Corrosion and Deposits From Combustion of Solid Waste

Part II–Chloride Effects on Boiler Tube and Scrubber Metals

H. H. KRAUSE, D. A. VAUGHAN and P. D. MILLER

ABSTRACT

Chlorides play an important role in corrosion of heat-transfer surfaces and wet-scrubbers in municipal incinerators. The nature of the deposits and the extent of corrosion have been investigated in a combined field and laboratory study. Corrosion by flue gases and accumulated deposits has been measured by probes exposed in large municipal incinerators. The corrosion rates of various metals by incinerator scrubber waters also have been determined. Parallel laboratory experiments were conducted to provide additional data under controlled environments for interpretation of corrosion reactions. General surface wastage, pitting, or stress-corrosion cracking was observed in different samples, depending on the exposure conditions.

INTRODUCTION

There has been increasing interest in steam-generating incinerators, as evidenced by recent construction of plants in Chicago and Harrisburg, plus several planned units. In addition, there is interest in the use of municipal refuse to replace some of the coal or oil now being burned in large power plants. This substitution offers a method of disposal of solid waste and provides a limited supply of low-cost, low-sulfur fuel. The deposit and corrosion problems which can occur in such a combustion system will include those that normally result from the coal or oil, plus the added effects of chlorides and metals such as lead and zinc that are present in significant amounts in refuse.

The first paper in this series [1] discussed the nature of the deposits that occur in large municipal incinerators and the general corrosion effects that result from the action of these deposits and the flue gases on boiler tube materials. The influence of chlorides in these circumstances are considered in this paper. In addition, the corrosion encountered in wet-scrubber systems which have been used on some large incinerators is discussed. These systems can be very effective in reducing pollutant emissions to acceptable levels. However, the high acidity that results primarily from HCl absorption, and the potential for stress-corrosion cracking caused by the chlorides formed in the scrubber water, present serious corrosion problems in these scrubbers.

BOILER TUBE METALS

Corrosion probes were exposed to the flue gases in the incinerators at Miami County, Ohio, and at the Norfolk Naval Base to obtain the field data for this part of the program. The probes were designed to provide exposure of 34 specimens during each test

period. The specimens were machined form 1 in. schedule 40 pipe or equivalent tubing, and were nested together end-to-end on the probe. The specimens were cooled by air flowing inside them and over an internal support tube designed to provide a temperature gradient along the probe between 350 and 1100 deg F. Actual specimen temperatures ranged from about 300 to 1200 deg F under different incinerator operating conditions. Details of the probe design and operation have been published previously [2, 3].

INCINERATOR EXPOSURES

Analyses of the incinerator flue gases in the probe exposure zone were made at intervals during the exposure periods. The HCl content of the gases ranged from a few ppm to several hundred ppm, depending on the nature of the refuse being burned. Chlorides accumulated rapidly in the deposits, even at moderate HCl concentrations in the flue gases. Probe deposits obtained at the Miami County, Ohio, incinerator during short exposure times in a 4-day period were found to contain very large amounts of chloride:

Exposure time, hr	Chloride concentration, wt. percent
1.5	22.0
8.5	27.3
24	21.6
88	13.3

The 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 (dry basis) ranged from 0.32 to 0.79 weight percent, with an average of 0.49 percent. Based on an average daily (24 hr) processing of 150 tons of waste at this incinerator, there would be about 1500 lb of chlorine in the refuse. The sources of the chlorine are both inorganic, primarily as NaCl, and organic, of

which polyvinyl 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 lb of the 1500 lb of chlorine in the refuse consumed daily. The remainder would be of inorganic origin. From these values it is obvious that large amounts of chloride are available to cause corrosion.

As the exposure time increased and the deposit aged, the amount of chloride decreased. This change results from the action of SO_2, which converts the chlorides to sulfates, but unfortunately this reaction releases HCl in the deposit, where it can attack the metal surface. A temperature effect also was observed, because the amount of chloride generally was greatest in the deposits found on lower-temperature specimens. These effects can be noted in the chloride contents of deposits accumulated at the Miami County incinerator during exposure times from 122 to 828 hr, as shown in Table 1.

