

CORROSION MECHANISMS IN MUNICIPAL INCINERATORS
VERSUS REFUSE COMPOSITION*

by

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Corrosion of heat recovery tubes exposed to combustion products from burning of municipal and industrial wastes has been a major problem with respect to utilizing heat energy created in disposal of solid waste by incineration. Influence of Cl⁻ and S content is discussed, and effects of temperature are evaluated.

Introduction

Increasing attention is being given to the disposal of refuse by incineration with energy recovery. We can expect it to become an economical process if the incineration does not create difficult to solve pollution problems. The heat (energy) can be extracted by water-wall tubes and convection pass tubes inserted in the hot gas. The technology of water-wall incinerators has advanced to a state of rather extensive use in Europe and several are operating in the United States. However, corrosion problems have been reported in most of the operating units. Municipal refuse is also being considered as a supplementary fuel to existing fossil-fuel power generating stations and for industrial needs for process steam. To provide guidance in materials selection for both pollution-control and heat-recovery systems, the magnitude of the corrosive attack by the hot gases and deposits has been investigated in a conventional ceramic-lined incinerator operating with typical municipal refuse.

Previous Battelle research 1-10 described the mechanism and extent of fireside metal wastage by incineration of municipal refuse. On the basis of these studies, corrosion mechanisms were proposed to explain the attack, which occurred over a range of metal temperatures. Furthermore, it was shown that chlorine, as HCl and/or solid chloride deposits, contributes significantly to high- and low-temperature corrosion of structural material in incinerators.

Because of the wide variations in refuse composition and the possibility of adverse effect upon metals employed in heat-recovery systems by these variations, a program was initiated to evaluate specific variables such as chlorine and sulfur. As it is difficult to control refuse collection and/or sort sufficient quantities of classified refuse to maintain operation at an operating incinerator, it was concluded that the most

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feasible approach was to add significant amounts of the variables of interest to the refuse. The increase of HCl and/or chloride content in the combustion products by the addition of PVC to the refuse incinerated was considered to be of potential interest with respect to its effect upon fireside corrosion and with respect to potential problems in disposing of plastic wastes. Although burning of plastics in well-designed incinerators at normal operating temperatures [1700-2000.°F (930-1100°C)] with an excess of air would not be expected to present difficulties, some grate damage has been observed. However, combustion of PVC, which accounts for 15-20% of plastic production, and approximately 10% of the plastic waste, has been reported by Meimburg¹¹ and Fessler, Lieb, and Spohn¹² to cause severe corrosion of furnace components and heat exchangers. Therefore, the initial investigation of refuse composition on fireside corrosion in municipal incinerators was designed to determine the effects of increasing the amount of chlorine in the combustion products by increasing the PVC content of the refuse.

Variations in the sulfur content may occur when the amounts of some kinds of refuse, such as plastics, rubber, etc., change, but in general the sulfur content is low (0.2%) in most refuse. For test burnings, the addition of elemental sulfur appeared to be the most appropriate method of attaining sulfur contents equivalent to that of fossile fuels. Also, there is considerable interest in the combined burning of coal and refuse for power generation as this method has been practiced in Europe for several years. An experiment of this kind is being conducted in the United States by Union Electric at their Meramec station near St. Louis. However, the objective of this research program was to obtain a better understanding of factors that contribute to the corrosion of structural and energy-recovery systems associated with municipal refuse incinerators.

Experimental Program

As it was not feasible to conduct experiments with controlled additions of specific materials (PVC or S) over long periods of time, this program consisted of exposing corrosion probes for one working day. Because previous experience with fireside corrosion in municipal incinerators showed an increasing corrosion rate with decreasing time (Figure 1), the magnitude of attack in these short exposure periods was expected to be sufficient to reveal differences as a function of refuse composition. Hence, a short (<10-hour) exposure time was selected for the investigation of corrosion rate versus induced variables in refuse composition. These short-time experiments are not intended to establish long-term performance but to show differences in the corrosiveness of the combustion environment.

The data illustrate the corrosion rates as a function of exposure time and metal temperature, the latter being controlled by the internal flow of cooling air through the corrosion probe, which is described later. Also, the effect of furnace-gas temperature variations on the corrosion of heat-recovery tubes was investigated. This was accomplished by inserting

corrosion probes, simultaneously, at the two positions shown in Figure 2 where the furnace gas temperatures differed by 100-150°F (55-85°C). Because the operational parameters in the incinerator vary with refuse, it was necessary to average the temperature records over the period of exposure. During any experiment, the gas temperature, as measured near the probe or taken from the incinerator instrument chart record, differed by 100-300°F (55-165°C), depending upon location of the corrosion probe. The average temperature for seven experiments consisting of 11 probe exposures are shown in Table I.

It is evident that the furnace gas temperature, as measured by thermocouples extending through the probes, differed significantly from that obtained on the chart record of the incinerator instrument panel. This is undoubtedly a result of thermocouple location and position of over-fire air entry ports. However, where two probes were inserted, marked differences in temperature were measured. This difference in gas temperature resulted in some variations in the temperature of corresponding specimens by any two corrosion probes.

TABLE I

Experiment Number	Probe Number	Location of Probe	Addition wt. %	Average Gas Temperature Probe, C°	Incinerator, C° (1)
72-1	16	1	0	770 (2)	700
72-2	17	1	2-PVC	782 (2)	710
72-3	18	1	1-PVC	943 (2)	870
72-4	19	1	0.5-PVC	760	680
72-4	20	2	0.5-PVC	816 (3)	680
73-1	21	1	0	770	727
73-1	22	2	0	904	727
73-2	23	1	1.5-S	770	704
73-2	24	2	1.5-S	820	704
73-3	25	1	.75-S	782	710
73-3	26	2	.75-S	843	710

- (1) The incinerator temperature is that recorded at the instrument panel from a permanently installed thermocouple.
- (2) Estimate from incinerator versus probe measured temperatures.
- (3) The thermocouple attached to probe failed but an auxiliary thermocouple inserted in the furnace at this location gave the reported value.

The probe was designed to include 34 cylindrical specimens nested together end to end and then inserted into the incinerator through a side wall. The section of the probe extending through the wall was water cooled, while the specimens exposed within the furnace were cooled by air flowing inside the tubular specimens. A computer analysis had been used in a previous program to ascertain the geometry of the internal support tube required to give the most linear specimen temperature variation over the range of about 350° to 1300°F (175-700°C) for a probe with 34 specimens. Each specimen was about 1.25 inches (32mm) in OD, 1.00 inch (25mm) in ID, and

1.5 inches (38mm) long. The composition of the alloys used to make up the corrosion probes is given in Table 2.

TABLE 2 - Nominal Compositions of Steels Tested

Alloys	Weight Percent										
	C	Cr	Ni	Si	Mn	Mo	Ti	Cu	P	S	Fe
A 106 Grade B ⁽¹⁾	0.30	-	-	0.10	0.65	-	-	-	0.48	0.058	Bal
A 213-T11	0.15	1.0-1.5	-	0.75	0.5	0.5	-	-	0.03	0.03	Bal
316	0.07	17.4	12.2	0.36	2.0	2.12	-	-	0.08	0.01	Bal
203 EZ	0.05	16.6	5.5	0.37	5.8	0.15	-	1.9	0.02	0.31	Bal
310	0.15	24-26	19-22	0.75	2.0	-	-	-	0.02	0.31	Bal
321	0.08	17-20	9-13	0.75	2.0	-	0.60	-	0.03	0.03	Bal
Incolony 825	0.03	21.5	42.0	0.25	0.5	3.0	-	2.25	-	-	Bal
431	0.15	16.0	2.2	0.34	0.6	0.16	-	-	0.02	0.01	Bal
446	0.11	27.2	0.3	0.47	1.1	-	-	-	0.02	0.02	Bal

(1) Specimens of the steel were coated with Cr or FeAl by plasma spray and diffusion heat treated at 2150°F (1180°C) or 1885°F (1030°C), respectively, to produce metallurgical bond and surfaces to be corrosion evaluated.

Figure 3 is a schematic of the final exposure probe apparatus. The specimens were nested together with lap joints, as shown in Detail A, and retained axially at the cooling-air-outlet end by a retainer which was fixed to the internal support tube with webs as shown in Section A-A. The axial restraining force in the internal support tube was obtained by compressing the spring on the air-inlet end of the probe at assembly. Also, the spring compensated for differential thermal expansion between the specimens and the internal support tube.

Specimen temperatures were measured at four stations with Type K thermocouples either welded into the wall of the specimens or inserted into recesses drilled lengthwise into one end of the appropriate specimens. The thermocouple lead wires were brought out of the probe through the center of the internal support tube, so that temperatures could be recorded continuously on a strip-chart potentiometer recorder. Since the computed results indicated that the temperature variation is linear for regions with a constant gap between the internal support tube and the specimens the four temperatures accurately reflect the specimen temperatures.

The specimen temperatures were controlled by regulating the amount of cooling air admitted to the probe. The output from a control thermocouple, which was attached to the specimen at the same axial location as Thermocouple 3, was monitored by a proportional temperature controller. At the start of a test, the controller maintained this temperature by varying the amount of cooling air bypassing the probe through a motorized butterfly valve located between the blower and the probe. A Roots-blower air pump delivering up to about 34 cfm (1000 l/min) was used with a 5-horsepower (3.7kw) motor as a drive.

Although the temperature of corresponding specimens varied from one probe to another, the specimen temperature employed in the analysis of corrosion-rate data was obtained by interpolation of temperatures recorded for Specimens 1, 9, 17, 27, and 34 on each probe.

