

Corrosion and Deposits From Combustion of Solid Waste Part III—Effects of Sulfur on Boiler Tube Metals

H. H. KRAUSE, D. A. VAUGHAN and W. K. BOYD

ABSTRACT

Sulfur plays a significant part in the corrosion of heat transfer surfaces in municipal incinerators. The nature of the deposits and the extent of corrosion on simulated boiler tube surfaces has been investigated in a combined field and laboratory study. The corrosion resulting from the accumulation of deposits and the action of flue gases on boiler tube metals has been measured by probes exposed in large municipal incinerators. In addition, laboratory experiments were conducted under controlled environments to provide additional data for determination of reaction mechanisms. The amount of sulfur in the solid waste was found to be a controlling factor in the corrosion, and increasing the amount of sulfur resulted in reduced corrosion rates on boiler tube metals. This effect has important implications for the combined firing of refuse and fossil fuels.

INTRODUCTION

In recent years there has been increasing interest in the use of municipal refuse to replace some of the coal or oil now being burned to provide electrical power. There has also been interest in following the rather common European practice of using solid wastes to fuel steam-generating incinerators. Both of these approaches provide for disposal of solid waste and

offer a limited supply of low cost, low sulfur fuel. However, the components of solid wastes which are not present in fossil fuels, particularly chlorine, lead, and zinc create additional deposit and corrosion problems.

The first paper in this series [1] discussed the general nature of the deposits and corrosive effects that occur in large municipal incinerators. The particular influence of chlorides in these circumstances was presented in the second paper [2]. This discussion emphasizes the effects of sulfur, both as it normally occurs in the refuse and when it was added to the solid waste in significant amounts.

INCINERATOR EXPOSURES

Corrosion probes were exposed to the flue gases in the incinerators at Miami County, Ohio, and at the Norfolk Naval Base for periods up to 1300 hr to obtain the field data for this research program. The probes were designed to provide exposure of 34 metal specimens of controlled temperatures during each test period. The specimens were machined from 1-in. Schedule 40 pipe or equivalent tubing, and were nested together end-to-end on the probe. The specimens were cooled internally by high velocity air which flowed over a tapered center body designed to provide a temperature gradient along the probe between 350 and 1100°F. (175-595°C). Under different incinerator

operating conditions, the actual specimen temperatures ranged from about 300-1200°F (150-650°C). Details of the probe design and operation have been published previously [3, 4]. The incinerator flue gases in the regions where the probes were exposed were analyzed at intervals during the long term exposures and a cumulative sample was taken during the periods in which sulfur additions to the refuse were made. The sulfur dioxide content of the flue gases ranged from a few ppm to a few hundred ppm, depending on the nature of the refuse being burned. When sulfur was added to the refuse in amounts up to 1.5 weight percent, the sulfur oxide content of the flue gases in the probe exposure zones was found to be about 700 to 800 ppm.

Refuse sortings made at four different times at the Miami County, Ohio, incinerator showed that the

nature of the refuse being burned during the experimental period was typical of municipal refuse in this country as reported by other investigators. On this basis the sulfur content of the refuse can be taken as 0.2 weight percent, as some recent analyses of refuse by the Solid and Hazardous Waste Research Laboratory showed a sulfur content ranging from 0.10 to 0.37 percent in 21 samples, averaging 0.19 percent.

In spite of the relatively low sulfur content of normal refuse, sulfur accumulated rapidly in the probe deposits. In a few hundred hours the amount of sulfur that was found in the incinerator deposits had reached levels equal to those found on boiler tubes where coal containing much larger amounts of sulfur was burned. As shown in Table 1 the sulfur content of the probe deposits quickly reached levels of 8 to 9 weight percent (20 to 22.5 percent SO₃). In each temperature zone on the probe as the exposure time increased and the deposit aged, the amount of sulfur in the deposit decreased slightly. This effect is the result of increasing amounts of heavy metals in the deposit with time rather than any occurrence of chemical reactions in the deposit. However, the decrease in sulfur content with increase in temperature which occurred consistently in all of the probes is the result of decomposition of some of the sulfates. The amount of sulfur found on the probe exposed for 390 hours was anomalous in that it was unusually high. Probably this change occurred because of some difference in the refuse being burned during that time. It was observed that occasionally the incinerator received waste which contained large amounts of plaster board, consisting primarily of calcium sulfate. The presence of this