The data shown in Table 1 are average chloride contents throughout a fairly large section of deposit on the probes. However, the chloride is not equally distributed, and the bulk of it diffuses into the inner deposit layer, at the metal-deposit interface. The deposits from the 828 hr probe exposure, which showed a uniform low average chloride content of 0.2 weight percent (Table 1), were sectioned horizontally to separate the bulk of the deposit from the corrosion-product scale at the interface with the metal. Analysis of the two sections of the deposit demonstrated that the chlorine, sulfur, potassium, lead, zinc, and iron are concentrated in the inner layer, as shown in Table 2. The relatively high concentration of chlorine that occurs at the metal-deposit interface also was revealed

Temperature zone, deg F	Chloride content (wt. percent) after time indicated (hours)						
	122	205	310	390	420	490	828
250-500	0.5	2.2	1.1	3.8	1.5	0.4	0.2
500-750	0.6	1.5	0.5	0.2	1.2	0.4	0.2
750-1000	0.1	0.1	0.3	0.2	0.4	0.3	0.2
1000-1250	0.5	0.5	0.6	0.1	0.2	0.2	0.2

TABLE 1. CHLORIDE CONTENT OF PROBE DEPOSITS FROM MIAMI COUNTY, OHIO, INCINERATOR

TABLE 2. COMPOSITION OF THE INNER AND OUTER LAYERS OF PROBE DEPOSIT[a]

| | Deposit analysis, weight percent | | | | | | | |
| | 300-500 F | | 500-700 F | | 750-1000 F | | 1000-1175 F | |
Material	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer
Cl	4.2	0.2	2.6	0.2	1.4	0.2	0.6	0.2
SO_3	26.2	16.3	25.0	15.0	22.6	14.5	25.4	13.0
Na_2O	9.0	10.2	9.1	10.5	10.8	10.0	10.4	11.2
K_2O	16.2	9.2	15.3	9.2	16.0	9.2	18.3	9.4
CaO	6.6	6.3	5.5	7.2	5.8	7.3	5.5	6.5
PbO	11.7	0.5	10.7	0.6	5.3	0.5	1.1	0.5
ZnO	8.8	7.5	9.4	7.9	8.1	8.2	8.5	8.5
Fe_2O_3	8.6	7.4	10.8	7.4	20.0	7.5	19.3	8.4
Al_2O_3	4.8	28.8	5.8	28.4	4.8	29.0	5.8	28.6
SiO_2	4.2	12.8	5.4	11.8	4.1	11.0	3.9	13.2
Total	100.3	99.2	99.6	98.2	98.9	97.4	98.8	99.5

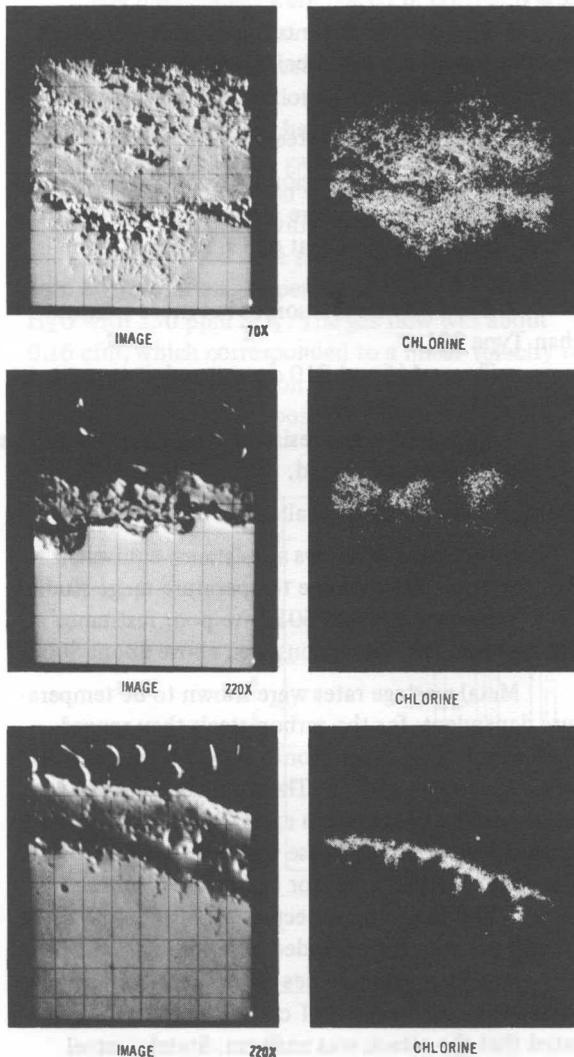[a]828-hr exposure in Miami County, Ohio, incinerator.

