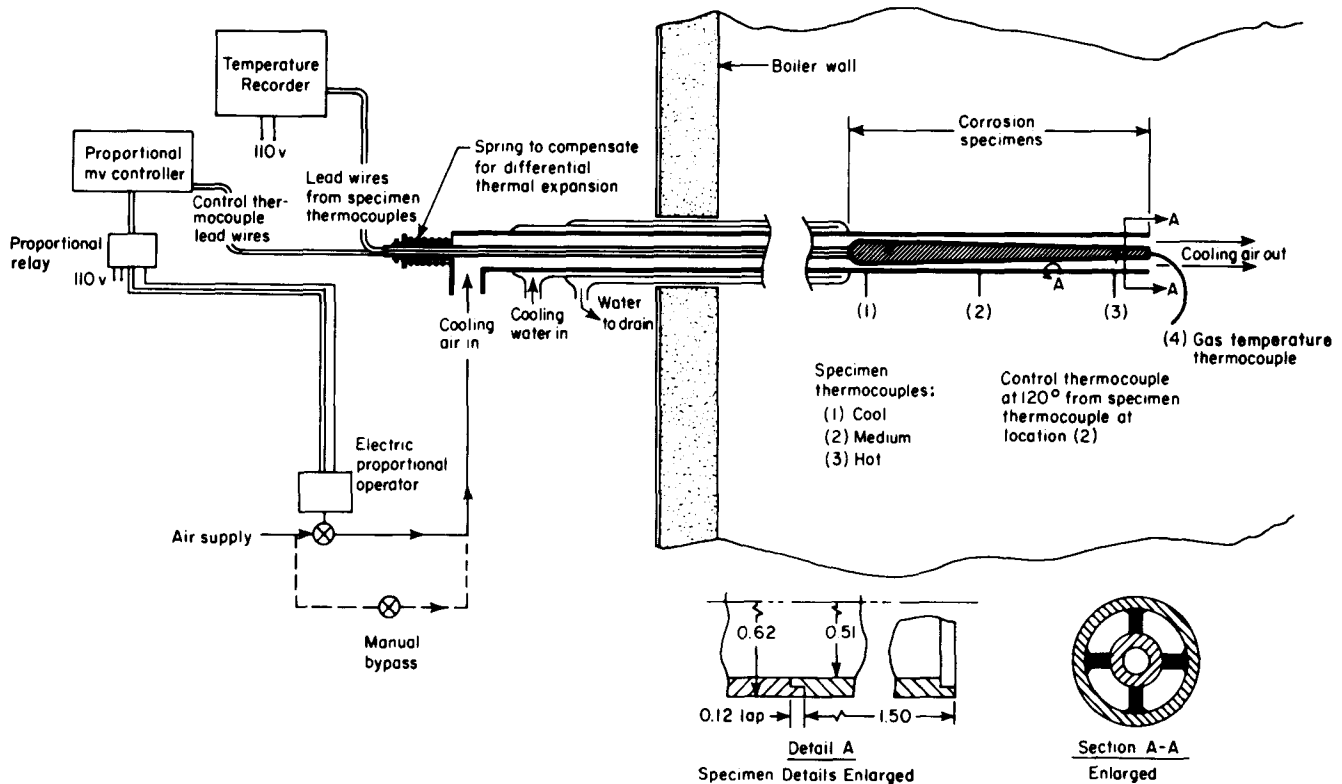


Fig. 1 — Schematic diagram of corrosion probe apparatus.

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. 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 valve.

Corrosion probe exposures up to 828 hours were carried out, and the corrosion rates of the various steels used as specimens were determined by the weight losses that resulted from the exposure. The data for the 828 hour exposure calculated to a basis of mils per month are presented in Figure 2. As seen from the figure, the weight losses increased with temperature and were especially high for the

carbon steel and the low alloy steel. Over a metal temperature range of 250 to 1200 °F (121 to 649 °C) the high-chromium ferritic and austenitic stainless steel showed the best corrosion resistance. As a function of exposure time, the corrosion rate of carbon steel was found to be very high initially and then to drop rapidly, leveling off after about 800 hours, as shown by the upper three curves in Figure 3. The effect of metal temperature is also shown by these data, which illustrate the increase in the corrosion rates as the temperature of the metal specimens was increased from 350 to 950 °F (177 to 510 °C).

Deposit and Scale Analysis. Both the bulk deposits and the corrosion product layers formed on the specimens were analyzed to determine the reaction leading to metal wastage. The deposits were removed from all the probe specimens in numbered sequence. Thus the variations in composition

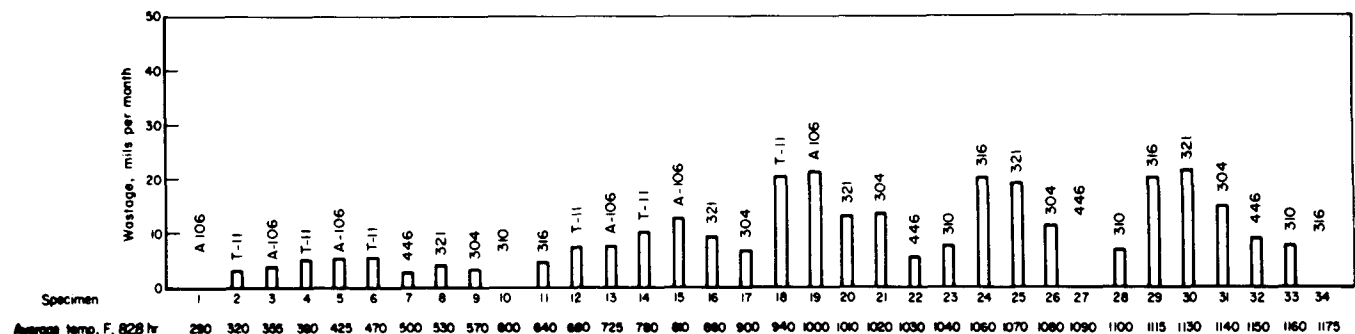


Fig. 2 — Corrosion rates of alloys exposed in bulk refuse incinerator.