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

Probe Temperature Zone, Deg.F	Sulfur content (wt. %) ^a after time indicated (hrs.)						
	122	205	310	390	420	490	828
250 - 500°F (120 - 260°C)	8.5	8.0	8.4	7.3	7.0	6.1	7.0
500 - 750°F (260 - 400°C)	8.6	9.0	7.4	12.8	8.5	6.5	6.5
750 - 1000°F (400 - 540°C)	6.2	6.0	6.5	8.4	5.0	4.0	5.1
1000 - 1250°F (540 - 675°C)	6.3	7.0	6.2	9.4	4.3	3.8	3.8

^aAs elemental sulfur

TABLE 2. COMPOSITION OF THE INNER AND OUTER LAYERS OF PROBE DEPOSIT^(a)

Material	Deposit Analysis, weight percent							
	300 - 500°F (150-260°C)		500 - 700°F (260-400°C)		750 - 1000°F (400-540°C)		1000 - 1175°F (540-635°C)	
	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 ₂ O	9.0	10.2	9.1	10.5	10.8	10.0	10.4	11.2
K ₂ O	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 ₂ O ₃	8.6	7.4	10.8	7.4	20.0	7.5	19.3	8.4
Al ₂ O 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 hours exposure in Miami County, Ohio, incinerator

material in the refuse could account for the unusually high concentration of sulfur in the deposit.

The sulfur concentrations shown in Table 1 are averages taken throughout a fairly large section of deposit on the probes. However, the sulfur is not equally distributed throughout the deposit, and the bulk of it diffuses into the inner deposit layer, nearer the metal-deposit interface. The deposits from the 828-hr probe exposure 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 showed that the sulfur, chlorine, potassium, lead, and iron are concentrated in the inner layer, as shown in Table 2. In each of the four temperature zones the sulfur content of the inner deposit layer was almost twice as great as that in the outer layer.

The probe deposits collected during the 8-hr periods during which sulfur was added to the refuse contained only 4 to 6 percent sulfur, indicating that longer periods of time are required for the sulfur content to build up to maximum levels. It is believed that with large amounts of sulfur present the interaction of sulfur dioxide with metal chlorides to form sulfates takes place to a greater extent in the flue gas stream, thus reducing the amount of sulfate formation in the deposit. The distribution of sulfur at the metal-deposit interface also was investigated by electron microprobe analysis. In Fig. 1 the image photographs on the left give the magnification and show the position of the metal-deposit interface. The relative sulfur 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. It can be seen that the sulfur is spread throughout the inner layer of the deposit in the first two cases, and follows the surface of the corroded metal. In the third case the sulfur is distributed in two layers, one along the metal interface and the other further out in the corrosion product layer with little in between. X-ray diffraction investigations of the zones where sulfur was concentrated near the metal identified the sulfur compound as FeS. Further out in the deposit the sulfur was present as sodium potassium sulfate, lead sulfate, potassium lead sulfate, and zinc sulfate.

Examination of deposit sections by optical microscopy shows that in the low temperature zone (400-800°F) (205-425°C) on the corrosion probe the FeS reaction product invariably forms between an iron chloride layer and an iron oxide layer. In the high temperature zone (800°-1200°F) (425-650°C) the