FIG. 1. ELECTRON MICROPROBE PULSE-MODE PHOTO-
GRAPHS SHOWING RELATIVE CHLORINE
CONCENTRATIONS AT METAL-DEPOSIT
INTERFACES

by electron microprobe analysis. The photographs shown in Fig. 1 demonstrate how the chlorine concentrates near the metal. The image photographs on the left give the magnification and show the position of the interface. The relative chlorine concentrations through the inner layer are shown in the photographs on the right. The top and center photos are sections of failed boiler tubes from an incinerator, and the bottom photo is a probe specimen exposed in the Miami County incinerator. X-ray diffraction investigations of these zones where chlorine was concentrated identified the chlorine compound as $FeCl_2$. The scale in contact with the substrate metal was found to contain $FeCl_2$ throughout the entire probe temperature range. At the moderately high-temperature end of the probe, it was found that the $FeCl_2$ layer melted and collected into small pools. Further out into the deposit the chlorine was found to be present as NaCl and KCl. These compounds can volatilize directly from the refuse or be formed by the action of HCl on sodium or potassium oxide. The $FeCl_2$ is obviously the corrosion product resulting from chloride attack on the metal specimen.

Deposits from the boiler tubes and other surfaces of the Mayson incinerator Atlanta, Georgia, also were analyzed. This boiler was selected for comparison because very little corrosion has been experienced in it. The average tube life there has been about 7 years. The tube deposits were taken from four places in the boiler along the main convection path. Other samples were taken from the bridge wall and the inspection door.

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The compositions of the deposits are shown in Fig. 2. The distribution of elements in the deposits is fairly typical of that found in municipal incinerators, except for the very high lead content. The boiler tube surfaces are maintained at a temperature determined by the operating pressure of the boiler (175 psi) and probably average about 420 F; the flue-gas temperature decreases from 1500–1800 F at the first tube bank to 550 F at the outlet. Larger amounts of lead and of chloride accumulate in the lower-temperature zones of the Atlanta boiler just as has been found with the probe deposits obtained in our program. The chlorine and sulfur concentrations in these Atlanta boiler deposits are sufficient to cause corrosion at the temperatures of the boiler tubes, although our work has demonstrated that the relatively low temperature gradient through the deposit to the tube surfaces will lessen corrosion.
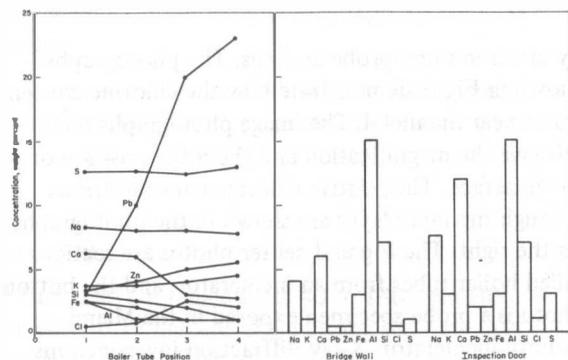

FIG. 2. ANALYSIS OF DEPOSITS FROM ATLANTA INCINERATOR

The other elements found in the Atlanta boiler tube deposits are in fairly typical distribution. Aluminum and iron are present in lower amounts than ordinarily encountered, however, and the potassium-to-sodium ratio is lower than usual.

The deposits on the bridge wall and the inspection door are predominantly calcium, sodium, aluminum, and silicon, which indicates that they constitute claylike particles that settle out of the gas stream and collect on these surfaces. The bridge-wall deposits, being subject to higher temperatures, are more completely oxidized, as indicated by the fact that the total metal content is about 15 percent less than that of the inspection door deposit. These deposits would be expected to be only slightly corrosive to metal surfaces.

CORROSION RESULTS

Eleven different metals and alloys were evaluated in the field probe studies. Two 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 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.

Measurements made on the probe specimens showed that for the A106 and T11 carbon steels:

• The rate of corrosion increases as the temperature increases and can range from 5 to 15 mils per month at 325 F to about 20 to 50 mils per month at 950 F.

• The two steels are comparable in corrosion resistance with the A106 being slightly superior to the T11 grade.

Second, for the stainless steels:

• The rate of corrosion increases for Types 304 and 321 as the temperature increases and ranges from about 10 mils per month at 625 F to about 40 mils per month at 1200 F.

• Type 304 steel is somewhat more resistant than Type 321.

• Types 446 and 310 are somewhat superior to Types 304, 321, and 316.

• Type 416 is less resistant than the other grades of stainless steels evaluated.