Description of the Alloys and Coatings

Most of the alloys (Table 2) were available as tubes, from which the specimens were cut and machined to a lap fit. In some cases, only rod material was available. The machined specimens were degreased in acetone, rinsed with alcohol, air dried, and weighed before assembling on the corrosion probe. For experiments run in 1972 (72-X), all of the specimens were exposed in the as-machined and cleaned condition, except for one experiment in which a representative specimen of each alloy was preoxidized at 1150°F (620°C) for 1/2 hour in air before making the probe assembly. During the 1973 experiments (73-X), the specimens of 316 stainless steel were heat treated for 3 hours at 1200°F (650°C) and 100 hours at 1550°F (845°C) to stabilize the material against sensitization during exposure to the hot incinerator gases. Also, two types of coatings (Cr or FeAl) were applied by a plasma spray to specimens of the A 106 steel. These coatings were metallurgically bonded to the base steel by heating in vacuum to high temperatures [1250 and 1880°F (1175 and 1030°C), respectively] for 10 hours. After the diffusion treatment, the coated specimens were wire brushed to remove any loose deposit, weighed, and assembled on the probes.

Corrosion Analyses

Corrosion rates were determined for most of the 34 specimens on each of the 11 probe experiments by comparing the initial weight with that obtained after removal of the corrosion products. The 34 corrosion specimens were first separated from each other by tapping with a fiber mallet. Then the amount of metal wastage was determined by chemically or electrochemically stripping the residual deposits and scale from each specimen using standard procedures. The specimens of T11 and A106 were stripped cathodically in 10% H₂SO₄ containing 1-ethylquinolinium iodide inhibitor, while the stainless steel specimens were descaled in a two-step process, first with 11% NaOH and 5% KMnO₄ at 212 F (100 C) and then with 20% HNO₃ with 2% HF at 130 F (54 C). These methods of scale removal were employed to avoid attack of the uncorroded substrate metals. Prior to removal of the corrosion products and the deposits, optical, and X-ray diffraction studies were made of the scale and deposits on several specimens to determine what phase changes occurred as a result of the type or the amount of addition to the refuse. Also, representative specimens were sectioned and examined metallographically to determine the mode of attack by the combustion environments.

Typical corrosion rate data versus metal temperature for T11 steel exposed to two furnace gas temperatures are presented graphically in Figure 4. These data show that the corrosion rates are affected by metal temperature up to approximately 750°F (400°C) above which furnace gas

temperature has a more dramatic effect than metal temperature. Although several specimens were preoxidized, the squared points in Figure 4, this did not alter their corrosion rates appreciably. Based upon plots of this type, it was possible to obtain corrosion rate data for various alloys at specific temperatures as a function of Cl⁻ and S content of refuse. Results of these analyses are presented in Tables 3 and 4.

The effects of increasing the chloride or sulfur oxide content of the combustion products on the corrosion rate of A 106 carbon steel are illustrated graphically in Figures 5 and 6. These results show that, for this steel, the corrosion rate increases with increasing chloride content, but decreases when a sufficient amount of sulfur is added to the refuse.

In the case of the stainless steels (316, 310, 321, and 446) and Incoloy 825, however, the corrosion rates were not significantly affected by the chloride content of the refuse. Furthermore, the corrosion rates for these alloys were not affected by specimen temperature but, as tabulated below, an increase in the furnace-gas temperature by 150° F (66° C) resulted in a large increase in corrosion rate:

Alloy	760°C Gas		~843°C Gas	
	mils/hr	µm/hr	mils/hr	µm/hr
310	0.032	0.81	0.170	4.3
446	0.050	1.3	0.136	3.4
825	0.056	1.4	0.259	6.6
316	0.056	1.4	0.203	5.2
321	0.109	2.8	0.201	5.1

When sulfur was added to the refuse, however, the corrosion rates of the stainless steel was markedly reduced as shown in the last two columns of Table 4. The data for Types 316 and 446 are presented graphically in Figure 7.

Table 3- Results of Corrosion Rate Analysis versus specimen temperature at various furnace gas temperatures

Percent Cl-Content of Refuse: 0.5		0.75					
Furnace-Gas Temperature (1)		(1420)	1400	1500	1730	(1440)	
Alloy	Temperature	Corrosion Rate, mils/hour (2)					
T11	300° F	150° C	0.02	0.14	0.10	0.24	0.16
	500	260	0.10	0.23	0.20	0.27	0.25
	700	370	0.12	0.25	0.25	0.30	0.27
	900	480	0.18	0.28	0.36	0.37	0.36
	1100	590	0.33	0.32	0.71	0.54	0.60
825	700	370	-	0.10	0.10	0.08	0.02
	1100	590	0.07	0.05	0.28	0.24	0.06
321	1100	590	0.08	0.14	0.29	0.19	0.13
310	1100	590	0.023	0.03	0.20	0.15	0.05

(1) Temperature in parentheses were estimated based upon incinerator chart record.

(2) 1 mil/hr = 25.4 µm/hr.

Mode of Attack

As it is important to establish whether the attack is uniform or localized at specific sites in the metal structure, metallographic examinations were made of the several alloys and coatings described in Table 2, after exposure to the various environmental conditions produced by combustion of refuse of normal and modified compositions. The results of these examinations are given below by material.

A106 low-carbon steel exhibited general attack, with some evidence of pitting when exposed to normal refuse, as shown in Figures 8a and 8b which are typical of two metal temperatures, Zones 400-800 F (200-430 C) and 900-1300° F (480-700° C), respectively. The higher metal temperature produced some surface decarburization as well as internal microstructural changes. When PVC was added to the refuse, similar attack was observed with more severe pitting. However, the addition of 1.5% sulfur essentially eliminated the pitting attack as shown in Figure 8c and, as the weight loss data show, reduced the general attack by a factor of three.

A213-T11 steel was attacked in the same manner as A106 in normal and PVC-enriched refuse, but was not included on the corrosion probe when sulfur was added to the refuse.

446 steel specimens exposed to normal refuse were attacked at grain boundaries, as shown in Figure 9a. Figure 9b illustrates the type of attack that occurred when PVC was added to the refuse. While the latter appeared to have a more irregular attack than is seen in Figure 9a, the magnitude of the weight loss was essentially the same. The addition of sulfur to the refuse greatly reduced the amount of the general attack and eliminated the intergranular dissolution, as shown in Figure 9c.

431 steel was evaluated in normal refuse and sulfur-doped refuse. This 16% Cr alloy was much less resistant to the combustion products of normal refuse than was the 27% Cr 466 alloy. The attack was of a general pitting type with little or no grain boundary penetration. The addition of sulfur to the refuse reduced the attack of 431 steel by a factor of two to three.

316 and 302EZ stainless steels had very similar behavior in that they were attacked intergranularly by the combustion products of normal refuse, and refuse to which PVC had been added. These steels were resistant and exhibited little or no grain boundary attack when exposed to combustion products of the refuse with an increased sulfur content. Photomicrographs of 316 steel exposed to the various environments are shown in Figures 10a, b, and c.

310 stainless was exposed with and without PVC added to the refuse and exhibited the best resistance of the steels investigated. However, when this steel was exposed to the higher temperature furnace gases, the attack increased and grain boundary attack similar to that of 316 steel occurred.

Previously¹, it was shown that austenitic stainless steels cracked by stress corrosion when exposed to a humid environment in contact with combustion deposit.

321 stainless steel and Incolony 825 were similar to 310 with only slight differences in magnitude of attack by the combustion products of normal refuse of PVC-doped refuse. These materials were not exposed to the combustion products of refuse with increased sulfur content.

Diffusion-bonded coatings of FeAl and chromium on A106 low-carbon steel were exposed to the combustion environment of normal refuse and high-sulfur refuse. In the case of the FeAl-coated specimens, a solid solution zone of approximately 10 mils [0.25mm] was developed by the diffusion treatment. The excess FeAl was removed in most cases before exposing the specimen to combustion environment. In normal refuse-combustion environments, there was considerable general surface attack, plus grain boundary penetration to a depth of 6-8 mils (0.15-0.20mm). Similar attack occurred when sulfur was added to the refuse, but the magnitude of both types of attack was somewhat less. It is interesting to note that when the FeAl compound layer (50% Al, 50% Fe) was not removed before exposure, the attack was very slight and an adherent oxide film formed on the surface.

The diffusion treatment of chromium-coated A106 steel produced a slight decarburization of the steel and an interface layer of chromium carbide between the substrate and the chromium coating. Although only slight attack of the chromium by the combustion environment was observed, it is unlikely that the chromium layer would maintain adherence on this steel in extended exposure times. Perhaps this type of coating, if applied to another steel where the carbide interface did not form, would provide beneficial corrosion resistance to the refuse combustion environments.

Deposit and Corrosion Product Analysis

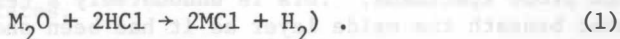
As the corrosion probes were inserted into the fireside chamber of the incinerator above the effluent end of the grate, the airflow carried sufficient particulate matter to produce a deposit 1/4 to 1/2-inch (6-12mm) thick over approximately one-third of the 1.25-inch (31mm) diameter tube in the 10-hour exposure periods. The remaining two-thirds of the surface contained only a thin deposit and an oxide layer, the oxide layer extending completely around the tube beneath the deposit. The thickness of the oxide layer varied for the various alloys and depended to some extent upon specimen temperature. These layers of deposit and oxide were removed mechanically and collected, by temperature zones, for optical emission spectroscopy analysis of the metallic element present. Wet chemical techniques were employed to determine the chlorine (Cl^-) and sulfur ($SO_4^{=}$) content in the deposits. X-ray diffraction analyses were made of the deposit at one or two temperature zones on the probe. Also, the scales, which formed at the metal-deposit interface, were identified by X-ray diffraction and by optical microscopy examinations.