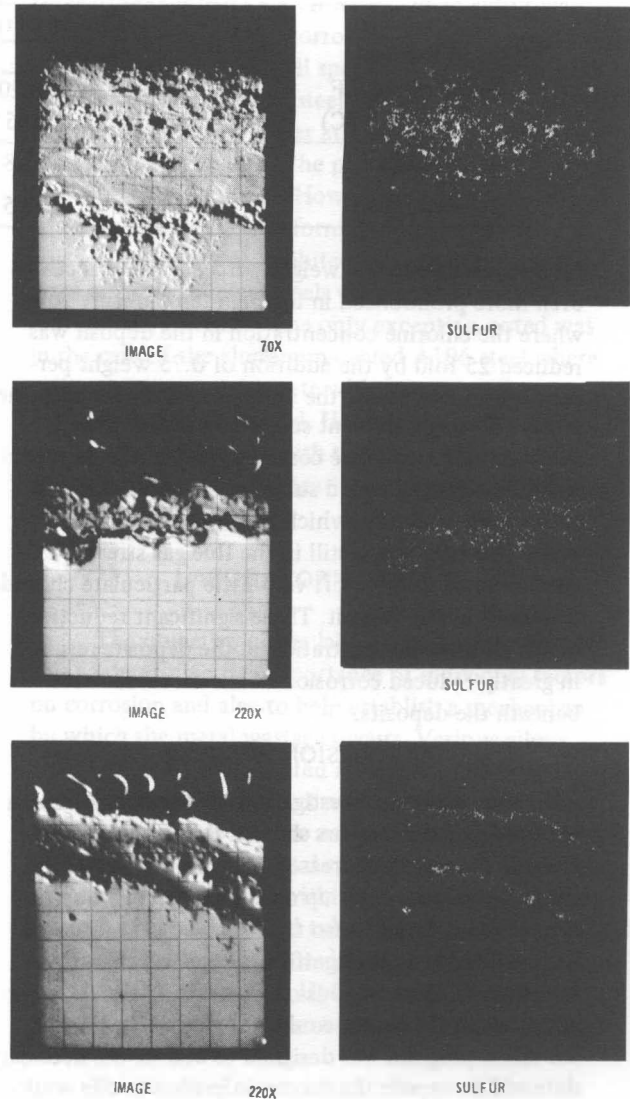


FIG. 1. ELECTRON MICROPROBE PULSE-MODE PHOTOGRAPHS SHOWING RELATIVE SULFUR CONCENTRATIONS AT METAL-DEPOSIT INTERFACES

The effect of adding sulfur to the refuse is particularly noted in a decrease of chlorine in the deposits as shown in Table 3. The effect was particularly pronounced in the 700° (370°C) temperature zone where chlorine reached a concentration of 7.5 weight percent in the deposits obtained after 8 hr of operation with normal refuse. When 0.75 weight percent sulfur was added to the refuse the chlorine concentration dropped to 1.9 percent, and when 1.5 weight percent sulfur was added, the chlorine concentration was FeS forms on the metal substrate where the iron chloride agglomerates to form islands on the metal surface. The FeS is then found on the metal surface between these islands.

TABLE 3. SULFUR AND CHLORINE CONTENT OF DEPOSITS WITH SULFUR ADDITIONS TO REFUSE

Substrate	Concentration (wt. %) with indicated sulfur addition (wt. %)					
	None		0.75% S		1.5% S	
Temperature, F (C)	745 (395)	1120 (605)	730 (390)	1125 (605)	740 (395)	1175 (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

further reduced to 0.1 weight percent. The effect was even more pronounced in the high temperature zone where the chlorine concentration in the deposit was reduced 25 fold by the addition of 0.75 weight percent sulfur, and below the detection limits for chlorine when 1.5 weight percent sulfur was added. This decrease in the chlorine concentration in the deposits indicates 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 formation of sulfates left very little particulate chloride to collect in the deposit. These significant reductions of the chlorine concentration in the deposits resulted in greatly reduced corrosion of the metal surfaces beneath the deposits.

CORROSION RESULTS

Our previous investigations of fireside corrosion in municipal incinerators showed that the corrosion rates of the metals decreased with time as protective oxide layers were built up on the surface. Extrapolation of these data to zero time showed that it would be possible to obtain significantly measurable corrosion rates in short periods of time during which sulfur additions to the refuse could be made. Accordingly, the latest program was designed to collect the necessary data and to expose the corrosion probes in one working day at the incinerator. A base line 10-hr exposure of the corrosion specimens with normal municipal refuse was carried out in order to demonstrate the validity of the extrapolation. The results are shown in Fig. 2 which gives corrosion rates for ordinary carbon steel (A106) as a function of time at four different specimen temperatures. The corrosion rates for the 10-hr exposure were very high as anticipated and the resultant curves fit the data for the longer term exposures. These short time experiments were not intended to establish long-term performance, but to show differences in the corrosiveness of the combustion environment.