Third, for the nickel-base alloys:

• Incoloy 825 shows a resistance equivalent to that for Type 304 over the temperature range studied.

• Inconel 600 and 601 have poor resistance in the high-temperature regions, i.e., above about 800 F.

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

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

changes and varying degrees of intergranular attack.

Not all of the corrosion can be attributed to attack by chlorides, however. Qualitative tests on the probe specimens showed the presence of sulfide on most of them. FeS was identified on the high-temperature specimens by X-ray diffraction. These results point to the participation of sulfur in the corrosion reactions, probably through the action of sulfates, bisulfates, and pyrosulfates. However, the important role that chlorine can play was emphasized by the investigations in the laboratory.

LABORATORY STUDIES

The approach taken in the laboratory research was to subject alloys to simulated flue gases with and without direct contact with known salt mixtures. Weight losses were used to assess the amount of corrosion which occurred.

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 corresponded to a linear velocity of 0.2 fps. HCl was added on occasion in amounts of 220 and 2000 ppm. Exposure times were 50 hr for most of the runs.

Details of the experimental conditions and the corrosion mixture compositions are summarized in Fig. 3, in which metal wastage rates found at 1000 deg F are plotted. The lower line on this figure also shows the results of the azide test for the presence of sulfide on the corroded metals. The strength of a positive test is indicated by the number of + marks. The corrosion is expressed in units of mils/month as obtained by linear extrapolation from the weight loss values for 50 hr of exposure.

A baseline experiment (Run 0) was made with no material in contact with the specimen. As can be seen in Fig. 3, Run 3, the K_2SO_4-Na_2SO_4-Fe_2O_3 mixture did not accelerate corrosion above that obtained in flue gas alone (Run 0).

The run with the K_2SO_4-Na_2SO_4-Fe_2O_3 mixture was made to determine whether reactions to form alkali iron trisulfates took place. Such compounds are known to be corrosive in the temperature range 900-1100 F. Since the mixture did not accelerate corrosion, it was concluded that the formation of alkali-metal ferric trisulfates from sodium and/or potassium sulfates, iron oxide, and sulfur trioxide was not of major concern under the experimental conditions used.

The addition of 1 percent NaCl to the sulfate-iron oxide mixture (Run 1) greatly increased the corrosion rates. Without the Fe_2O_3 the corrosion rates were still very high (Runs 5 and 20). Increasing the chloride content (Run 10) had negligible effect although the action of KCl on A106 and T11 steels at 5 percent level seemed to be somewhat less than for NaCl (Run 11). As shown by Run 7, K_2SO_4 with 1 percent NaCl was less corrosive than the mixture of

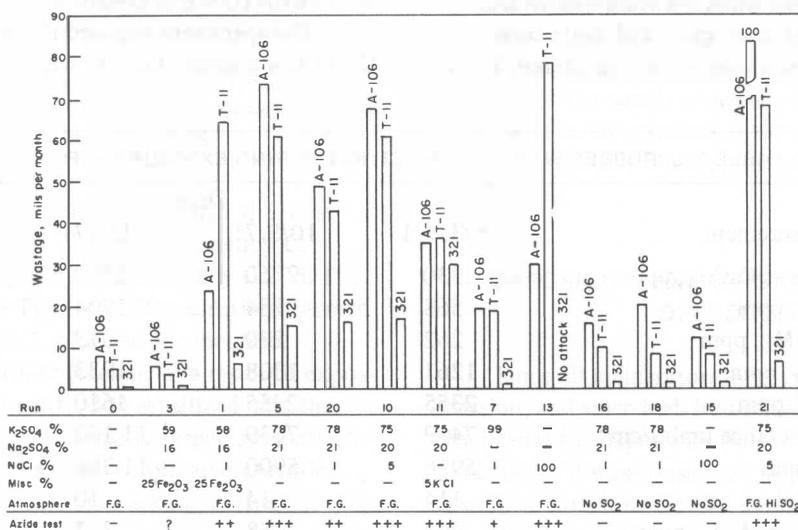| Run	0	3	1	5	20	10	11	7	13	16	18	15	21
K_2SO_4 %	–	59	58	78	78	75	75	99	–	78	78	–	75
Na_2SO_4 %	–	16	16	21	21	20	20	–	–	21	21	–	20
NaCl %	–	–	1	1	1	5	–	1	100	1	1	100	5
Misc %	–	$25 Fe_2O_3$	$25 Fe_2O_3$	–	–	–	5 KCl	–	–	–	–	–	–
Atmosphere	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	F.G.	No SO_2	No SO_2	No SO_2	F.G. Hi SO_2
Azide test	–	?	++	+++	++	+++	+++	+	+++	–	–	–	+++

FIG. 3. LABORATORY CORROSION RESULTS WITH
SYNTHETIC FLUE GASES AT 1000 F

K_2SO_4 and Na_2SO_4 with NaCl.