The results of the analysis of the deposits obtained from runs with PVC additions to the refuse are presented in Table 5, in which low and high temperature zones on each probe are averages for given. Of particular interest is the increasing chloride content in the deposit with increasing PVC content of the refuse. It was noted, however, that the chloride content was somewhat low for Probes 17 and 20, which were exposed to a higher temperature furnace gas. Omitting the analyses for these two probes, the chloride content in the deposit versus PVC content of the refuse is illustrated in Figure 11. It is seen here that the chloride content of the deposit increases with PVC content of the refuse, but decreases with increasing metal temperature. As pointed out above, increasing the gas temperature also decreases the chloride content of the deposit. Phase studies of these deposits by X-ray diffraction reveal (Table 5) sulfate, silicates, and chlorides; the intensity of the chloride phases increase with the amount of PVC added to the refuse. The chloride permeates the semiprotective oxide that forms between the deposits and the substrate metal and forms iron chloride on the substrate metal surface. The scale that forms next to the metal consists of the phases described in Table 6. When large amounts of PVC were added to the refuse, the iron chloride, on specimens at temperatures of 400-800°F (200-430°C), was found to form a continuous layer adjacent to the metal substrate, by optical microscopy examination, also this examination showed the FeS reaction product (Table 6) to form between the iron chloride layer and the oxide layer in the low temperature [400-800°F(200-430°C)] zone on the corrosion probe. The FeS forms on the metal substrate in the high temperature [800-1200°F (480-650°C)] zone where the iron chloride agglomerates to form islands on the metal surface, with the FeS forming between the islands. The composition of the deposits on probes exposed to combustion products of refuse with and without sulfur additions are presented in Table 7. There are fluctuations in the amounts of all elements present from one area to another in the deposit as well as from one probe to another. It is surprising, however, that the S⁼ content increased by only 1% when sulfur was added to the refuse. On the other hand, the Cl⁻ content decreased by nearly 5%, to less than 0.1%, with the addition of 1.5% sulfur. These data along with the corrosion rate data, described previously, suggest that the corrosiveness of the incinerator combustion products varies directly with the Cl⁻ content of the resulting deposit. Presumably, the lack of an increase in S concentration in the deposit with increasing sulfur in the refuse is related to the type of compound formed. For example, the increase in some of the heavy metal elements such as Pb and Zn, will result in a low weight percent of sulfur in the deposit. These heavy metal elements were found to be present in even higher concentrations in the fly ash particulates collected with the gas samples taken from the furnace and from the stack.

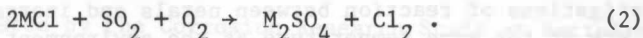
Discussion of Results

The results of these investigations of refuse composition on fireside corrosion of heat recovery tubes show strikingly opposite effects by chlorine and sulfur in the refuse. An increase in the available chlorine increases the corrosion rate of low alloy steels, whereas an increase in sulfur decreases the corrosion rate of all steels investigated. The major

contribution of these compositional variables to the corrosion reaction responsible for these changes in corrosion rates is in the type of compounds that deposit on the simulated heat recovery tube, the corrosion probe. The analysis of probe deposits, particulates, and gaseous species shows that increasing the chlorine or sulfur contents in the refuse increases the amount of these elements in the deposit and in extracted particulates in proportion to the amounts added. The corrosion rate and combustion product analyses reported confirm the importance of the chloride reaction described in References 1 and 13. It is evident, however, that the role of the HCl, generated by combustion of PVC, is to increase the inorganic (alkali) chlorides by the reaction:



The chlorides that deposit on the corrosion probes are mainly sodium and potassium salts, but also contain other metals such as lead and zinc. The mixture of these salts forms low-melting-point eutectic compositions that permeate and destroy the initial oxide scale that normally forms on metals exposed at the temperatures explored in this study. It is important to note that, although the metal temperatures were controlled, the deposits were exposed to much hotter incinerator gases. The deposit temperatures were undoubtedly 300°F (165°C) higher than the highest metal temperature. At the higher temperatures [1600°F (870°C)], the chlorides decompose and/or react with other incinerator gases releasing chlorine which attacks the substrate metal. One of the possible reactions that would account for the production of chlorine is



In the present investigation, which was for short (10-hour) exposure times, the amount of chloride in the deposit with or without PVC additions was much larger than in a previous investigation¹ which was for long (100-800 hour) exposure times. The chloride content of the deposit was shown earlier,¹ however, to decrease with increasing of exposure time. This would be expected through Reaction (2) where the SO₂ content in the combustion products is low. Perhaps part of the reduction in corrosion rate with exposure time, as shown in Figure 1, results from the reduction in chloride content of the deposit with time. The short and long exposure time corrosion rates, shown in Figure 1, from our corrosion probe experiments, are in good agreement with those of superheater tubes which failed at the Harrisburg, Pennsylvania incinerator. After 3000 hours of operation, the 165-mil (4 mm) tubes failed in an area where the soot blower was used to remove the deposit and protective oxide scale at least daily. Thus the clean tube metal was exposed in much the same manner as the short time (10-hour) exposure of the Battelle probes. The corrosion rate of 0.055 mil/hour (1.4 μm/hr) at the Harrisburg tube failure is comparable to the 0.10 mil/hour (2.5 μm/hr) corrosion rate obtained with normal refuse in the present study. In an area away from the soot blower, the Harrisburg tubes had lost ~ 15 mils (0.38 mm) in 3000 hours or 0.005 mils/hour (0.13 μmeters/hour), which agrees quite well with the long time [800 hour] Battelle data of 0.005 mils/hr (0.13 μmeters/hour) at 400°F (200°C) [Figure 1].

Increasing the sulfur content of the refuse from the normal 0.2% level to 1.0 and 1.7% level increased the amount of SO₂ and sulfate compounds in the combustion products but reduced significantly the chloride content of the deposit on the corrosion probe. These observations show that, where sulfur oxides are present the combustion favors the formation of sulfates.

The lower corrosion rates observed when sulfur was added to the refuse show, as expected, that sulfates are more stable than chlorides. However, 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 a result of the reducing environment beneath the oxide layer as it has been shown¹⁴ that FeS will form at very low sulfur pressure (10⁻¹³ atmosphere) if the SO₂ or O₂ pressures are below 10⁻¹⁴ atmosphere. At higher SO₂ or O₂ pressures, iron oxides form. Several reactions have been proposed¹ for bisulfate, pyrosulfate, and alkali trisulfates attack of iron to give FeS. However, the present study has shown these reactions to be slow, compared to the chloride reaction, as the corrosion rates of steel exposed to the combustion product of high sulfur refuse were very low [0.05 mil/hr (1.3 μm/hr)] compared to those [0.15-0.20 mil/hour (3.8-5.1 μm/hr)] for normal refuse, or to the higher corrosion rates obtained when the chloride content of the refuse was increased. The very low corrosion rates of steels exposed to the combustion products of sulfur enriched refuse were undoubtedly attributable to the low (0.1%) chloride content in the tube deposit. This is consistent with other data¹⁵ which show the negligible effect of this amount of chloride in Na₂SO₄ on the corrosion rate of a 18Cr-12Ni-1Nb steel. However, in these and most other investigations of reaction between metals and inorganic compounds, the specimens are at the same temperature as the environment. In the case of heat recovery tubes, the furnace temperature is considerably higher than the tubes, in which case, deposit decomposition reactions 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 1400 to 1550 F (760 to 840°C). This is particularly evident for metal temperatures above 800 F (430 C), but laboratory investigations under more controlled conditions are needed to evaluate this effect in detail.

Conclusions

The results show that the sulfur and chlorine contents of refuse have significant effects on the corrosion of metal surfaces exposed to hot combustion products. Corrosion was accelerated when the chloride content of the refuse increased, but was reduced when the sulfur content of the refuse was increased.

The amounts of inorganic chloride or sulfate formed in the tube deposits and in the fly ash were found to be proportional to the amounts of chlorine of sulfur in the refuse.

Inasmuch as the chlorine content of normal refuse is high, relative to the sulfur content, a small (0.25%) addition of chloride

produced a greater increase in the corrosion rates of low alloy steels at 400-800°F (200-430°C) metal temperature than did larger additions of chloride. At metal temperatures above 900°F (480°C), the corrosion rates of these steels increased linearly with the amount of chloride added to the refuse. However, the corrosion rates of stainless steels were not affected by the chloride content of the refuse, but increases with furnace gas temperature.

On the other hand, 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, the sulfur addition must be sufficient to reduce the chloride content of the deposit to the 0.1% level in order to achieve low corrosion rates.

It is concluded that through control of refuse composition by additives and/or selection of refuse mixture, the corrosion rates for several of the materials investigated can be held to an acceptable level, providing that the metal temperatures do not exceed 800°F (430°C) and the furnace-gas temperature does not exceed 1450°F (790°C). It is important to note, in addition, that the corrosion rates obtained for 10-hour exposure times cannot be extrapolated to long time service.

Additional Comments from Battelle

R. B. Engdahl

The data accumulated by the Corrosion Research Staff at Battelle: Boyd, Miller, Vaughan, and Krause, show that the overwhelming factor in refuse-fired boilers is chloride attack. This goes on whether the furnace conditions are oxidizing or reducing. That is, even when the furnace atmosphere is on the oxidizing side, conditions within the mineral deposit on the tube surface may be devoid of oxygen. Where reducing conditions do occur right next to the tube metal, of course, attack on the metal does occur.