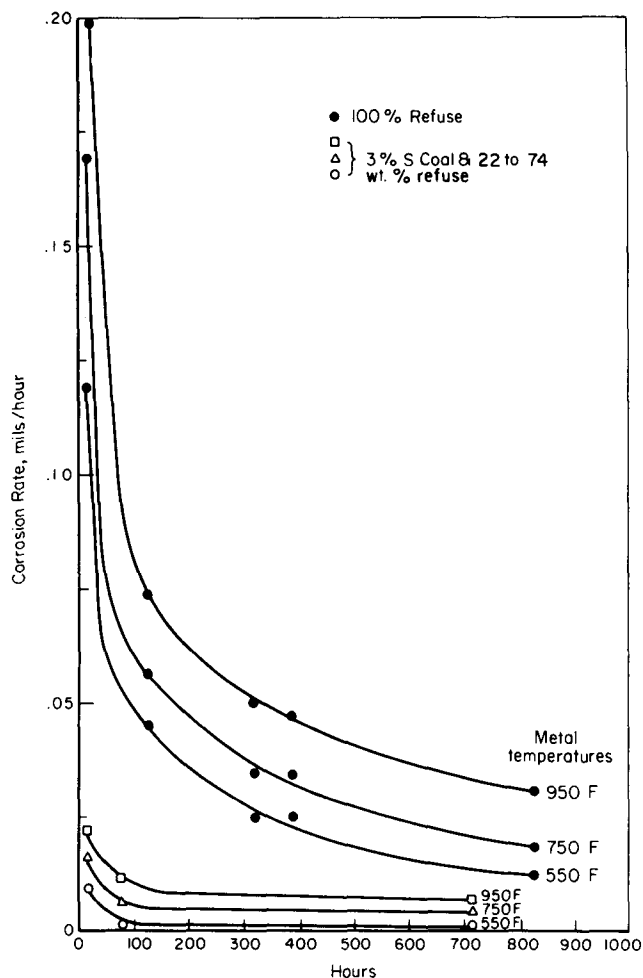


Fig. 3—Comparison of corrosion rates for refuse incineration and co-firing of refuse and high sulfur coal.

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. Electron microprobe analysis and X-ray diffraction were used to obtain additional detailed information on the nature of the deposits. Analyses of the bulk deposits showed that chlorides accumulated rapidly even at moderate HCl concentrations in the flue gases. Chloride concentrations ranging from 21 to 27 percent by weight were found on probes which were exposed for short periods of time ranging from 1.5 to 24 hours. Flue gases contained from 40 to 140 ppm HCl (corrected to 12 percent CO_2) during the time that these deposits were formed.

Eight analyses of typical refuse samples from the incinerator showed that the chloride content of the solid waste on a dry basis ranged from 0.32 to 0.79 weight percent, with an average of 0.49 percent. Based on an average 24 hour processing of 150 tons (136,080 kg) of waste at this incinerator, there would be about 1500 pounds (682 kg) of chlorine in the refuse. The sources of the chlorine are both inorganic, primarily as NaCl, and organic, of which poly-

vinyl chloride plastic is the predominant item. Practically all of this chlorine is volatilized at combustion temperatures, as the ash contained only 0.01 to 0.02 weight percent chlorine. Refuse sortings made at four different times at the incinerator gave values for plastic content of 3 to 6 percent. Of this, about one-fifth was estimated to be polyvinyl chloride. Using the lowest value of 3 percent total plastic, the polyvinyl chloride would account for 900 pounds (409 kg) of the 1500 pounds (682 kg) of chlorine in the refuse consumed daily. The remainder would be of inorganic origin. From these values it is obvious that large amounts of chlorine are available to cause corrosion.

As the exposure time increased and the deposit aged, the amount of chloride decreased. This change resulted from the action of SO_2 , which converted the chlorides to sulfates. A temperature effect also was observed, because the amount of chloride generally was greatest in the deposits found on lower temperature specimens. Average chloride values in bulk deposits of long-term runs ranged from a few tenths of a percent at temperatures from 750 to 1250 °F (399 to 677 °C) up to 3.8 percent in the 250 to 500 °F (121 to 260 °C) temperature zone. However, the chloride was not equally distributed throughout the deposit, and the bulk of it diffused into the layer at the metal-deposit interface. The deposits from the 828 hour probe exposure, which showed a uniform low average chloride content of 0.2 weight percent, were sectioned horizontally to separate the bulk of the deposit from the corrosion product scale at the interface with the metal. Analyses of the two sections of the deposit demonstrated that the chlorine was concentrated in the inner layer. The outer layer contained only 0.2 weight percent chlorine, while the inner layer showed values up to 4.2 weight percent. The other elements which were found to be concentrated in the inner layer were sulfur, potassium, lead, zinc, and iron.

The sulfur resembled chlorine in that its concentration built up rapidly in the deposits and leveled off after about 100 hours, with higher concentration on the cooler specimens. The inner layers of the deposit contained approximately twice as much sulfur as did the outer layers. Electron microprobe analyses of the corrosion scale layer showed that significant amounts of chlorine, sulfur, zinc, and lead were present at the interface of the tube metal and the scale (Figure 4).

Investigation by X-ray diffraction demonstrated that a continuous layer of FeCl_2 formed at the interface with the metal. FeS occurred between the FeCl_2 and the overlying Fe_2O_3 layer. Various other compounds, mostly sulfates, were identified in the deposits. About 20 different compounds have been identified as shown in Figure 5. On the higher temperature specimens, it was found that the FeCl_2 layer melted and collected into small pools. The electron microprobe showed that a zinc compound was also present