It is significant that sodium chloride alone in the presence of flue gas was quite corrosive to the carbon steels, i.e., Run 13. Of even greater significance is the fact that sulfide was revealed by the azide test, 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.

In order to get a better understanding of the possible reactions involving sulfur and SO_2 several experiments were conducted without SO_2 in the gases. In addition, experiment No. 21 was carried out where the SO_2 content of the flue gas was increased from 250 to 2500 ppm.

As can be seen from Runs 15, 16, and 18, the elimination of SO_2 from the flue gas decreased markedly the corrosion for chloride alone and for sulfate-chloride mixtures. Runs 16 and 18 were duplicate experiments and it can be seen that results are in quite good agreement. It is important to note that no sulfide was detected on the metal surfaces of the specimens for the three runs just mentioned, i.e., with SO_2 absent.

SCRUBBER METALS

There is general agreement that the corrosion in wet scrubbers for incinerators is an extremely severe problem. The rapid attack of most metals and alloys is not too unexpected when the composition and complexity of the effluent gases and dusts coming from the combustion chamber are considered. These gases include corrosive constituents such as HCl, SO_2, SO_3, HF, and organic acids. Extensive measurements of incinerator effluent gases have been reported by Carrotti and associates during the past few years [4, 5, 6]. One of their earlier measurements at the East 73rd Street Incinerator in New York City indicated an HCl evolution of up to 8 lb/ton of refuse. Our data from the Miami County, Ohio, incinerator suggest that about 6 lb of HCl may be obtained from a ton of municipal refuse.

The presence and concentration of HCl are of particular concern because this material accelerates pitting of most construction materials. It also limits the use of austenitic stainless steels because of the possibility of stress-corrosion cracking. In order to gain a better understanding of corrosion in scrubber systems, a fairly extensive exposure program was carried out in the North Montgomery County, Ohio, incinerator. The specimens were immersed in the hot water (170-190 F) passing through the concrete flume at the base of the scrubbers. The racks holding the specimens were alternated between Units 1 and 2 as the incinerator operation schedule dictated. The pH of this scrubber water varied from 4.0-5.1 as shown in Table 3, which gives compositional data on the effluent water. A duplicate set of specimens was also exposed in the same water at Columbus, Ohio, under static, aerated, conditions at pH 2.0-2.5 to determine the effect of lower pH. Three specimen configurations were used: stressed C-rings cut from pipe, U-bends cut from sheet stock, and flat plates containing 2-in-dia circular welds.

INCINERATOR EXPOSURES

The specimens exposed in the scrubber water at North Montgomery County were examined after 8,

Measurement	8/31/71	10/8/71	11/2/71	12/8/71[a]
Total hardness as $CaCo_3$, ppm	2330	2760	6250	272
Calcium as Ca, ppm	568	784	1704	71
Magnesium as Mg, ppm	262	230	573	27
Sulfate as SO_4, ppm	1261	1308	1933	231
Chloride as Cl, ppm	2355	2355	1610	183
Specific conductance μmho/cm	7499	7639	11,160	833
Total solids, ppm	5916	5900	11,386	732
Suspended solids, ppm	114	14	10	114
Total acidity as $CaCO_3$, ppm	402	388	352	68
pH	4.4	4.3	5.1	4.0

TABLE 3. SCRUBBER WATER COMPOSITION DURING EXPOSURE PERIOD (Date)

[a]On this date the scrubber water was not being recirculated.

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17, 38, 63, 96, and 129 days. These specimens rapidly became coated with a very adherent deposit which could be removed only by vigorous scrubbing with a bronze-wire brush. This coating very likely afforded some corrosion protection to the specimens. Spectrographic analyses of the coating showed a major amount of calcium and appreciable amounts of lead, barium, silicon, and aluminum. The low solubilities of calcium, barium, and lead sulfates are consistent with the presence of these deposits. X-ray diffraction studies confirm the presence of $PbSO_4$ and $CaSO_4 \cdot 2\text{-}H_2O$.