In subsequent experiments sulfur was added to the refuse by introducing elemental sulfur with each grapple load placed in the feed hopper. The effect of these sulfur additions on the corrosion rate of A106 steel is shown in Fig. 3. At 300°F (150°C) metal temperature the corrosion rate decreased linearly with the

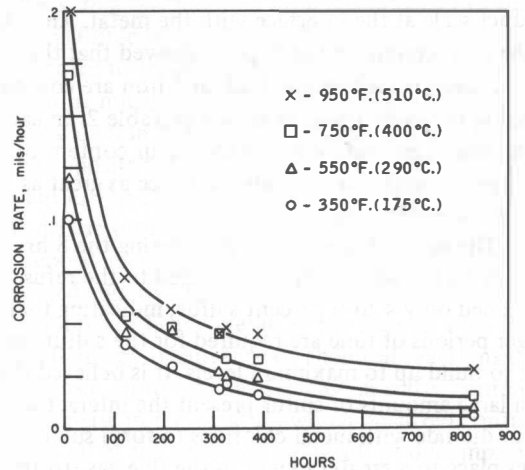


FIG. 2. CORROSION RATES OF A106 STEEL AS A FUNCTION OF EXPOSURE TIME AT THE MIAMI COUNTY, OHIO, INCINERATOR—NOTE: MILS/HOUR TIMES 25.4 = MICRONS/HOUR.

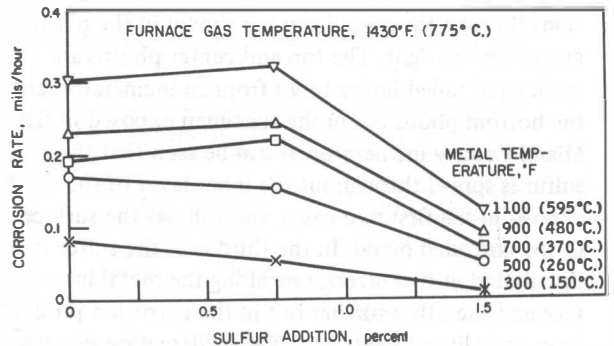


FIG. 3. CORROSION RATES OF A106 STEEL AS A FUNCTION OF SULFUR ADDITIONS TO REFUSE —NOTE: MILS/HOUR TIMES 25.4 = MICRONS/HOUR.

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.

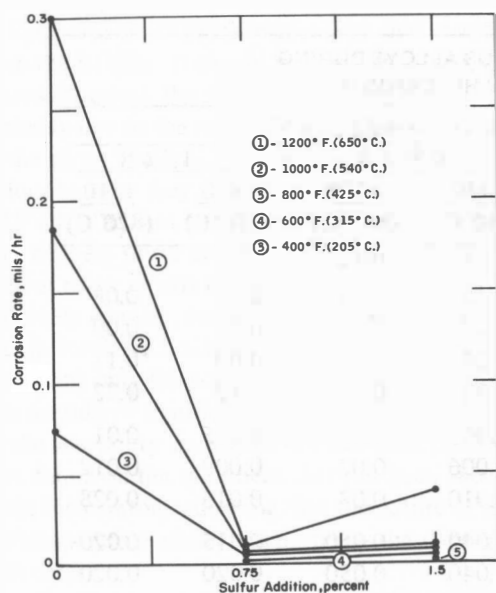


FIG. 4. CORROSION RATES OF TYPE 316 STAINLESS STEEL AS A FUNCTION OF SULFUR ADDITIONS TO REFUSE—NOTE: MILS/HOUR TIMES 25.4 = MICRONS/HOUR.

An even more dramatic effect of sulfur addition to the refuse was noted for 316 stainless steel, as shown in Fig. 4. At 800°F (425°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 (540 and 650°C) decreased about 25- and 30-fold, respectively, with the 0.75 percent sulfur addition. There was a slight increase in the corrosion rate at 1200°F (650°C) when the sulfur addition was increased to 1.5 percent.