For example, electron probe analysis of the layers on corroded tubes shows that minerals exist there which could only be formed under reducing conditions, but at the same time, furnace gas analysis in the vicinity showed strongly oxidizing conditions.

In general, the European practice has been to "solve" the wall tube corrosion-erosion problem by covering them. Hence, the remaining corrosion problem is primarily on the superheaters. Although there may be momentary excursions into reducing conditions in spots around superheaters, it seems to be unlikely that many superheaters are subjected to severe and massive flows of oxygen-deficient gases. Yet superheater corrosion is common. And so are chlorides common in refuse - the 0.5 percent in the bulk refuse quickly accumulates to become several percent of the tube deposits, hence, their corrosive action at high temperatures. Closely related to this situation

is the "protective" action of sulfur in the fuel. If there is sufficient sulfur in the fuel, sulfates will be formed prior to deposition and they are relatively innocuous compared to chlorides in a deposit. Strongly reducing furnace atmospheres could interfere with this sulfate formation and thus promote corrosion by chlorides and unoxidizing sulfur.

To summarize this subject: even in the very common condition with refuse burning where very strongly oxidizing furnace gases are typical, there is a distinct possibility that the zone next to the tube metal is indeed reducing, hence reaction of the deposit with the metal surface can take place.

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**TABLE 4 — Results of Corrosion Rate Analysis Versus Specimen Temperature
at Various Furnace Gas Temperatures
(Normal, PVC and/or S Doped Refuse)**

Percent Cl and S in Refuse: Furnace-Gas Temperature, F: ⁽¹⁾		0.5-0.25			0.75-0.25		1.5-0.25	2.5-0.25	0.5-1.0		0.5-1.75	
		(1420)	1480	1660	1400	1550	(1730)	(1440)	1440	1550	1420	1510
Alloys	Temperature, F	Corrosion Rate, mils/hour ⁽³⁾										
A106	300	0.05	0.11	0.13	0.11	0.10	0.15	0.10	0.05	0.14	0.01	—
	500	0.16	0.19	0.17	0.22	0.19	0.24	0.23	0.15	0.26	0.05	0.08
	700	0.18	0.22	0.24	0.25	0.23	0.28	0.27	0.22	0.34	0.07	0.09
	900	0.20	0.28	0.37	0.28	0.31	0.34	0.33	0.24	0.39	0.09	0.11
	1100	0.23	0.42	0.69	0.31	0.51	0.43	0.55	0.32	0.53	0.12	0.22
316SS	700	—	0.04	0.01	—	—	—	—	0.005	0.02	0.005	0.01
	900	—	0.14	0.09	—	—	—	—	0.006	0.02	0.009	0.012
	1100	0.06	0.23	0.17	0.12	0.25	0.18	0.07	0.010	0.03	0.015	0.028
203EZ	700	—	0.155	0.10	—	—	—	—	0.040	0.050	0.015	0.020
	400	—	0.17	0.125	—	—	—	—	0.040	0.060	0.060	0.030
	1100	—	0.185	0.15	—	—	—	—	0.045	0.060	0.060	0.030
431	700	—	0.16	0.43	—	—	—	—	0.025	0.055	0.005	0.025
	900	—	0.125	0.25	—	—	—	—	0.025	0.055	0.010	0.025
	1100	—	0.19	0.165	—	—	—	—	0.05	0.065	0.015	0.035
446	700	—	0.07	0.05	0.11	0.09	0.20	0.09	0.03	0.05	0.003	0.01
	900	0.05	0.07	0.06	0.07	0.11	0.20	0.09	0.03	0.055	0.004	0.01
	1100	0.05	0.07	0.06	0.03	0.13	0.20	0.09	0.03	0.06	0.005	0.01
Cr coated ⁽²⁾	700	—	0.10	0.14	—	—	—	—	0.07	0.17	0.005	0.02
	900	—	0.15	0.15	—	—	—	—	0.07	0.17	0.01	0.02
	1100	—	0.22	0.16	—	—	—	—	0.07	0.20	0.015	0.02
Al coated ⁽²⁾	700	—	0.105	0.20	—	—	—	—	(2)	(2)	0.025	0.01
	900	—	0.125	0.31	—	—	—	—	(2)	(2)	0.025	0.015
	1100	—	0.25	0.50	—	—	—	—	(2)	(2)	0.045	0.03

(1) Furnace temperatures in parentheses are estimated from incinerator records while the others were measured at probe locations.

(2) Some spalling of the Al and Cr coatings caused error in corrosion rate analyses, numbers shown are maximum and include spalling losses.

(3) 1 mil/hr = 25.4 μm/hr.

$$^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32)$$

TABLE 5 – Chemical Assay of Deposits Versus PVC Addition to Refuse

Elements Detected	Probe 16, 0% PVC		Probe 19, 0.5% PVC		Probe 20, 0.5% PVC		Probe 18, 1% PVC		Probe 17, 2% PVC	
	400 F - 800 F	800 F - 1200 F	400 F - 800 F	800 F - 1200 F	400 F - 800 F	800 F - 1200 F	400 F - 800 F	800 F - 1200 F	400 F - 800 F	800 F - 1200 F
Concentration, Weight Percent										
Na	7.5	7.5	6.9	7.5	6.9	7.5	6.5	4.5	5.0	4.0
K	11.5	19.0	3.7	3.6	4.4	3.7	10.8	7.5	8.5	8.0
Ca	6.0	7.5	6.4	12.5	6.7	12.5	10.8	12.5	7.5	10.0
Mg	2.0	3.0	1.0	2.0	0.6	2.0	3.3	3.0	2.5	3.5
Pb	2.5	1.0	3.2	0.3	3.1	0.3	3.0	0.3	2.0	0.5
Zn	6.0	6.5	6.9	7.5	6.9	7.5	6.5	4.5	6.0	4.5
Fe	5.0	6.0	12.3	7.1	12.6	6.6	8.5	6.3	6.5	6.0
Al	14.5	12.5	3.0	5.6	3.3	6.0	6.5	7.3	7.5	8.5
Si	4.5	5.5	3.4	7.5	3.9	7.5	7.5	7.5	6.0	6.5
Cl ⁻	4.0	1.5	7.6	3.6	4.8	1.9	5.8	1.3	11.5	4.5
S ²⁻	8.0	9.0	7.8	8.3	4.9	7.6	6.9	8.6	6.5	5.5
O ₂	Balance		-		-		-		-	
Phase Studies in Deposits										
-	CaSO ₄	CaSO ₄	CaSO ₄	CaSO ₄	CaSO ₄	CaSO ₄	-	-	CaSO ₄	CaSO ₄
	+	+	+	+	+	+			+	+
-	SiO ₂	Ca ₂ SiO ₄	Ca ₂ SiO ₄	-	SiO ₂	-	-	-	NaCl	NaCl
	+	+	+		+				+	+
-	K ₃ Na(SO ₄) ₂	NaCl	K ₃ Na(SO ₄) ₂	-	Ca ₂ SiO ₄	-	-	-	KCl	SiO ₂
									+	
									SiO ₂	

$$OC = \frac{5}{9} ({}^{\circ}F - 32)$$

TABLE 6 - Phase Studies of Scale Next to Metal

Probe Number	Phases by Layers Between the Metal and the Oxide Layer	
	400 F - 800 F	800 F - 1200 F
16	FeCl ₂ · 4H ₂ O + FeOOH + FeS ⁽³⁾	(FeCl ₂ · 4H ₂ O + FeOOH + FeS) ⁽¹⁾
17	FeCl ₂ · 4H ₂ O + KCl	(FeCl ₂ · 4H ₂ O + FeOOH + NaCl) ⁽¹⁾
18	As 17 - no evidence of sulfide layer ⁽²⁾	As 17 ⁽²⁾
19	FeCl ₂ · 2H ₂ O + FeCl ₂ · 4H ₂ O + FeOOH + FeS ⁽³⁾	(FeCl ₂ · 2H ₂ O + FeOOH + FeS) ⁽¹⁾
20	As 19	(FeCl ₂ · 2H ₂ O + FeS) ⁽¹⁾

(1) Phases in this temperature zone do not form successive layers but are present in discrete areas.

(2) Analyzed by optical method.

(3) This FeS is found at the interface between the ferrous chloride and the oxides that separates the deposit from the scale.