A large portion of the water in this scrubber was recirculated, but a sizable makeup was required. This is evident from the data in Table 3 which includes analyses over a 4-month period. The results for 12/8/71 in Table 3 show extremely low concentrations of dissolved salts. This is because the scrubber during that period was being operated on a once-through water flow.

A photograph of the more severely corroded specimens from the incinerator scrubber exposure is presented in Fig. 4.
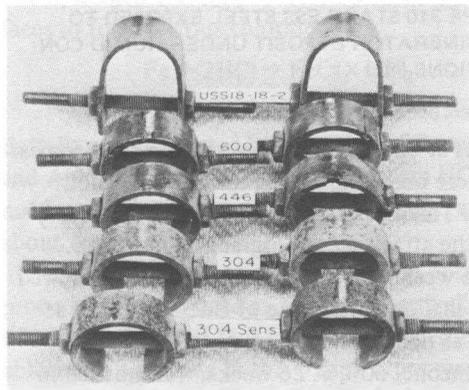

FIG. 4. SEVERELY CORRODED SPECIMENS EXPOSED TO SCRUBBER WATER AT NORTH MONTGOMERY COUNTY, OHIO, INCINERATOR

The corrosion results showed that the most durable materials were Ti-6Al-4V, Hastelloy C, Inconel 625, Hastelloy G, and Hastelloy C-276. The least resistant were Type 304, 304 sensitized, Armco 22-13-5, USS 18-18-2, 445, and Inconel 600.

The only definite cracking as a result of exposure was on the Type 304, 304 sensitized, and the Inconel 600 specimens. In many respects the attack had the appearance of stress-accelerated corrosion rather than stress-corrosion cracking, particularly for the Inconel.

Cracking was not observed in the circular welded panels, but many of them were pitted, often pre-

dominantly in the area near the weld.

Selective attack at the support hole crevices and the pits in the weld area on the back of the Type 310 stainless steel panel were evident.

Type 304 stainless steel was similarly affected, except that more linear strings of pits were present.

Inconel 600 was usually severely attacked at corners, edges, and crevices.

LABORATORY STUDIES

The scrubber solutions used in the exposures made at Columbus, Ohio, were obtained from the scrubber effluent stream at the North Montgomery County incinerator. The solutions were changed three times during the 137-day period. A set of specimens identical to those exposed at North Montgomery County was used. The specimens were completely submerged in the scrubber water contained in a large Pyrex jar maintained at 170-180 F. Air was slowly sparged through the solution during the exposure. The pH of the solutions was maintained at 2.0-2.5 by means of occasional additions of sulfuric or hydrochloric acids. Specimens were examined at 20, 42, 95, and 137 days. The following materials furnished the best resistance when rated on the basis of good performance in all configurations in which they were run: Ti-6Al-4V, Hastelloy C, Inconel 625, Alloy S-816, and Hastelloy F, Hastelloy G, and Hastelloy C-276.

Stress-corrosion cracking was found on the Type 304 panels and C-rings. Cracking was also noted at an area in the weld and base metal of the Type 316L panel.

Stress-accelerated corrosion (trenches) running across the face of the specimen was found for the Inconel 600 and 601 specimens.

Pitting occurred on many of the specimens, and most of the panels which showed bad pitting were also severely attacked at the crevices under the Teflon spacers near the support holes in the corners of the panels.

CORROSION FROM MOIST INCINERATOR DEPOSITS

Since all incinerators must be shut down on occasion, and since high humidity conditions can often cause the deposit on the tube surfaces to become moist, it was considered important to assess the severity of attack under these conditions. The most damaging forms of attack to be anticipated are stress-corrosion cracking (SCC) and pitting. Probably the most hazardous of these is stress-corrosion cracking.

While SCC of stainless steels can occur in caustic environments, the most important substance promoting the SCC of stainless steels is chloride ion in an acid medium. Trace quantities of this substance are enough to cause austenitic stainless steels to develop stress-corrosion cracks rapidly. While higher temperatures generally favor SCC, Type 304 will crack even at room temperature. Stainless steel alloys will crack when stressed to as low as 2000 psi in the presence of a few parts per million of chloride ions.