For all of the alloys studied there were significant decreases in corrosion rate when sulfur was added to the refuse. The corrosion results are summarized in Table 4 which shows both the effect of increasing the amounts of sulfur in the refuse and of flue gas temperature. In some cases such as for the 446 stainless steel and the chromium-coated A106 steel there was an order of magnitude decrease in the corrosion rate between the addition of 0.75 percent sulfur and the addition of 1.5 percent sulfur. Lesser decreases in corrosion rate were observed with the other alloys used.

The effect of flue gas temperature on the corrosion rate of the various alloys also can be related to the refuse composition. With no sulfur added, the carbon steel showed very little change in corrosion rate with flue gas temperature up to specimen tempera-

tures of 900°F (480°C). However, when sulfur was added to the refuse the corrosion rates increased with flue gas temperature at all specimen temperatures. For the various stainless steels, with normal refuse the corrosion rates were lower at higher flue gas temperatures, probably because the protective oxidation layer formed more rapidly. However, when sulfur was added to the refuse, the formation of the protective layer apparently was inhibited because the corrosion rates of these stainless steels were greater at the higher flue gas temperatures. The only exception noted was in the case of the aluminum-coated A106 steel where a decrease in corrosion rate with increasing flue gas temperature was observed. However, there were some problems with spalling with these coatings and these results need further verification.

LABORATORY STUDIES

The objective of the laboratory experiments was to determine the importance of individual factors on corrosion and also to help establish a mechanism by which the metal wastage occurs. Various alloys were subjected to simulated incinerator 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 located within quartz tubes passing through resistance-heated tube furnaces. The synthetic flue gas composition used was: 80 percent air, 10 percent CO₂, 10 percent H₂O, and 250 ppm SO₂. In some experiments HCl also was added in amounts of 200 or 2000 ppm.

The attack of the synthetic flue gases alone on carbon steel was not significant at temperatures up to 800°F (425°C). At higher temperatures the corrosion rates increased rapidly due to the oxidation of the carbon steel specimens. The corrosion of 321 stainless steel was insignificant under these conditions.

Experiments were conducted at 600°F (315°C) with KHSO₄ and K₂S₂O₇ in contact with the metal specimens while the synthetic flue gases were passed over them. These compounds were selected because the corrosion probe studies in the incinerator showed that sulfur-containing salts were involved in the low temperature corrosion, and these are the salts most likely to be involved. Pyrosulfates in particular have been demonstrated to be the cause of corrosion in wall tubes of boilers fired by fossil fuels. The results of the experiments are shown in Table 5 together with data taken at 800 and 1000°F (425 and 540°C) for other sulfur-containing compounds. The corrosion by

TABLE 4. CORROSION RATES OF VARIOUS ALLOYS DURING SULFUR ADDITIONS TO REFUSE (TEN-HR. EXPOSURE)

Refuse additions: Furanc-gas temp. F: Alloys Temp., F		Corrosion rates, mils/hour ^(b)					
		None		0.75% S		1.5% S	
		1480 (805°C)	1660 (905°C)	1440 (780°C)	1550 (845°C)	1420 (770°C)	1510 (820°C)
A106	300(150°C)	0.11	0.13	0.05	0.14	0.01	—
	500(260°C)	0.19	0.17	0.15	0.26	0.05	0.08
	700(370°C)	0.22	0.24	0.22	0.34	0.07	0.09
	900(480°C)	0.28	0.37	0.24	0.39	0.09	0.11
	1000(540°C)	0.42	0.69	0.32	0.53	0.12	0.22
316SS	700(370°C)	0.04	0.01	0.005	0.02	0.005	0.01
	900(480°C)	0.14	0.09	0.006	0.02	0.009	0.012
	1100(595°C)	0.23	0.17	0.010	0.03	0.015	0.028
203EZ	700(370°C)	0.155	0.10	0.040	0.050	0.015	0.020
	900(480°C)	0.17	0.125	0.040	0.050	0.020	0.020
	1100(595°C)	0.185	0.15	0.045	0.060	0.060	0.030
431	700(370°C)	0.16	0.43	0.025	0.055	0.005	0.025
	900(480°C)	0.125	0.25	0.025	0.055	0.010	0.025
	1100(595°C)	0.19	0.165	0.05	0.065	0.015	0.035
446	700(370°C)	0.07	0.05	0.03	0.05	0.003	0.01
	900(480°C)	0.07	0.06	0.03	0.055	0.004	0.01
	1100(595°C)	0.07	0.06	0.03	0.06	0.005	0.01
A106-Cr coated ^(a)	700(370°C)	0.10	0.14	0.07	0.17	0.005	0.02
	900(480°C)	0.15	0.15	0.07	0.17	0.1	0.02
	1100(595°C)	0.22	0.16	0.07	0.20	0.015	0.02
A106-Al coated ^(a)	700(370°C)	0.105	0.20	(a)	(a)	0.025	0.01
	900(480°C)	0.125	0.31	(a)	(a)	0.025	0.015
	1100(595°C)	0.25	0.50	(a)	(a)	0.045	0.03