TABLE 7

Probe No. - Addition:	21-0% S		25-0.75% S		23 1.5% S	
	745	1120	730	1125	740	1175
Substrate Temp., F:						
Elements Detected	Concentration, Weight Percent					
B	<0.1	0.1	<0.1	<0.1	<0.1	<0.1
Na	2.0	4.0	2.0	2.0	2.0	1.0
Mg	0.7	3.0	0.5	0.2	0.7	0.1
Al	2.0	4.5	3.0	4.5	2.0	4.5
Si	3.0	7.5	1.0	4.0	3.0	4.0
K	2.0	4.0	2.0	4.0	2.0	2.0
Ca	4.5	15.0	4.5	15.0	4.5	7.5
Ti	0.3	1.0	0.3	0.4	0.4	0.5
Cr	<0.1	2.0	0.1	0.1	<0.1	<0.1
Mn	0.2	0.3	0.2	0.3	0.3	0.5
Fe	25.0	15.0	25.0	15.0	20.0	15.0
Cu	<0.1	<0.1	0.1	0.1	0.1	0.2
Zn	3.0	3.0	3.0	2.0	7.5	3.0
Sn	0.1	0.1	0.3	0.1	0.3	0.1
Sb	<0.1	0.1	0.1	<0.1	<0.1	<0.1
Pb	0.4	0.1	1.5	0.3	2.5	1.5
Cl ⁻	7.5	2.5	1.9	0.1	0.1	<0.1
S ²⁻	4.6	2.8	3.5	6.0	5.0	3.8
O ₂	Bal	Bal	Bal	Bal	Bal	Bal

$$^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32)$$

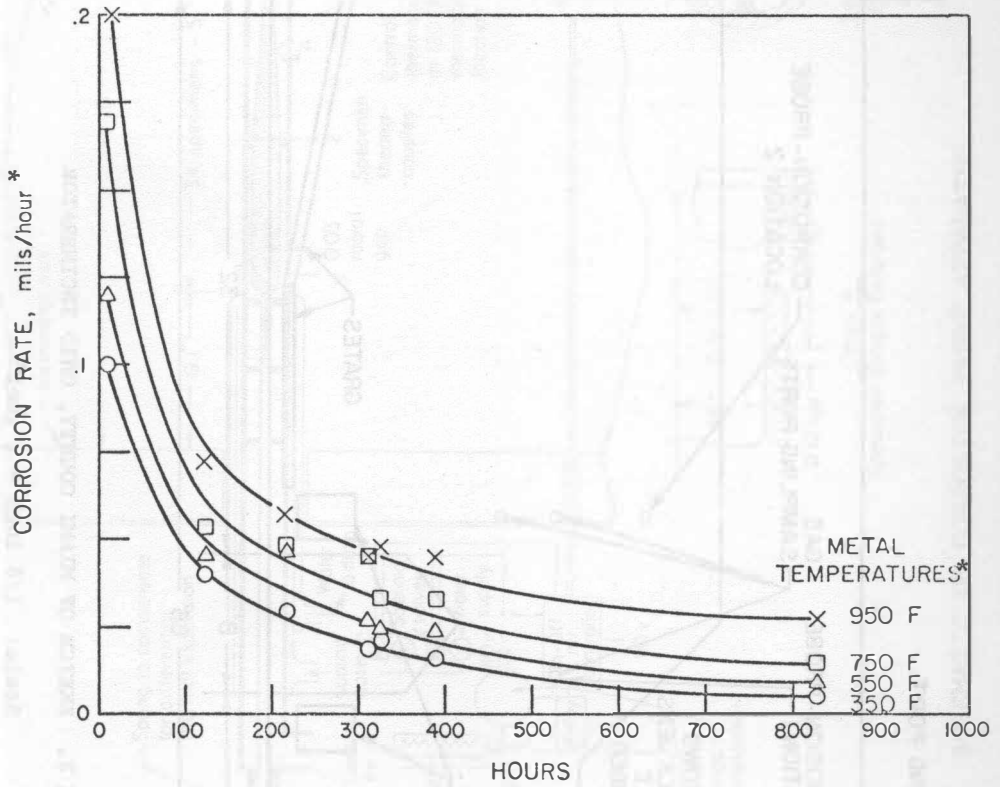


FIGURE 1. ISOTHERMAL CORROSION-RATE DATA FOR A106 STEEL VERSUS TIME OF EXPOSURE TO SOLID-WASTE COMBUSTION PRODUCTS

*Conversion Factors: $(\text{cm/hr}) = 3.94 \times 10^2 (\text{mils/hr})$
 $(\text{K}) = 5/9 (\text{F}-32) + 273.15$

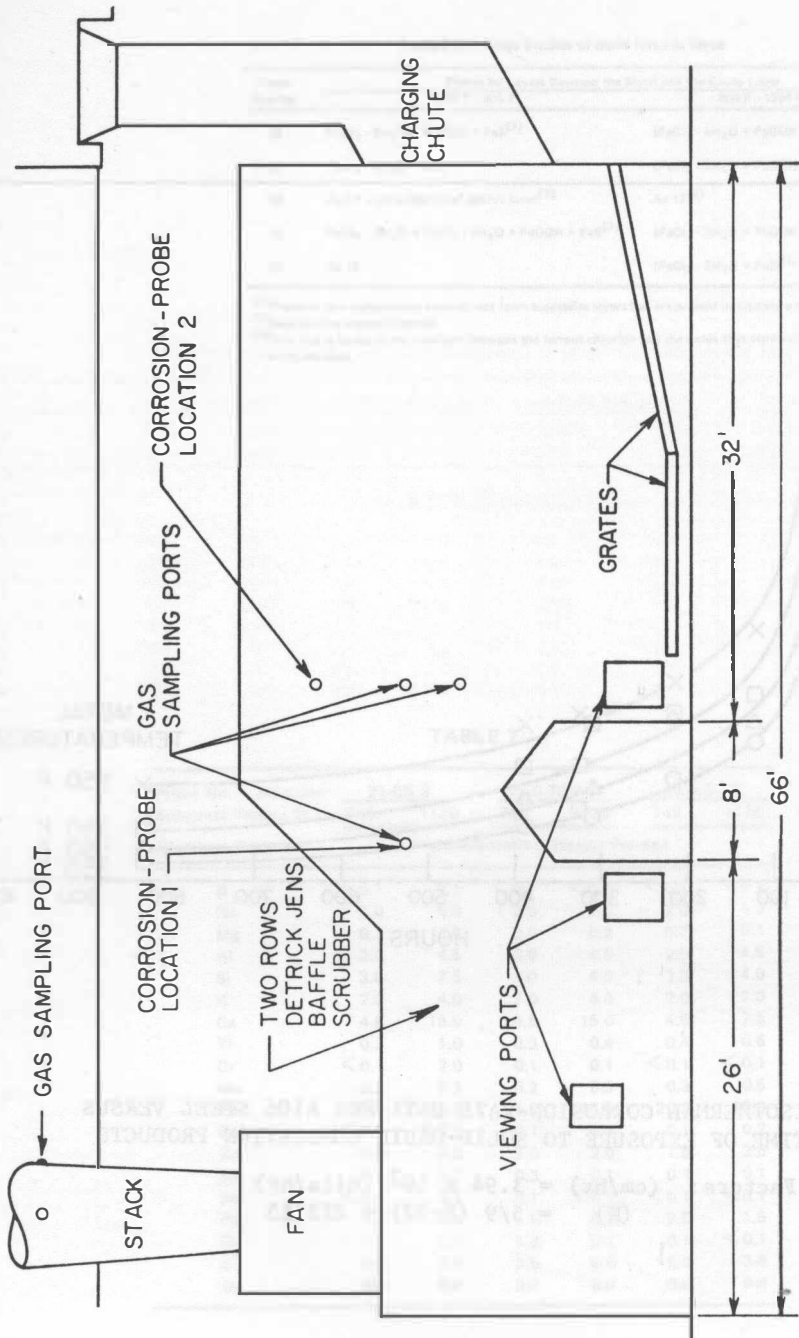


FIGURE 2. SKETCH OF MIAMI COUNTY, OHIO INCINERATOR

Scale: 1/8 inch = 1 foot*

*Conversion Factor: (meter) = 3.28 (foot)