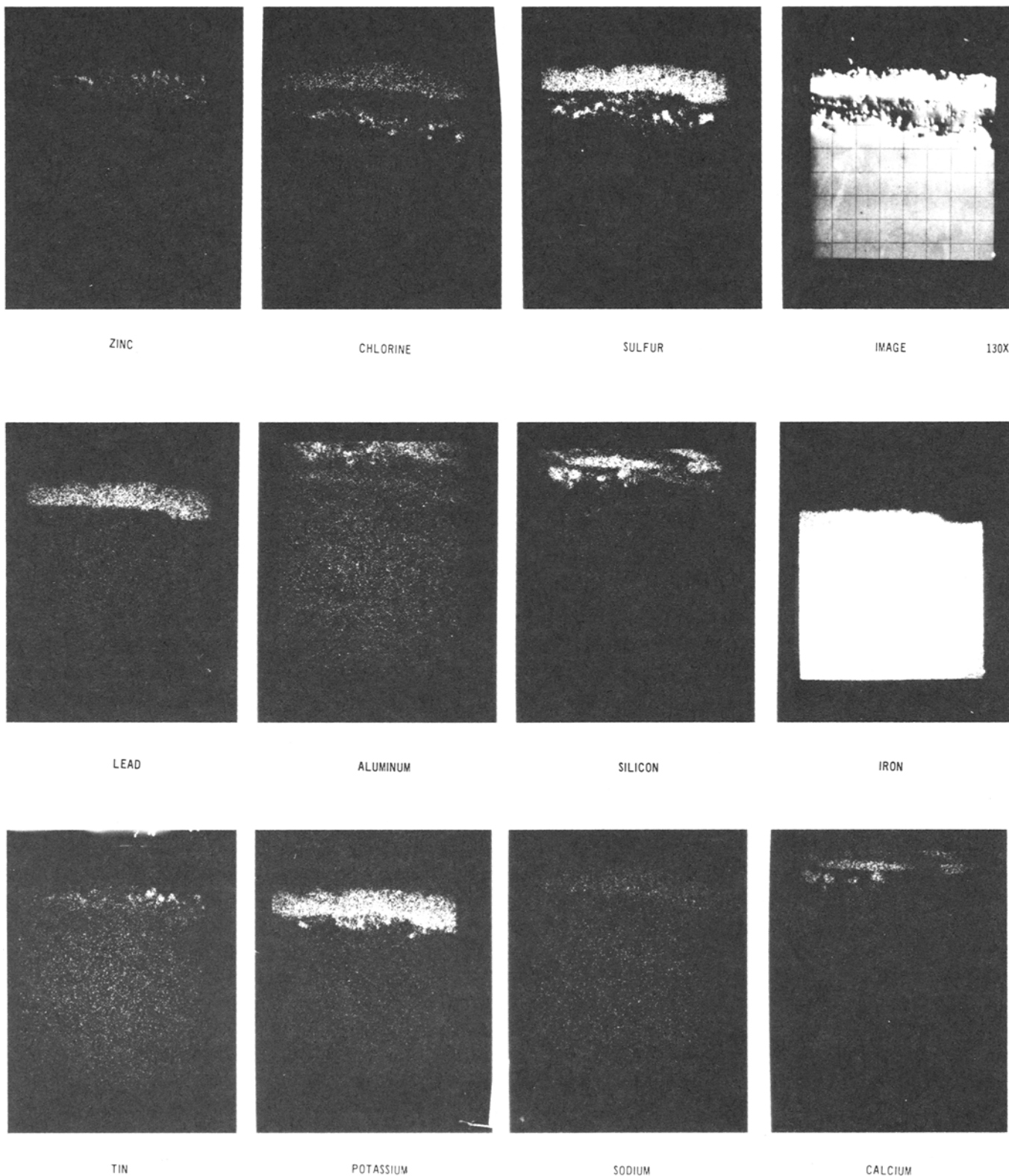


Fig. 4— Electron microprobe pulse mode photographs of corrosion product layer from refuse incineration.

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 FeCl_2 or in the FeS as a replacement for some of the iron atoms in the host structures. These interface layers are of the order of 6 to 10 micrometers thick on the

low temperature specimens. The thickness increased somewhat with temperature.

Between the interface scale and the bulk deposit was a multilayered scale of Fe_2O_3 and Fe_3O_4 . It is interesting to note that a thin layer of $\alpha\text{-Fe}_2\text{O}_3$ formed at the interface