(a) Some spalling of the Al and Cr coatings caused error in corrosion rate analyses; numbers shown are maxima and include spalling losses.

(b) Mils per hour times 25.4 = microns/hour.

TABLE 5. RESULTS OF LABORATORY CORROSION STUDIES^(a)

Alloy	Corrosion rates (mils/month) ^(b) with indicated temperature and salt mixture					
	600°F (315°C)		800°F (425°C)		1000°F (540°C)	
	KHSO ₄	K ₂ S ₂ O ₇	75 K ₂ SO ₄ 25 Na ₂ SO ₄	75 K ₂ SO ₄ 20 Na ₂ SO ₄ 5 NaCl	No SO ₂ 78 K ₂ SO ₄ 21 Na ₂ SO ₄ 1 NaCl	250 ppm SO ₂ 78 K ₂ SO ₄ 21 Na ₂ SO ₄ 1 NaCl
A106	7	24	1	18	18	73
T11	8	31	1	15	9	52
321	18	26	0	0.5	1	16

(a) Synthetic flue gas: 80% air, 10% CO₂, 10% H₂O, 250 ppm SO₂.

(b) Mils/month times 25.4 = microns/month.

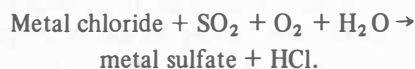
$K_2S_2O_7$ was much more serious than that resulting from the $KHSO_4$. It should be noted that both of these salts attack the 321 stainless steel significantly, probably due to the sulfidation of the nickel content of the alloy. The attack by these salts is particularly serious because they are in the fused state at $600^\circ F$ ($315^\circ C$). It has not been possible to verify the presence of these sulfur compounds in the deposits in spite of many efforts to find them. These salts are extremely reactive, and it is likely that they participate in corrosion reactions as rapidly as they are formed, leaving only the corrosion products to be observed. It is considered significant that sulfides were detected on the laboratory specimens in these cases just as they were found on the specimens that had been exposed in the incinerator, indicating that the nature of this low temperature attack was probably the same in both cases.

In experiments conducted at $800^\circ F$ ($425^\circ C$) with the metal specimens subjected to a mixture of K_2SO_4 and Na_2SO_4 (3 to 1 ratio) very little attack was observed on the carbon steels until sodium chloride was added to the mixture. As shown in Table 5, the corrosion rates for A106 and T11 steels increased rapidly when sodium chloride was included in the mixture in contact with the metal specimens. By contrast the 321 stainless steel showed negligible corrosion when the sodium chloride was added. The increased corrosion on the carbon steels cannot be completely attributed to chloride attack because the test for sulfide by the sodium azide technique was approximately twice as strong on the specimens exposed to sodium chloride. This result indicates that more of the sulfur participated in the corrosion reactions in the latter case, although the actual reaction mechanism is uncertain.