Since chloride ions are present in incinerator deposits, two groups of materials were evaluated for SCC while in contact with incinerator deposit under humid conditions. The first group of alloys included Types 304, 310, and 446 stainless steels and carbon steels A106, Grade B, and A213, Grade T-11. The Group 2 specimens included Type 316L stainless steel and three other alloys more resistant to SCC in chloride environments, namely, Inconel 600, Inconel 601, and Incoloy 825. Bent specimens (C-rings) were stressed to a level halfway between the yield stress and the ultimate tensile strength (at the SCC test temperature). Some U-bend configurations were also used. Some specimens of Type 304 stainless steel were sensitized for 2½ hr at 1200 F to increase their susceptibility to SCC. Other specimens were tested as received.

The apparatus for these moist-air SCC experiments was similar to a double boiler: the specimens are placed on dry pulverized incinerator deposit in the inner vessel while distilled water in the outer vessel is heated to humidify the atmosphere.

In the Group 1 alloys, the Type 304 specimens (both sensitized and annealed) showed cracks after an exposure of one week. Fracture occurred on the sensitized Type 304 piece during the eighth week of exposure. Cracks were first observed in Type 310 steel after 10 weeks. Deep stress-corrosion cracks developed in all three materials during 20 week's exposure. There were fewer cracks on the Type 310 specimens but they were very deep. The attack on this material was predominantly transgranular as is illustrated in Fig. 5.

No SCC was observed with Type 446 steel after 22 weeks of exposure. The specimen, however, was quite rusty and pitted. After 12 weeks, the A106 and T-11 steels were quite rusty and scaled but no stress-corrosion cracking was observed. The surface roughening on these steels was noticeable at 15X but was not great. There was no indication of deep pitting as is sometimes seen in corrosive environments.

The Group 2 alloys were exposed for 26 weeks. Only the Type 316L specimens exhibited cracking

FIG. 5. STRESS-CORROSION CRACK IN C-RING OF TYPE 310 STAINLESS STEEL EXPOSED TO INCINERATOR DEPOSIT UNDER HUMID CONDITIONS (100 X)

and this was at 22 weeks. However, some rusty appearing spots were observed on this specimen in about four weeks. The cracking started at one of the rusty areas, and the attack was transgranular in nature.

At 26 weeks, the Inconel 601 specimen showed many fine, shallow pits. Some of these appeared at four weeks as rusty spots.

The Inconel 600, at 26 weeks, was mottled in appearance as if it were etched in spots. This alloy also showed a few rusty spots after four weeks.

The Incoloy 825 showed good resistance throughout the 26-week period. It is, therefore, concluded that this alloy is a good choice when resistance to downtime conditions is considered.

The austenitic-type stainless steels such as 304, 310, 316, etc., do not appear to be good choices because of the likelihood of the incidence of stress-corrosion cracking.

The ferritic-type stainless steels, as exemplified by 446, have the limitation of possibly being subject to severe pitting under the downtime conditions.

Apparently, these laboratory conditions were more severe than those experienced in the field because the corrosion probe specimens exposed at Miami County did not show bad pitting even when downtime occurred weekly.

CORROSION MECHANISMS

CORROSION BY CHLORIDE DEPOSITS

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 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 [7], particularly as they apply to burning fossil fuel containing chlorine.

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

$$2(Na,K) Cl + SO_2 + \tfrac{1}{2}O_2 + H_2O \rightarrow$$

$$(Na,K)_2 SO_4 + 2HCl. \qquad (1)$$
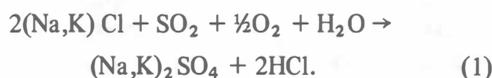
The hydrogen chloride then reacts with the iron surfaces to form ferrous chloride:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2. \qquad (2)$$
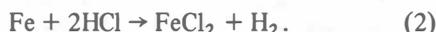
As indicated by the laboratory studies at Battelle and supported by the work of Brown, DeLong, and Auld [8], the corrosive effects from HCl would not be expected to be severe below temperatures of about 600 F.

Since $FeCl_2$ has been detected on corrosion-probe samples exposed at temperatures well below 600 F, it is believed that corrosion by elemental chlorine is operating in this temperature range.

Although elemental chlorine has not been identified in incinerator furnace gases, it is believed that it may play a role in the corrosion reaction. It is postulated that metal oxides, possibly Fe_2O_3 or PbO, on the tube surfaces catalyze the reaction:

$$2HCl + \tfrac{1}{2}O_2 \rightarrow H_2O + Cl_2. \qquad (3)$$

The chlorine, which is formed only near the catalytic surface, then combines directly with the iron:

$$Fe + Cl_2 \rightarrow FeCl_2. \qquad (4)$$

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 $FeCl_2$ would react with oxygen to form Fe_2O_3. 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 within the adherent scale.