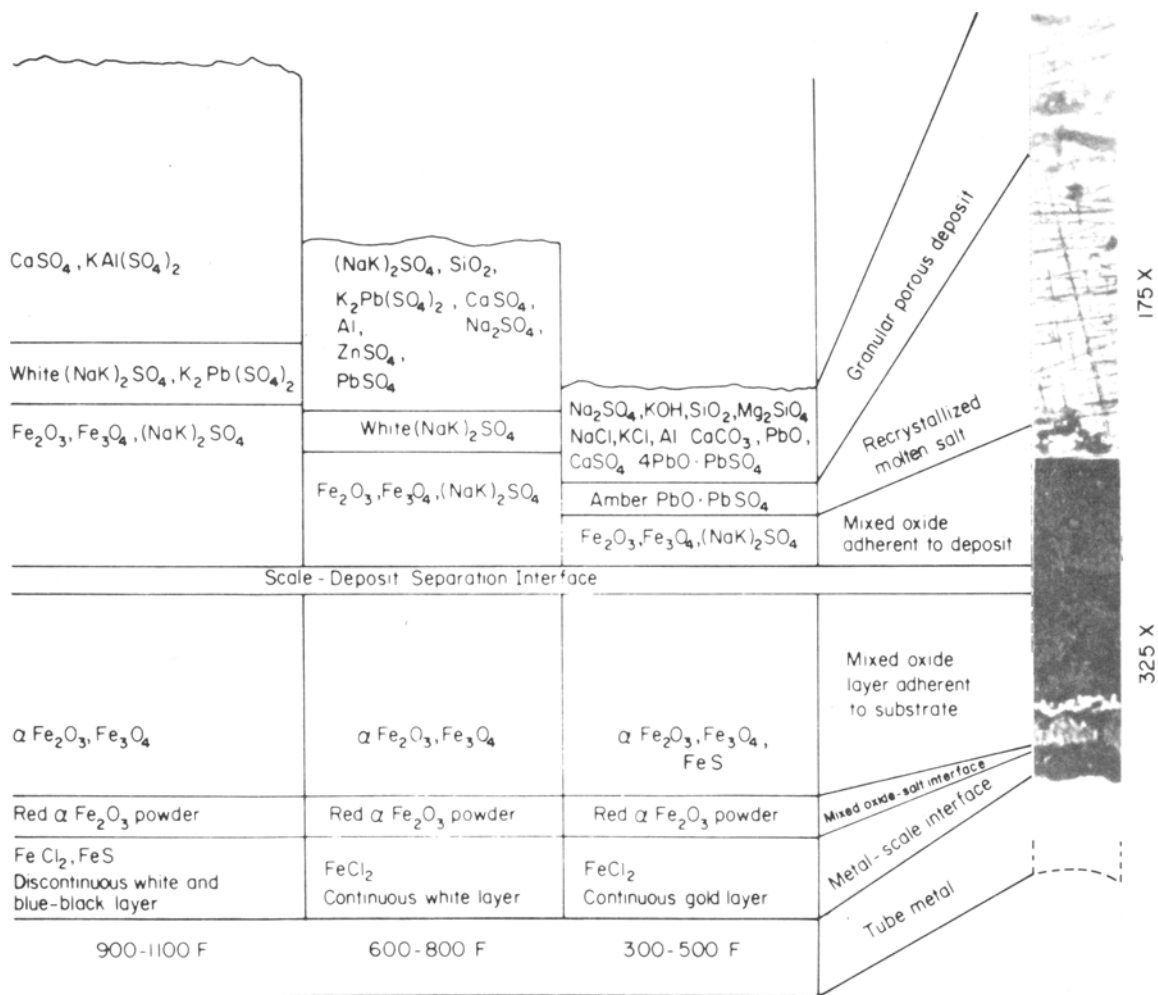


Fig. 5—Compounds identified by X-ray diffraction of deposit and scale layers on corrosion probe specimens exposed to bulk refuse incineration.

between the FeCl_2 and mixed oxides. At low temperatures FeS formed between the FeCl_2 and Fe_2O_3 layers. Part of the mixed oxide scale adhered to the substrate and part to the external deposit. The mixed oxide layer was a hard, brittle, magnetic, gray-black material which thickened with temperature and was made up of several layers with loose red Fe_2O_3 between layers. This suggests that reduction or reaction with other elements occurred in or below this layer. At the higher temperature where FeCl_2 melted and FeS formed on the substrate, the mixed oxide scale was less adherent, and in this area more of the mixed oxide was removed with the outer deposit.

Examination with the optical microscope indicated that some melting had occurred in the deposit near the mixed oxide scale. These studies showed the presence of recrystallized continuous phases of the compounds $(\text{Na}, \text{K})_2\text{SO}_4$ and $\text{PbO} \cdot \text{PbSO}_4$ on the external surface of the mixed iron oxide scale. The sodium-potassium sulfate phase was also dispersed throughout the iron oxide scale and adhered to the bulk deposit. It appears that separation in the iron oxide scale occurred at the depth to which this salt phase perme-

ated in sufficient quantity to destroy the iron oxide. It is proposed that in the initial stage of incinerator operation, various salt phases permeate the iron oxide scale and destroy its protective characteristics. These phases are the mixed alkali sulfates, alkali chlorides, and possibly ZnCl_2 and PbCl_2 , whose mixtures rich in PbCl_2 (90 wt pct) melt as low as 572°F (300°C). In addition, PbCl_2 and FeCl_3 form low-melting mixtures, with a eutectic at 50 weight percent each, having a melting point of 347°F (175°C).

The flue gas compositions in the vicinity of the corrosion probes were measured in order to determine the gaseous environment to which these specimens were subjected. The range of values found for the various components is presented in Table I. HCl was by far the main component found in the flue gases, with the SO_2 concentration significantly lower. The other gaseous components found in the furnace were not considered to be making any significant contributions to corrosion.

Corrosion Mechanisms. A number of chemical reactions are proposed to account for the formation of chlorides and sulfates in the deposits, as shown in Figure 6. Initial depos-

Table I. Concentration Ranges of Chemical Species in Incinerator Flue Gases (in Dry Gases, Corrected to 12 Percent CO₂)

Component	Range of Concentration, ppm
Sulfur dioxide, SO ₂	59 to 195
Hydrogen chloride, HCl	214 to 1250
Hydrogen fluoride, HF	3 to 34
Nitrogen oxides, as NO ₂	53 to 115
Phosphate, PO ₄ ⁻	0.5 to 6
Organic acids	35 to 178
Aldehydes and ketones	1 to 12

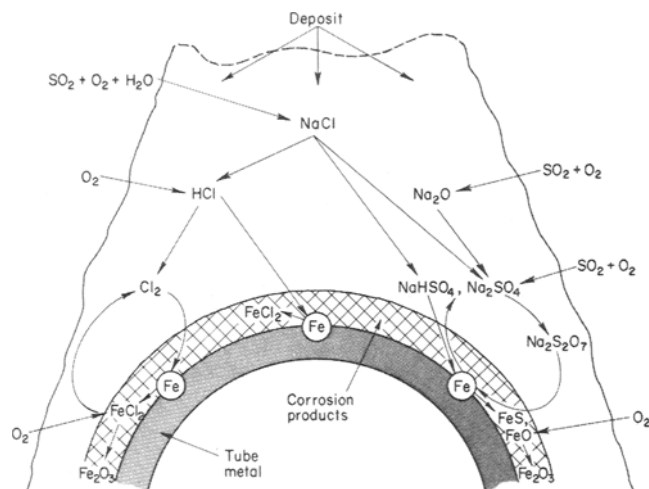
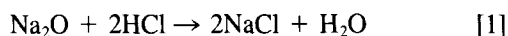
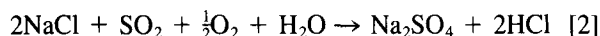


Fig. 6—Sequence of chemical reactions explaining corrosion on incinerator boiler tube.

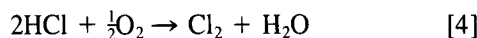
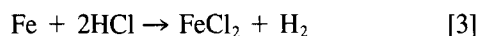
its are alkali metal oxides, which are then converted to chlorides by the action of HCl:



Some chloride such as NaCl may be volatilized in the flame and deposited directly as such. Corrosion is initiated by conversion of chlorides in deposits to sulfates by the action of SO₂, oxygen, and moisture, thereby releasing HCl at the metal surface:



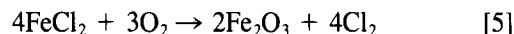
The HCl formed can then react with the iron surface to form FeCl₂, or it may be oxidized to elemental chlorine:



As indicated by laboratory studies at Battelle and supported by the work of Brown, DeLong, and Auld,⁹ the corrosive effects from HCl would not be expected to be severe below temperatures of about 600 °F (316 °C). Since FeCl₂ has been detected on corrosion probe samples exposed to temperatures well below 600 °F (316 °C), it is likely that

corrosion by elemental chlorine is operating in the lower temperature range. Although elemental chlorine has not been identified in incinerator and furnace gases, recent laboratory work by Mal'tseva *et al.* showed that several percent of chlorine can be formed by burning organic compounds which contain chlorine.¹⁰ Metal chlorides on the tube surface also can catalyze reaction [4], as is done in the Deacon process. Chlorine would attack the iron to form FeCl₂.