The most significant result in the experiments run at $1000^\circ F$ ($540^\circ C$) was a demonstration of the importance of SO_2 to the corrosion reactions. When corrosive mixtures containing K_2SO_4 , Na_2SO_4 , and $NaCl$ were subjected to the synthetic flue gas mixture without SO_2 present, the corrosion rates were comparable to those at $800^\circ F$ ($425^\circ C$) in the presence of SO_2 as shown in Table 5. However, when 250 ppm of SO_2 were added to the flue gases as had been the case in the experiments at 600 and $800^\circ F$ (315 and $425^\circ C$), a very large increase in the corrosion rate occurred. For A106 steel the increase was fourfold, for the T11 steel the increase was almost sixfold, and for the 321 stainless steel it was sixteenfold. These large increases in corrosion rates can be explained in terms of HCl released within the deposit as a result of the action of SO_2 .

DISCUSSION

This investigation of the effects of sulfur content of the refuse on the corrosion of boiler tube metals in the incinerator environment has demonstrated clearly that the corrosion rates of a variety of steels are significantly reduced as the sulfur content is increased. Increasing the sulfur content of the refuse from the normal 0.2 percent level to 0.75 and 1.5 percent increases the amount of SO_2 and sulfate compounds in the combustion products. On the other hand, the increased sulfur content results in a significant reduction in the chloride content of the deposits and of the particulates extracted from the furnace or the stack. These observations indicate that the following chemical reaction is occurring in the flue gas stream rather than in the deposit:



Because this hydrogen chloride is released in the gas stream it does not have the opportunity to act on the metal as it would by *in situ* formation beneath a deposit which adheres strongly to the tube metal. It also was noted when sulfur was added to the refuse that the deposits formed on the corrosion probe were of a light powdery nature and much less adherent than in the case when normal refuse was burned. The conversion of the metal chlorides to metal sulfates before deposition on the tubes would account for this effect, and would result in the presence of compounds in the deposit which have much higher melting points than the corresponding chlorides.

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 very low sulfur pressure (10^{-13} atmosphere) if the SO_2 or oxygen pressures are below 10^{-14} atmosphere [5]. At higher SO_2 or oxygen pressures iron oxides form.

The very low corrosion rates of steels exposed to the combustion products of sulfur-enriched refuse are undoubtedly attributable to the low (0.1 percent) chloride content of the tube deposit. This result is consistent with other data which show the negligible effect of small amounts of chloride in Na_2SO_4 on the corrosion rate of 18Cr-12Ni-1Nb steel [6].

In these and most other investigations of reaction between metals and inorganic compounds, the specimens are at the same temperature as the environment. However, in the case of heat recovery tubes

the furnace temperature is considerably higher than that of the tubes, in which case deposit decomposition reactions can become important. The present study has shown further that a significant increase in corrosion rates of metals occurs when the furnace gas temperature is increased from about 1400 to 1550°F (760 to 845°C). This higher gas temperature increases reaction rates in the deposit and provides a driving force for diffusion of corrosive materials to the metal surface beneath the deposit.

The data from the laboratory experiments confirmed the importance of sulfur oxides in converting chlorides into sulfates, thereby releasing HCl. When this occurs in a deposit on the heat recovery tube the corrosion from the HCl released is particularly severe. If this same reaction occurs in the flue gas stream, the HCl is released at that point rather than in the deposit and chloride corrosion is minimal. In addition if the HCl is released beneath the deposit and in the presence of iron oxide catalysts, it can be oxidized to elemental chlorine with increasingly greater corrosive effects. The overall effect then of increasing the amount of sulfur in the refuse is to cause the most serious corrosion-promoting reactions to occur in the gas stream rather than in and underneath the deposits thus eliminating the primary cause of the corrosion.

The most important implication of the results of this research program is for combined firing of municipal refuse with a high-sulfur coal. In the efficient combustion of coal, most of its sulfur is converted to sulfur oxides and the coal would thus act in the same fashion as the sulfur addition to the refuse in reducing corrosion. The question of stack emissions of sulfur oxides remains, but there is evidence from European practice in combined firing of coal and refuse that sulfur oxide emissions can be reduced under these circumstances. Measurements made at the Munich incinerators, where such combined firing was used, showed that while 92 percent of the sulfur oxides from the coal went out the stack when the coal was fired alone, only about 30 percent of the sulfur oxides were found in the effluent when the coal was burned with refuse [7]. However, this was a peculiar circumstance in which the sulfur content of the refuse was higher than that of the coal, and is not quite comparable to the suggested firing of a high-sulfur coal with a low-sulfur refuse. Nevertheless, the relatively high content of alkaline oxides, namely, sodium oxide, potassium oxide, and calcium oxide in refuse combustion products should be able to react with the sulfur oxides in the flame zone to form sulfates and thus reduce the emissions of sulfur oxides. The result will probably be an increase in particulate loading of the stack gases, but