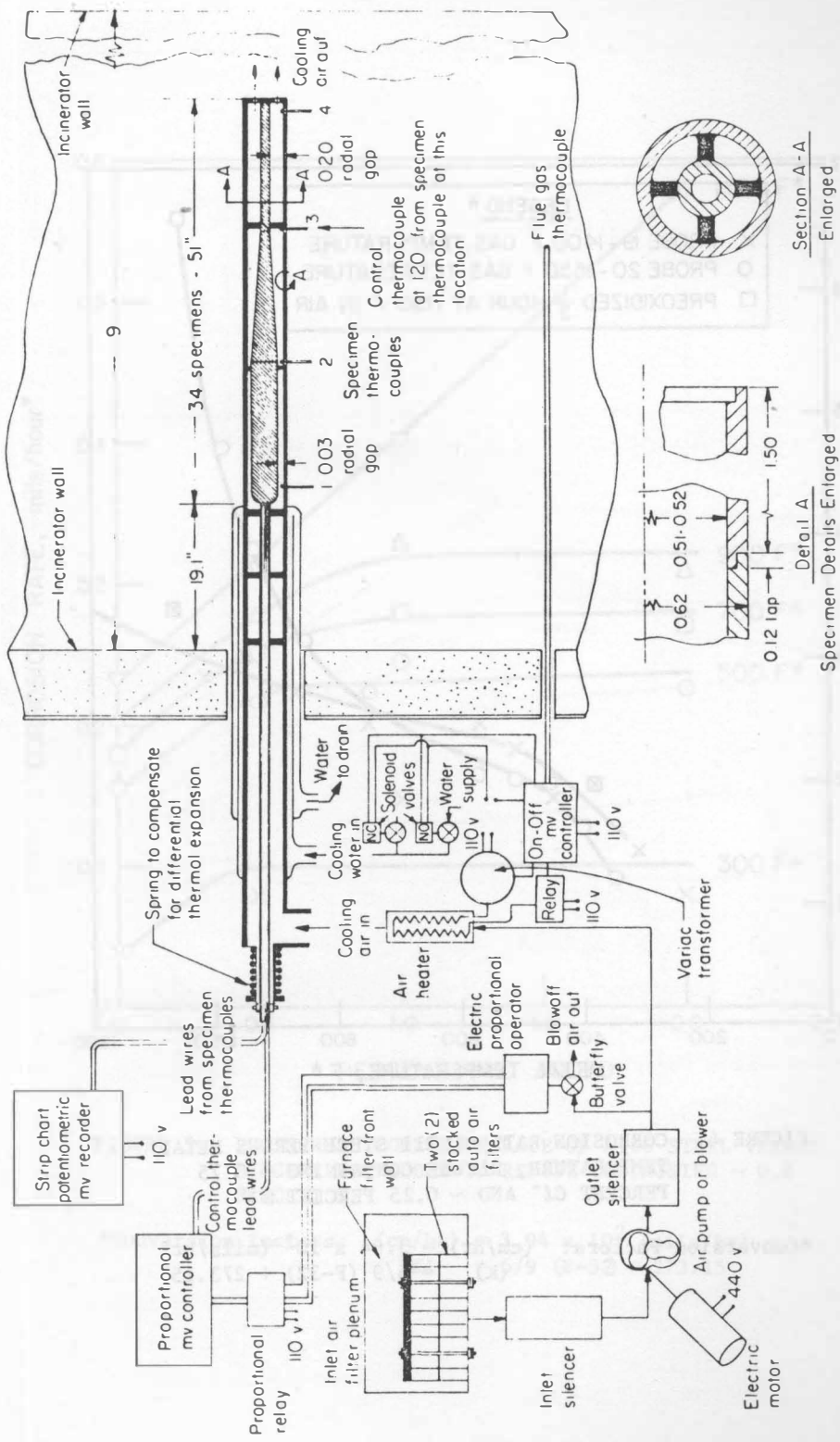


FIGURE 3. SCHEMATIC OF CORROSION PROBE APPARATUS

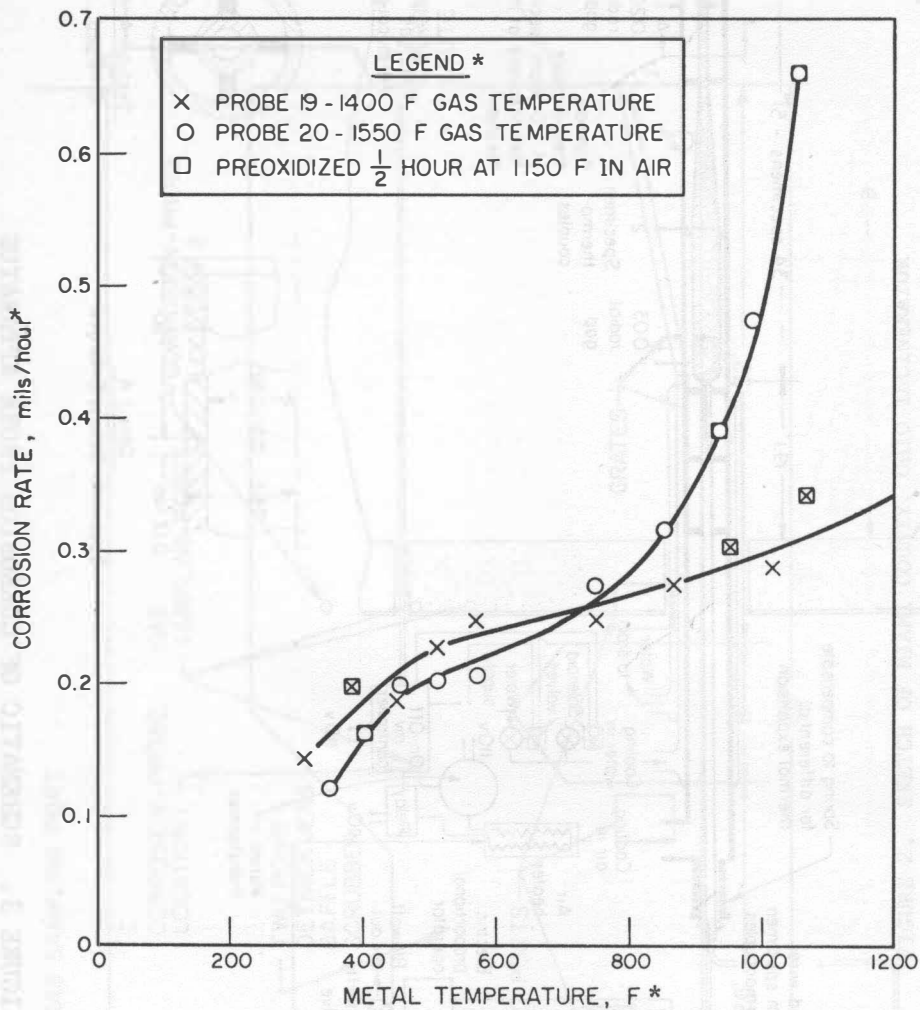


FIGURE 4. CORROSION RATE OF T11 STEEL VERSUS METAL TEMPERATURE, REFUSE CONTAINING ~ 0.75 PERCENT Cl^- AND ~ 0.25 PERCENT S

*Conversion Factors: $(cm/hr) = 3.94 \times 10^2 (mils/hr)$
 $(K) = 5/9 (F-32) + 273.15$

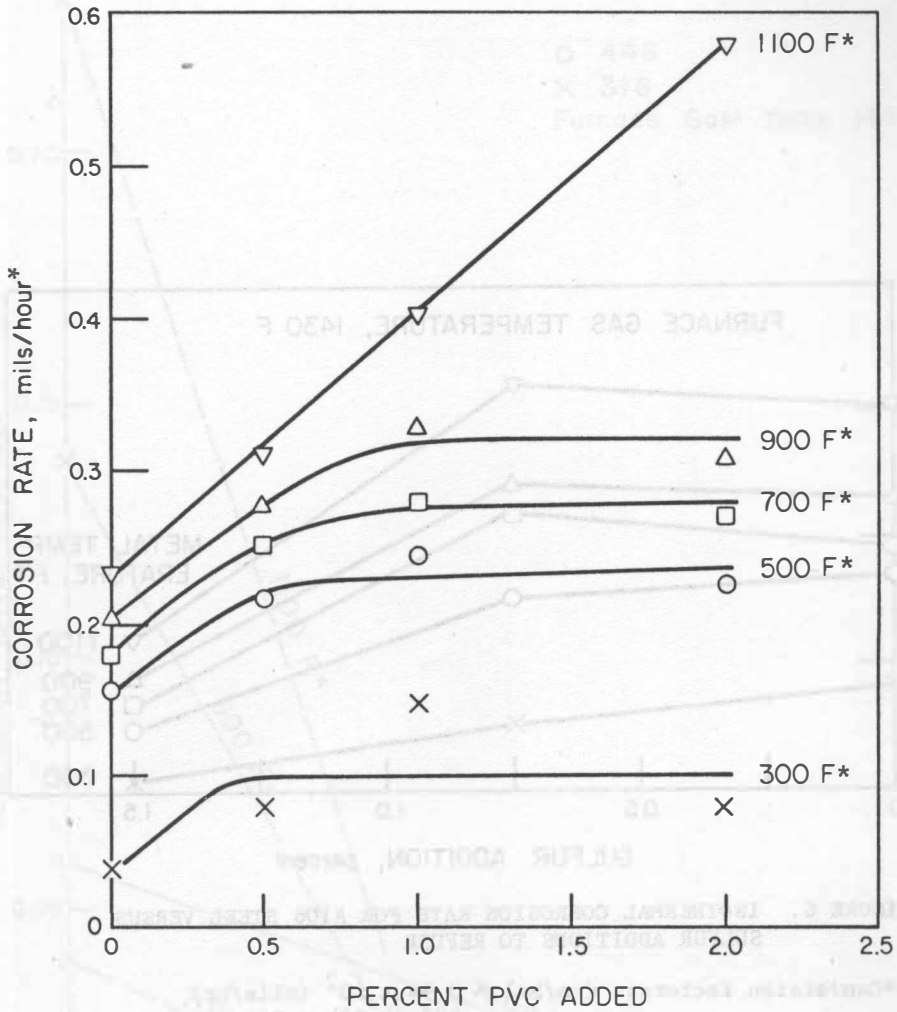


FIGURE 5. ISOTHERMAL CORROSION RATE OF A106 STEEL VERSUS PERCENT PVC ADDED TO REFUSE CONTAINING ~ 0.2 PERCENT S

*Conversion factors: $(\text{cm/hr}) = 3.94 \times 10^2 (\text{mils/hr})$
 $(K) = 5/9 (F-32) + 273.15$