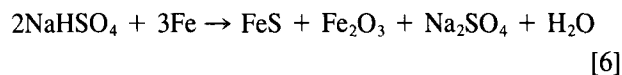
The molten salt phase which was found as an interface layer between the scale and deposit would act as a barrier to the motion of gases in and out of the layer adjacent to the metal surfaces. Under oxidizing conditions, it would be expected that FeCl₂ would react with oxygen to form Fe₂O₃ and release chlorine:



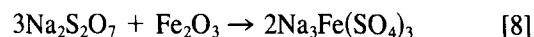
The chlorine would, in turn, react with the tube metal to form more FeCl₂, and a cyclic reaction would operate beneath the oxide scale.

Similar corrosive conditions from deposited chloride were demonstrated by Cutler *et al.*,¹¹ particularly as they applied to burning fossil fuels containing chlorine. The possibility of oxidizing FeCl₂ to release elemental chlorine also was shown by Fassler *et al.*¹²

The formation of FeS in the corrosion product layer indicates that sulfur is also playing a part in the corrosion reactions. The alkali pyrosulfates and bisulfates are known to be very corrosive materials, and the potassium compounds in particular have low melting points. Hence corrosion by these materials as shown below is a very likely possibility for the formation of FeS:



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 they are not present, since previous studies at Battelle-Columbus and elsewhere have shown that these materials are difficult to detect in small amounts. These sulfate salts can react directly with the tube metal to form iron sulfide, which was identified in the corrosion probe scale by X-ray diffraction. At higher temperatures, where the bisulfates and pyrosulfates are not stable, the corrosion by sulfur can proceed through formation of the alkali iron trisulfates which can be formed from pyrosulfates:



Trisulfates also attack the tube metal to form FeS. The system of reactions which can occur in a tube deposit to establish cyclic reactions and continue corrosion beneath deposits is shown in Figure 6.

On the principle that the chloride concentration of deposits could be reduced by causing the conversion to sulfates (reaction [2]) to occur prior to deposition, elemental sulfur was added to refuse to increase SO₂ in the flue gas. These runs also were conducted at the Miami County, Ohio incinerator, and were limited to 8 hours by the logistics of adding sulfur.

When sulfur was added to the refuse, the chloride content of the deposits decreased significantly as shown in Table II. The effect was particularly pronounced in the 700 to 750 °F (371 to 399 °C) temperature zone where chlorine reached a concentration of 7.5 weight percent in the deposits after 8 hours of operation with normal refuse. When 0.75 weight percent sulfur was added to the refuse, the chloride concentration dropped to 1.9 percent, and when 1.5 weight percent sulfur was added, the chlorine concentration was further reduced to 0.1 weight percent. The effect was even more pronounced in the high temperature zone where the chloride concentration was reduced 25-fold by the addition of 0.75 weight percent sulfur, and below the detection limits for chloride when 1.5 weight percent sulfur was added. This decrease in the chloride concentration in the deposits indicated that the added sulfur in the refuse formed sulfur oxides rapidly, which then reacted with the metal chlorides while still in the flue-gas stream. This rapid formation of sulfates left very little particulate chloride to collect in the deposit. The effect of the sulfur additions on the corrosion rate of Al06 steel is presented in Figure 7. At 300 °F (149 °C) metal temperature the corrosion rate decreased linearly with the amount of sulfur added. At higher temperatures the rapid decrease in corrosion rate began at the point of 0.75 weight percent sulfur addition. On the basis that the normal sulfur content of refuse is about 0.2 percent, these data indicate that when the total sulfur level in the refuse reaches 1 percent the corrosion rates can be expected to decrease.

An even more dramatic effect of sulfur addition to the refuse was found with Type 316 stainless steel, as indicated in Figure 8. At 800 °F (427 °C) the corrosion rate decreased by about an order of magnitude when 0.75 percent sulfur was added to the refuse, but no further decrease was noted with additional sulfur. The corrosion rates at 1000 and 1200 °F (538 and 649 °C) decreased about 25- and 30-fold,

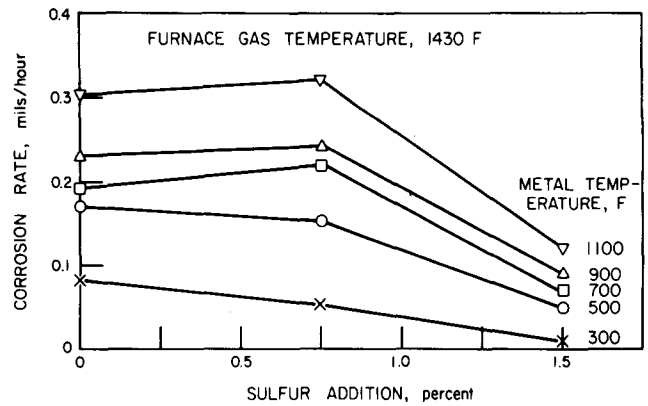


Fig. 7—Effect of sulfur additions to refuse on the corrosion rate of Al06 carbon steel.