this can be reduced to allowable limits by efficient electrostatic precipitators, which is usually preferable to sulfur oxide scrubbing.

CONCLUSIONS

The results of this research program show that the addition of sulfur to municipal refuse can produce a sharp decrease in the corrosion rates of both carbon steels and stainless steels. In the case of a low alloy steel, the sulfur addition must be sufficient to reduce the chloride content of the tube deposits to a concentration of 0.1 percent in order to achieve the low corrosion rates.

For metal temperatures in the range of 900 to 1200°F (480 to 650°C) increasing the furnace gas temperature from 1400-1550°F (760-845°C) increased the corrosion rates of both the carbon steels and the stainless steels by 2 to 4 times. In the case of metal temperatures from 400-800°F (205-425°C), the increase of gas temperature had little effect on the corrosion rates.

Two general operating procedures were indicated by this research program to minimize corrosion when municipal refuse is burned in steam generating systems:

- 1) It is advisable to process the refuse in such a manner as to avoid high concentrations of chlorine and/or to mix into the refuse sufficient quantities of sulfur-bearing material to minimize the amount of chloride deposit on tube surfaces.
- 2) Care should be taken to maintain metal temperatures well below 800°F (425°C) and to avoid exposure of tubes operating at high temperature, to furnace gas temperatures over 1450°F (790°C).

ACKNOWLEDGMENTS

This project has been financed in part with Federal funds from the Environmental Protection Agency under Grant Number R800055 from the Solid and Hazardous Waste Research Laboratory, Cincinnati, Ohio. The contents do not necessarily reflect the views and policies of the Environmental Protection Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

Mr. Donald Oberacker monitored this program for the Solid and Hazardous Waste Research Laboratory, EPA, and his assistance and encouragement is greatly appreciated.

The cooperation of the administrative and operating staff of the Miami County, Ohio, incinerator

also is appreciated.

The authors also wish to acknowledge the efforts of the Battelle-Columbus staff members: J. Faught, J. Hunt, W. Stieglmeyer, P. Webb, and E. White.

REFERENCES

- [1] Krause, H. H., Vaughan, D. A., and Miller, P. D., "Corrosion and Deposits From Combustion of Solid Waste," *Journal of Engineering for Power, Trans. ASME, Series A*, Vol. 95, 1973, pp. 45-52.
- [2] Krause, H. H., Vaughan, D. A., and Miller, P. D., "Corrosion and Deposits From Combustion of Solid Waste. Part 2—Chloride Effects on Boiler Tube and Scrubber Metals," *Journal of Engineering for Power, Trans. ASME, Series A*, Vol. 96, 1974, pp. 216-222.
- [3] Miller, P. D., and Krause, H. H., "Fireside Metal Wastage in Municipal Incinerators," ASME Winter Annual Meeting, Paper No. 70-WA/INC-2.
- [4] Miller, P. D., and Krause, H. H., "Factors Influencing the Corrosion of Boiler Steels in Municipal Incinerators," *Corrosion*, Vol. 27, 1971, pp. 31-45.
- [5] Ross, T. K., "The Distribution of Sulfur in Corrosion Products Formed by Sulfur Oxide on Mild Steel," *Corrosion Science*, Vol. 5, 1965, pp. 327-29.
- [6] Johnson, H. R., and Littler, G. J., *The Mechanism of Corrosion by Fuel Impurities*, London: Butterworth, 1963.
- [7] Roberts, R. M., et al., "Systems Evaluation of Refuse as a Low-Sulfur Fuel," U.S. Environmental Protection Agency Report No. F-1295, Vol. 1, Nov. 1971, p. II-32.