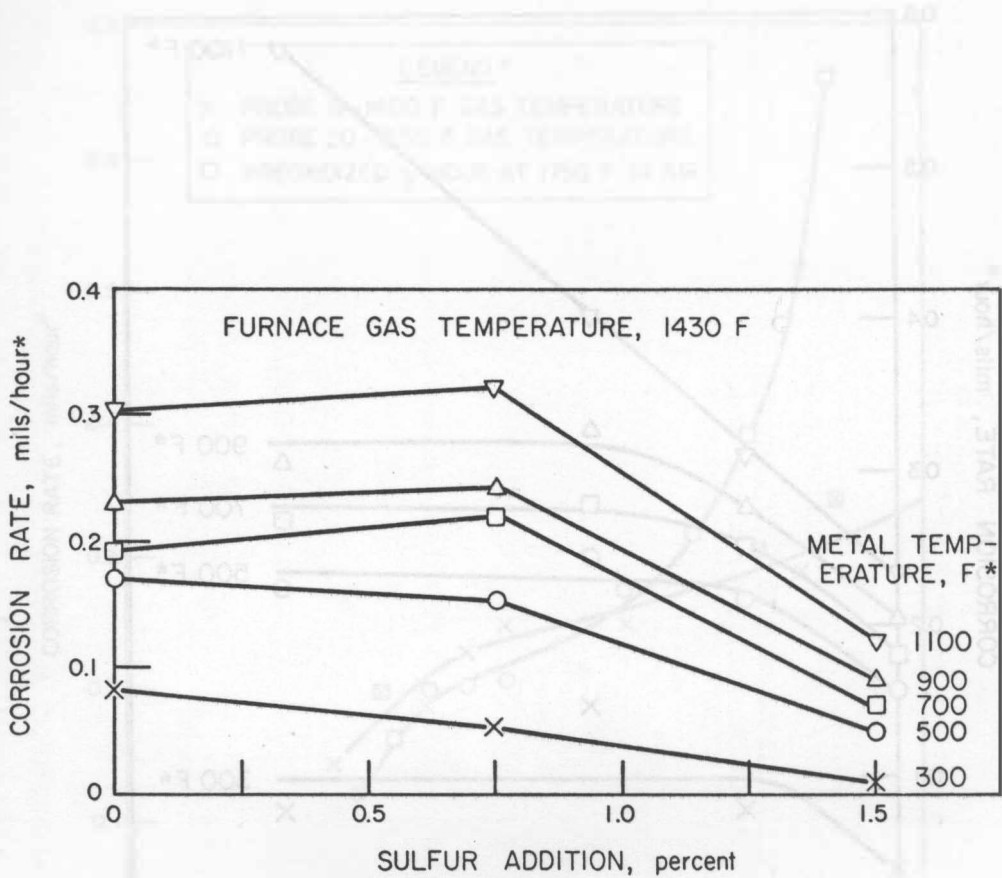


FIGURE 6. ISOTHERMAL CORROSION RATE FOR A106 STEEL VERSUS SULFUR ADDITIONS TO REFUSE

*Conversion factors: $(\text{cm/hr}) = 3.94 \times 10^2 (\text{mils/hr})$
 $(k) = 5/9 (F-32) + 273.15$

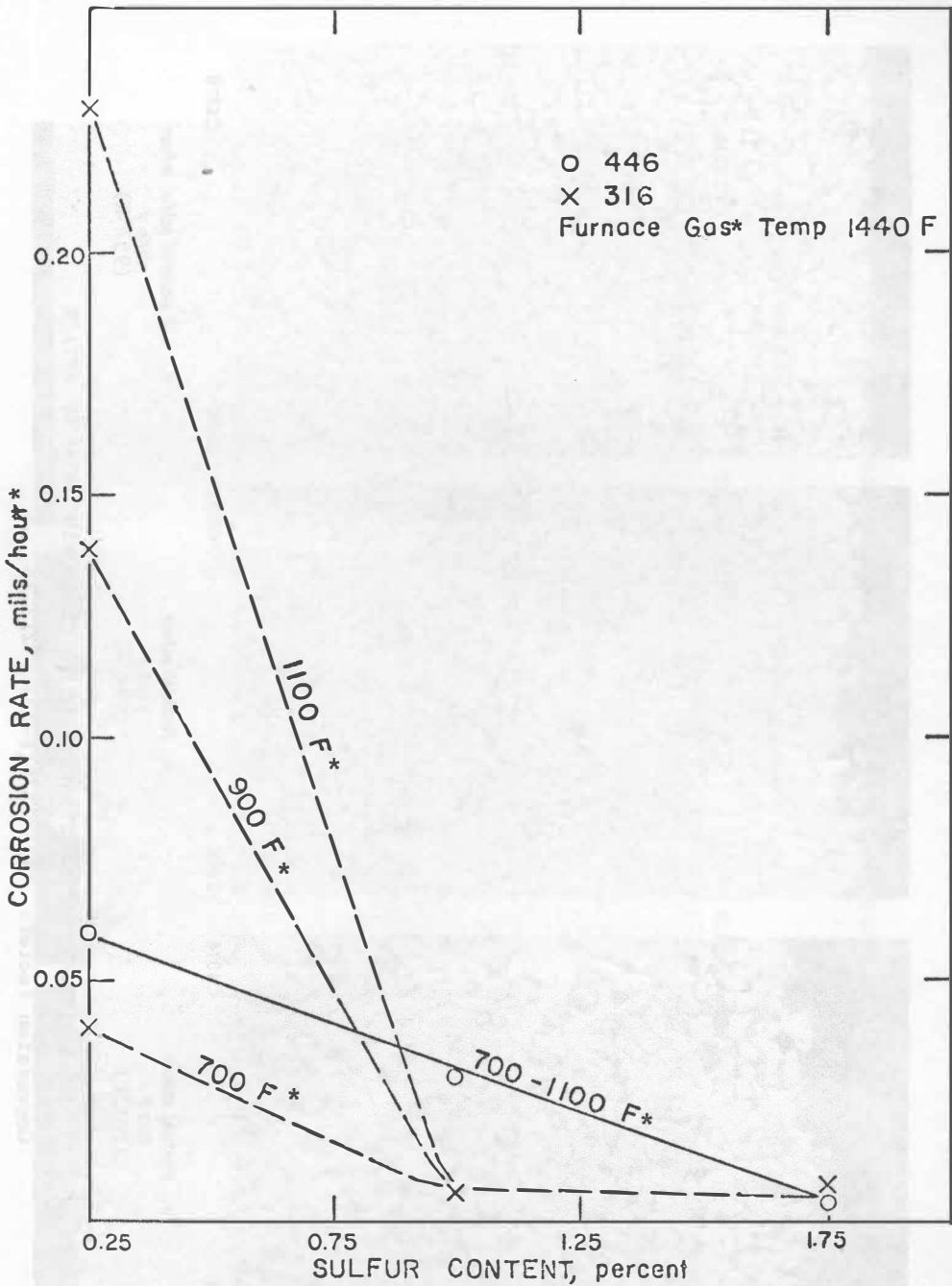
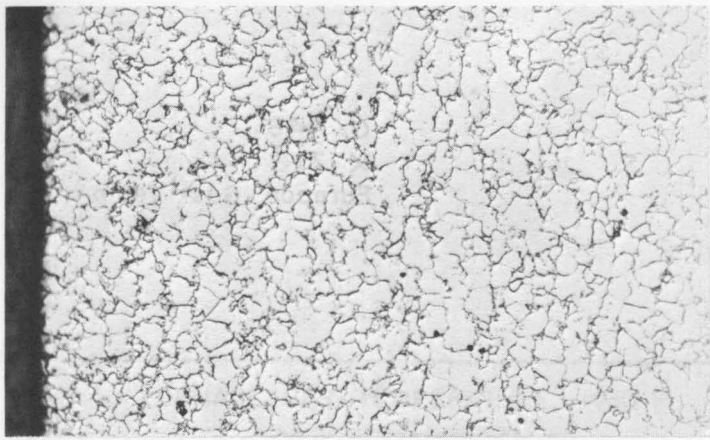


FIGURE 7. ISOTHERMAL CORROSION RATES FOR 316 and 446 STAINLESS STEEL VERSUS SULFUR CONTENT OF REFUSE CONTAINING 0.5 PERCENT Ca^{2+}

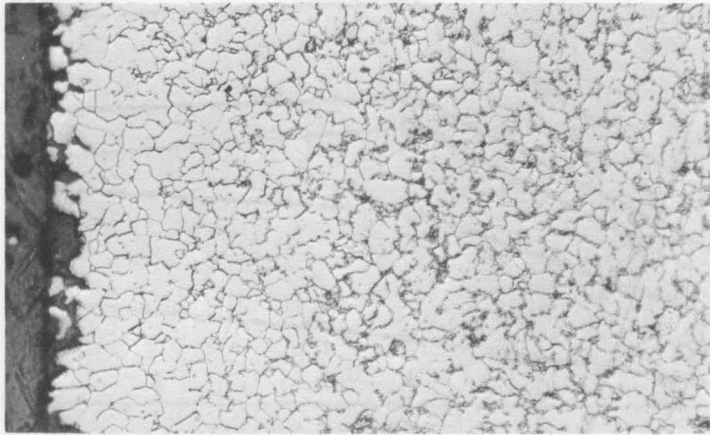
*Conversion factors: $(cm/hr) = 3.94 \times 10^2 (mils/hr)$
 $(K) = 5/9(F-32) + 273.15$



C4376

250X

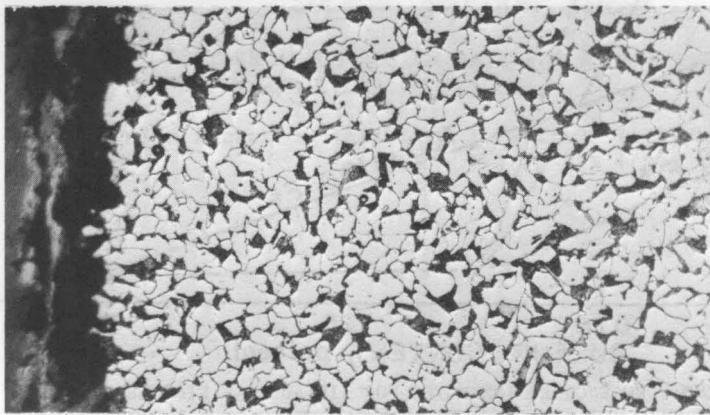
c. 1.5 percent sulfur refuse
1260 F
(957°K)



C4375

250X

b. Normal refuse
1235 F
(942°K)



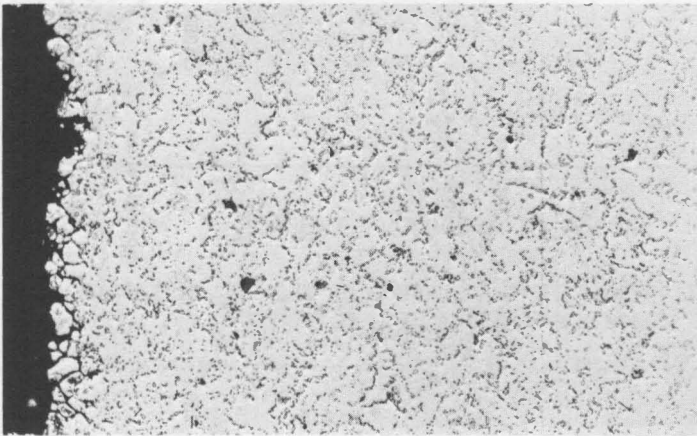
C4374

250X

a. Normal refuse
820 F
(705°K)