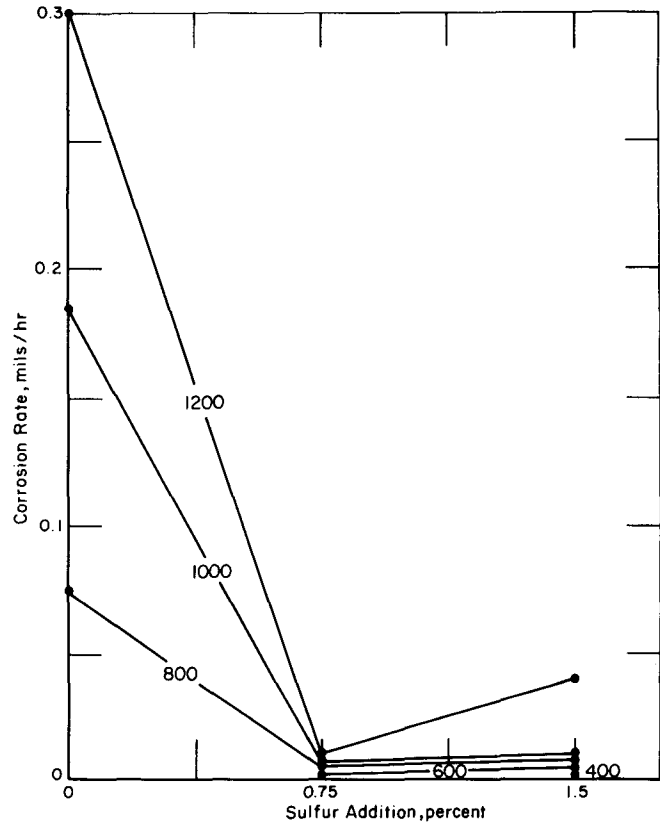


Fig. 8—Effect of adding sulfur to refuse on corrosion rates of Type 316 stainless steel.

respectively, with the 0.75 percent sulfur addition. There was a slight increase in the corrosion rate at 1200 °F

Table II. Sulfur and Chlorine Content of Deposits with Sulfur Additions to Refuse

	Concentration (Wt Pct) with Indicated Sulfur Addition (Wt Pct)					
	None		0.75 Pct S		1.5 Pct S	
Metal Temp., F	745	1120	730	1125	740	1175
(C)	(395)	(695)	(390)	(605)	(343)	(635)
Sulfur	4.6	2.8	3.5	6.0	5.0	3.8
Chlorine	7.5	2.5	1.9	0.1	0.1	<0.1

(649 °C) when the sulfur addition was increased to 1.5 percent. There also were significant decreases in corrosion rates of ferritic stainless steels when sulfur was added to the refuse.

The addition of sulfur to the refuse produced a sharp decrease in the corrosion rates of all types of steel investigated. In the case of low alloy steel, sulfur addition must be sufficient to reduce the chloride content of the initial deposit to the 0.1 percent level in order to achieve low corrosion rate. It is believed that the sulfur/chlorine ratio in the refuse must be about 4 in order to achieve this low chloride level in the deposits and thus eliminate corrosion from this source.

Nevertheless, it is important to note that with these sulfur additions, sulfides did form near the metal oxide interface beneath the deposit on all of the corrosion probe specimens. This is undoubtedly the result of the reducing environment beneath the oxide layer, as it has been shown that FeS will form at a very low sulfur pressure (10^{-13} atmosphere) if the SO_2 or oxygen pressures are below 10^{-14} atmosphere.¹³ At higher SO_2 or oxygen pressures the iron oxides form.

CO-FIRING OF REFUSE AND HIGH SULFUR COAL

It was a logical step to proceed from the addition of sulfur to refuse to employing high sulfur coal as the source of the SO_2 needed to suppress chloride corrosion. Consequently, additional work on the research program was directed to investigating the disposal of municipal refuse by co-firing with high-sulfur coal in a stoker-fired boiler, to demonstrate: (1) that corrosion of boiler tube materials in such a system would be minimal; and (2) that the sulfur oxide emissions from the coal would be reduced to acceptable levels by dilution of the coal with refuse and by the interaction of the alkaline components of the solid wastes with the sulfur oxides. The coal-fired boiler at the Municipal Electric Plant, Columbus, Ohio, was used for this program. This site was selected to represent boiler furnaces having grates on which final burnout of the refuse could occur. The boiler used had a spreader stoker and was rated at 150 thousand pounds (68,040 kg) of steam per hour, but it normally operated up to 125 thousand pounds (56,700 kg) per hour with a maximum electrical output of 12.5 MW. This program was directed ultimately toward determining the limitations and benefits of burning the solid wastes with high-sulfur coal and limiting the processing of the solid wastes to shredding and magnetic separation. The corrosivity of the combustion products obtained from the burning of coal and the refuse-coal mixes was evaluated by inserting the corrosion probes in the superheater section of the boiler. At this location the gas temperature varied from 1100 °F (593 °C) under low load conditions to 1400 °F (760 °C) for the higher loads.

The internal air cooling of the probe specimens maintained metal temperatures of 500 to 950 °F (260 to 510 °C). The initial corrosion rates of carbon steel and stainless steels were measured by 8-hour probe exposures during the combustion of coal containing up to 5 percent sulfur and in refuse-coal mixtures containing up to 70 weight percent refuse. With this maximum amount of refuse the heat input from the refuse constituted 60 percent of the energy supplied.

Initial corrosion rates of A106 carbon steel as a function of the metal temperature during the combustion of various coals, coals plus refuse, and 100 percent refuse are shown in Figure 9. The results presented in the upper part of the figure for burning of bulk refuse were obtained at the Miami County incinerator, Troy, Ohio. The corrosion rates with refuse alone proved to be an order of magnitude greater than those found with coal or coal plus up to 42 percent refuse. In the lower portion of the figure the two data points at about 750 °F (399 °C) which showed the highest corrosion rates, represent the coal with 5 percent sulfur and are the result of sulfide corrosion. It should be emphasized that these data represent corrosion rates obtained in 8-hour probe exposures and are useful for comparing materials and refuse-coal mixes but should not be extrapolated to represent long-term corrosion rates. These rates drop off rapidly with time as shown in the three lower curves of Figure 3. As corrosion