It has been shown by Fassler [9] that chlorine can be formed by oxidation of $FeCl_2$:

$$4FeCl_2 + 3O_2 \rightarrow 2Fe_2O_3 + 4Cl_2. \qquad (5)$$

The chlorine retained within the scale deposit then reacts further with the iron.

Three observations support this mechanism. 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 F and higher. Third, the Deacon Process (Reaction 3) is favored at temperatures near 500 to 700 F in the presence of catalysts. Thus it appears that chlorine reactions with steel are important at the low temperatures, and that both HCl and Cl_2 reactions take place at the high temperatures.

CORROSION BY CHLORIDE SOLUTIONS

The scrubber metals are subject to strongly acid chloride solutions. Carbon steels corrode rapidly under these conditions, primarily by acid attack. However, stress-corrosion cracking can be more serious than the general wastage and pitting. The austenitic stainless steels, which resist the acid attack, are particularly susceptible to stress-corrosion cracking induced by chlorides.

When an alloy is simultaneously subjected to surface-tensile stresses and a variety of specific corrosive environments, it may experience premature failure because of stress-corrosion cracking. This process is unique in that failure does not occur when the individual factors mentioned in the foregoing are acting alone.

One aspect of the phenomenon is that the metal at the failed areas does not exhibit ductile tearing, but instead exhibits a brittle fracture. Crack propagation, once initiated, is quite rapid. The propagation is in a plane perpendicular to the direction of the applied stress. The cracks may be either transgranular or intergranular, depending on the alloy and the composition of the environment.

The tensile stresses required for cracking may be either applied or residual. The latter may result from welding or from press fits or other assembly procedures. Also, the presence of crevices may favor the initiation of stress-corrosion cracks.

All common structural materials such as carbon steel, low-alloy steel, stainless steels, aluminum alloys, copper alloys, and nickel alloys are susceptible to SCC to varying degrees in some specific environments. The mechanism of the cracking is not completely understood. From an engineering standpoint, however, it is important to know which combinations of materials and environments will initiate cracking. The large concentrations of chloride ion, which are inevitable in the incinerator scrubber water, make it inadvisable to use austenitic stainless steels in these scrubbers. Neutralizing the acidity of the scrubber water with alkalis will decrease the stress-corrosion cracking, but it will not eliminate this type of attack.

CONCLUSIONS

The stainless steels, particularly Types 310 and 446, furnish good resistance to fireside corrosion but 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 chloride stress-corrosion cracking and the Type 446 can be severely pitted. However, only minor pitting occurred in incinerator operation. The other austenitic stainless steels evaluated—Types 304, 316, and 321— also were more resistant than the carbon steels but are subject to SCC by chlorides. 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 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 SCC than the austenitic stainless steels, so it could be considered for use in high-temperature areas where the carbon steels would not be recommended.

Pitting attack and selective attack at crevice areas constituted the major form of metal deterioration at the incinerator scrubber. In the low pH solutions (2.0) used for the laboratory studies stress-corrosion cracking was observed on Types 304 and 316L stainless, steel specimens. Specimens of Inconel 600 and 601 exhibited what is termed stress-accelerated corrosion at North Montgomery County.

The alloys most resistant to all types of corrosion of those evaluated were Ti-6Al-4V, Hastelloy C, Inconel 625, Hastelloy G, Hastelloy C-276, Hastelloy F, Ti75A, and Type S-816.

The less-resistant alloys were Carpenter 20, Incoloy 825, Types 316L, 310 stainless steels, Inconel 600 and 601, Armco 22-13-5, USS 18-18-2, and Type

304. Table 4 lists these 18 alloys and their general resistivity to corrosion in the scrubber solutions.

TABLE 4. EVALUATION OF ALLOYS UNDER INCINERATOR SCRUBBER CONDITIONS

Alloy	Performance
Ti6Al-4V	Good resistance
Hastelloy C	Good
Inconel 625	Good
Hastelloy F	Good
Hastelloy C-276	Good
Hastelloy G	Good
Ti75A	Good
S-816	Good
Carpenter 20	Pitted
Incoloy 825	Pitted
316L	Pitted, SCC
310	Pitted
446	Pitted
Inconel 600	Trenches
Inconel 601	Trenches
Armco 22-13-5	Pitted
USS 18-18-2	Pitted
Type 304	Pitted, SCC

R. D. Fischer, E. J. Schulz, W. N. Stiegelmeyer,
P. R. Webb, and E. L. White.

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