FIGURE 8. PHOTOMICROGRAPHS OF A106 STEEL SHOWING MODE OF ATTACK

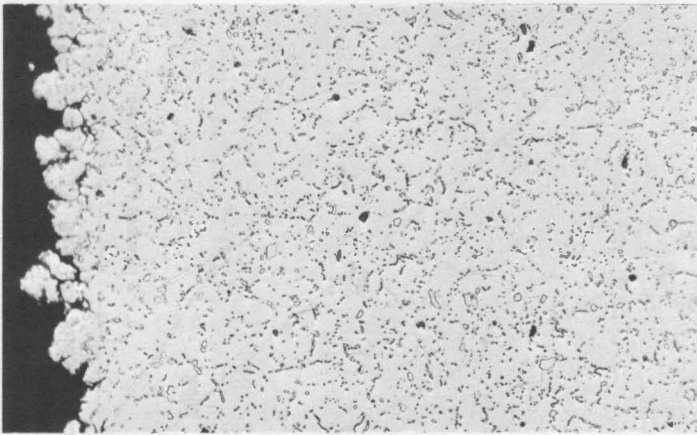
Conversion factor: (K) = 5/9(F-32) + 273.15



250X

C4377

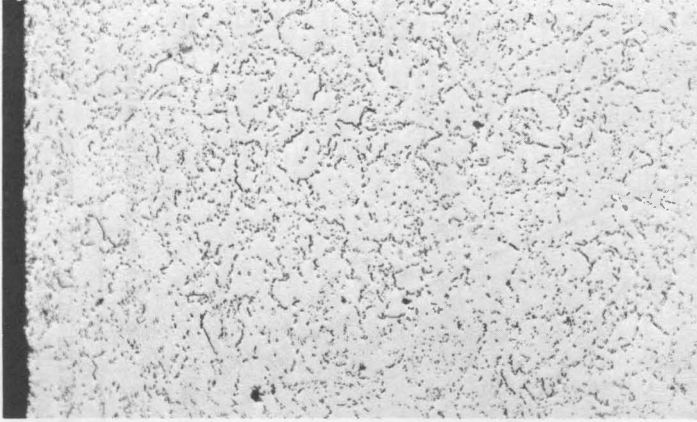
a. Normal refuse



250X

C4378

b. 2 Percent PVC refuse

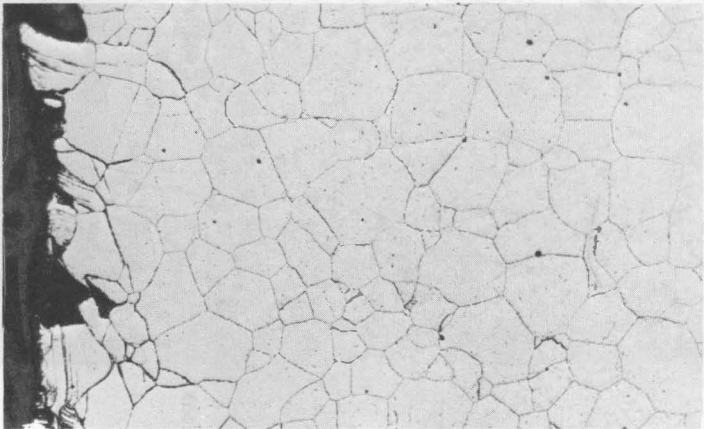


250X

C4379

c. 1.5 percent sulfur refuse

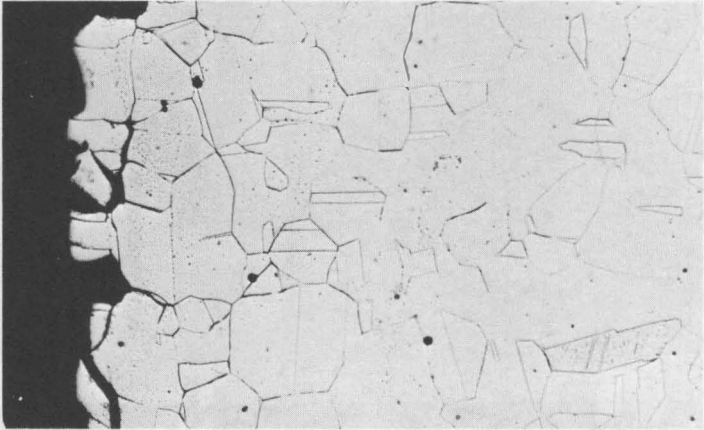
FIGURE 9. PHOTOMICROGRAPHS OF 446 STEEL SHOWING MODE OF ATTACK



250X

C4380

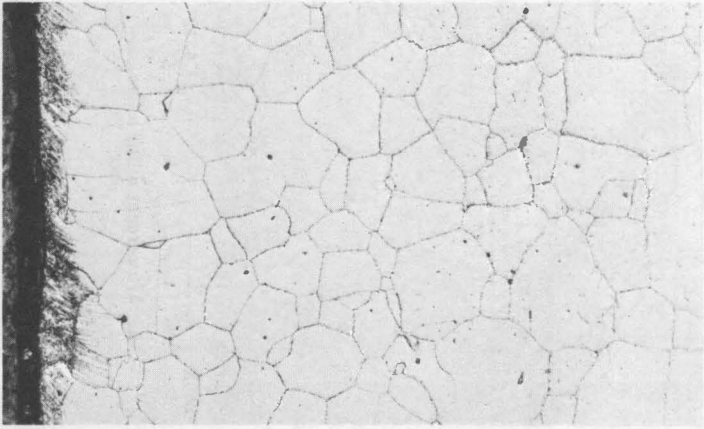
a. Normal refuse



250X

C4381

b. 2 percent PVC refuse



250X

C4382

c. 1.5 percent sulfur refuse

FIGURE 10. PHOTOMICROGRAPHS OF 316 STAINLESS STEEL SHOWING MODE OF ATTACK

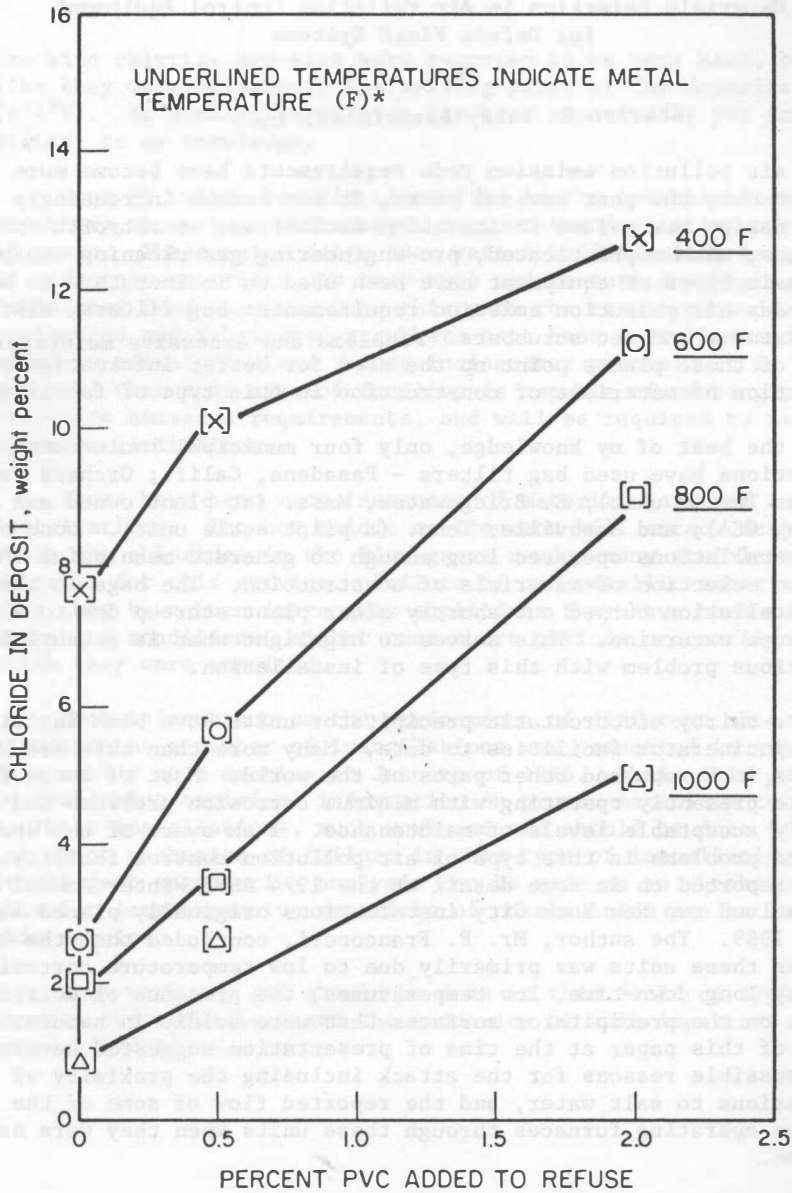


FIGURE 11. CHLORIDE CONCENTRATION IN DEPOSIT VERSUS AMOUNT OF PVC ADDED TO REFUSE

*Conversion factor: $(K) = 5/9(F-32) + 273.15$