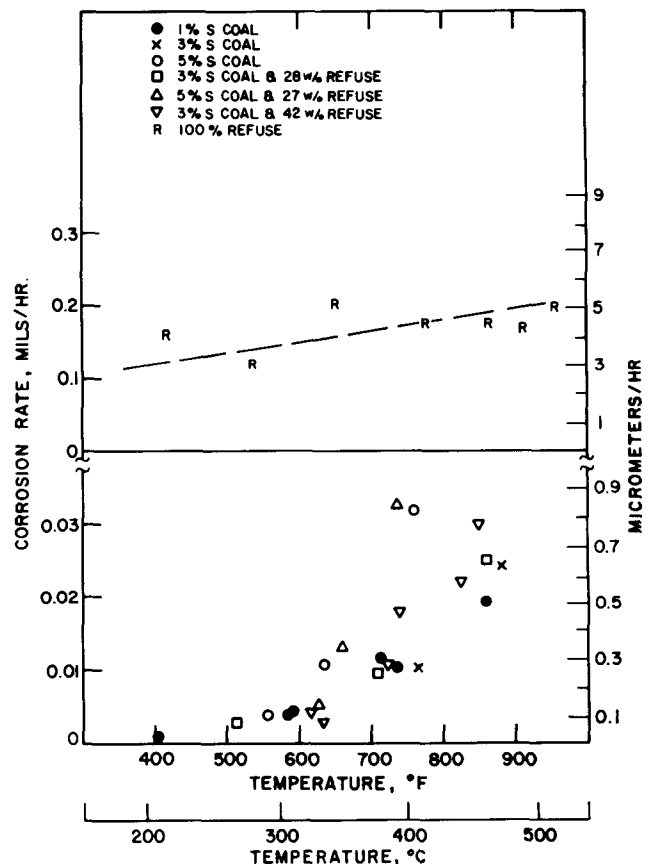


Fig. 9—Corrosion rates of A106 steel as a function of metal temperature with various fuels.

product layers are built up on the metal surfaces, the rates level off at a much lower wastage rate. It is significant that when the sulfur content of coal reached 5 percent the higher corrosion rate of carbon steel was from attack by the sulfur and not by the chlorine.

CO-FIRING OF REFUSE AND SEWAGE SLUDGE

This part of the work was carried out at the Harrisburg, Pennsylvania incinerator, where during initial operation, tube failures occurred every 3 to 5 months when only bulk solid waste was burned. However, no tube failures occurred during the period when municipal sewage sludge was burned along with the refuse. In addition, soot blowing was reduced in frequency and some of the carbon steel tubes were replaced with a low-chromium alloy. Consequently, the reason for the reduced metal wastage at the Harrisburg incinerator was uncertain and corrosion studies were needed to evaluate the effect of adding the sewage sludge to the refuse combustion environment. This facility has two identical boilers, each with a nominal capacity of 360 T/day (327 Mg per day) of refuse. At this rate of 15 tons (13.6 Mg) of refuse per hour, the normal steam production is 92,500 lb/hr (42.0 Mg/hr).

About 15 to 20 tons (13.6 to 18.3 Mg) of partially dried sewage sludge were delivered by truck to the incinerator every 24 hours, and the sludge was dumped onto the refuse in the pit. This material contains 20 to 22 percent solids, so the incinerator handled the equivalent of about 5 to 6 tons (4.5 to 5.5 Mg) per day of dry solids. During the course of these corrosion studies, the partially dried sludge was delivered at an average rate of 16.5 tons (15 Mg) per working day. During the 8-hour and 80-hour probe exposures, the weight ratio of sludge to solid waste was about 1:10 on an as-received basis, but during the long-term run the ratio dropped to about 1:20.

Considerable mixing occurred in the pit before the sludge and refuse were fed into the furnace charging chute. It seemed likely that sulfur and silica were present in the sludge in sufficient quantity and were burned effectively to reduce the corrosive effects of chlorine in the refuse.

Six corrosion probe exposures were made on this program, two with refuse alone and four during co-firing of refuse and sludge. Exposure times of 8, 80, and 816 hours were employed.

The addition of sewage sludge to the refuse reduced the initial corrosion rate of the carbon steel by about a factor of 2. However, as the exposure time increased, the corrosion rates for operation with and without sludge converged. Thus, at the 800-hour point, the rate experienced for the small amounts of sludge burned at Harrisburg was only slightly less than that for refuse alone at the Troy incinerator. Nevertheless, if the difference in the corrosion rates at the 1000-hour point were to be maintained indefinitely,

the result would be a 35 to 40 percent increase in boiler tube life for the system with the sludge added.

Effect of Metal Temperature. A plot of wastage rates for A106 carbon steel over the temperature range 300 to 800 °F for the 8 hours exposure to the burning refuse with and without sludge additions is shown in Figure 10. The line drawn on this figure from the studies conducted at the Troy, Ohio incinerator is based on 10 or more A106 specimens exposed at a gas temperature of 1500 °F (816 °C) which is comparable to that of the Harrisburg probe in the superheater inlet. The increase in corrosion rate starting at 800 °F (427 °C) is typical of that found for carbon steel and low alloy steels in our past experience with the burning of bulk refuse at high gas temperatures. The three data points obtained for the carbon steel exposed to comparable conditions in the Harrisburg incinerator fall close to the curve established for the Troy incinerator. The corrosivity of the environment was significantly reduced when the sewage sludge was burned with the refuse. As shown in Figure 10, the 8-hour corrosion rates with sludge present in the fuel are 2 to 2.5 times lower than those with refuse alone.

Both Type 310 and Type 347 stainless steel, as well as INCOLOY* alloy 825, showed very low wastage rates in

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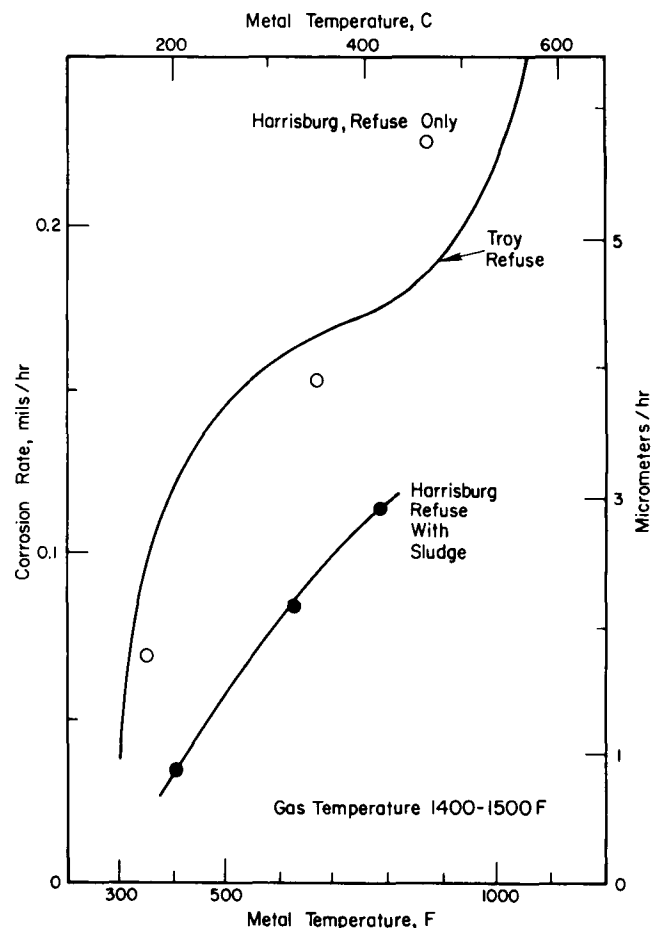


Fig. 10—Corrosion rates of A106 steel for burning of refuse alone and with sewage sludge.

the aggressive incinerator environment, as summarized in Figure 11. In comparable 8-hour exposures, the corrosion rates of these alloys at temperatures between 500 °F (260 °C) and 900 °F (482 °C) were only about one-fifth as great as those for the carbon steel and the low-alloy steel. These high chromium-nickel alloys afforded more protection as the temperature increased, probably due to more rapid diffusion of the chromium and nickel into the oxide layer with the formation of a thicker protective scale. The addition of sludge to the refuse had practically no effect on the corrosion rates of Type 310 and Type 347 stainless steel. The sludge did, however, slightly reduce the attack on INCOLOY alloy 825, particularly at lower temperatures.

Effect of Gas Temperature. At the Harrisburg site, two different locations for probe exposure were selected on the basis of their gas temperatures. The higher temperature location was in front of the first superheater bank and 6 feet below the location of the plant thermocouple for furnace temperature measurement. Gas temperatures in this zone were monitored and maintained near 1500 °F (815 °C).

Two of the 8-hour probe runs were made in a relatively cool location which was about 15 feet downstream of the hotter location. At this point, the tubes were practically black and the gas temperature as monitored by the probe thermocouple was in the range of 1100 to 1200 °F (593 to 650 °C). The corrosion rates of the carbon steel and the P22 alloy exposed at low gas temperature showed only a slight variation with metal temperature as compared to

1500 °F (816 °C) gas, where the corrosion rates increased rapidly with metal temperature. The corrosion data demonstrated that the same reduced temperature dependence existed at low gas temperature when the sludge was burned with the refuse. Under these low temperature conditions, there was no apparent difference in the corrosion rates between the carbon steel and the P22 alloy.

It should be noted that a reduction in gas temperature is more effective in reducing the corrosivity of the environment over the entire metal temperature range than is the addition of sludge to the fuel. Thus, although additives to the refuse may improve the life of boiler tubes, the design of the boiler to reduce the gas temperature in the steam generator section would also provide a significant improvement in boiler tube life.

EFFECT OF REDUCING ATMOSPHERE

The effect of a reducing atmosphere was not investigated in our work. However, excessive furnace wall corrosion noted in European incinerators was found to be associated with high CO levels in the flue gas as well as chloride in deposits.¹⁴ These observations did not include measurement of corrosion rates, although tube failures generally occurred in less than 1 year.

A recent investigation of the combined effect of HCl and CO on corrosion was reported by Brooks and Meadowcroft.¹⁵ In a simulated flue gas containing 400 ppm HCl, 10 percent CO, 10 percent H₂O, 0.5 percent SO₂, and the balance nitrogen, corrosion rates of mild steel were linear with time. At 752 °F (400 °C) the slope of the metal loss vs time curve was 45 mils/year (1.14 mm/yr). Without the HCl in the gas, a parabolic rate curve was obtained which leveled off at a maximum metal loss of only 5 mils (127 micrometers).

The reason for the synergistic action of HCl and CO has not been determined, but it is possible that the CO may cause defect structures in iron oxides which allow greater penetration by HCl.

CONCLUSIONS

The results of corrosion probe exposures have shown that the sulfur and chlorine contents of refuse have significant effects on the corrosion of metal surfaces exposed to hot combustion products. From the data collected it can be concluded that (1) the conversion of chlorides to sulfates in the incinerator deposits by the action of SO₂ releases chlorine and HCl at the metal surface, thereby causing serious corrosion; (2) chloride corrosion can be made negligible by increasing the total available sulfur to provide a sulfur to chlorine ratio of 4 in the fuel; (3) co-firing of refuse with high sulfur coal up to a 60/40 mix on a Btu basis will not

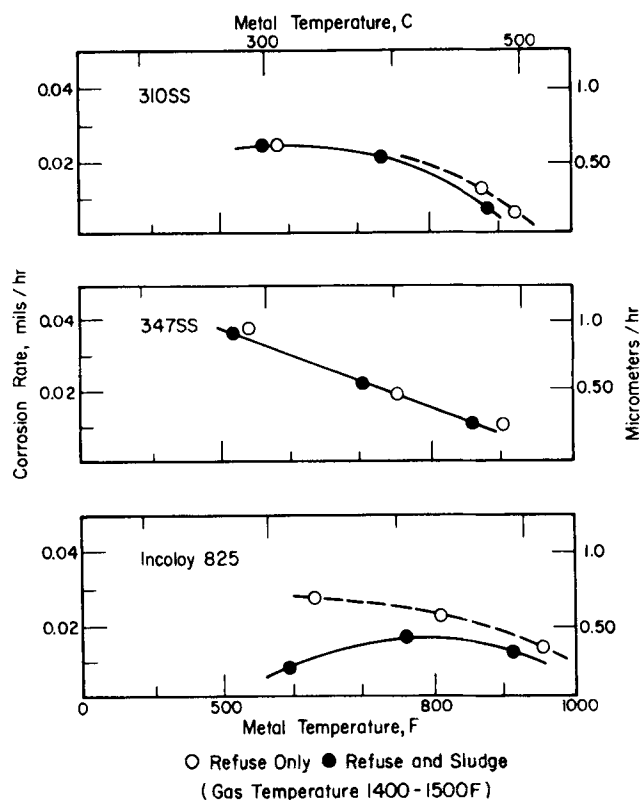


Fig. 11 — Corrosion rate of stainless steels and INCOLOY alloy 825 as a function of metal temperature (8-hour exposures).

increase the initial corrosion rate beyond that of coal alone; and (4) co-firing of refuse with a high-silica sludge will inhibit corrosion significantly.

These results have been obtained in probe exposures of less than 1000 hours, and the actual wastage rates reported cannot be extrapolated to determine the long-term corrosion that might be expected under these conditions.

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