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Atmospheric Corrosion Resistance of Steels Prepared From the Magnetic Fraction of Urban Refuse

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ATMOSPHERIC CORROSION RESISTANCE OF STEELS PREPARED FROM THE MAGNETIC FRACTION OF URBAN REFUSE

by

Stephen D. Cramer,[1] John P. Carter,[2] and Bernard S. Covino, Jr.[2]

ABSTRACT

The Bureau of Mines conducted a study in which the magnetic fraction of urban refuse was used as melting stock in the preparation of high-strength, low-alloy and carbon steel. Product steels, made from incinerated steel can scrap, nonincinerated-nondetinned steel can scrap, nonincinerated-detinned steel can scrap, and dilutions of these scraps with No. 1 heavy melting scrap, were used in continuing tests in industrial, rural, and marine environments to determine the effect of residual elements and atmospheric pollutants on their atmospheric corrosion resistance. The respective commercial steels were exposed at the same time to establish baseline corrosion data for the test sites.

Weight-loss data are reported for atmospheric exposures of 0.5, 1.0, 1.5, and 3.8 years. The marine environment was the most corrosive; the industrial environment was the least corrosive. The atmospheric corrosion resistance of the carbon steel was improved 25 pct by using incinerated scrap and nonincinerated-nondetinned scrap in the steelmaking process. In no case was the atmospheric corrosion resistance of carbon steel degraded by using the magnetic fraction of urban refuse as melting stock.

The presence of sulfur in the corrosion film was the most important factor affecting the corrosion resistance of the steels. With increasing sulfur concentration, the rate of the corrosion reaction was reduced and the corrosion film became more protective. The residual elements in the product steels most responsible for improving corrosion resistance were copper and tin. These elements tended to increase the concentration of sulfur in the corrosion film. At the levels present in the product steels, Cr, Ni, and Pb had no observable effect on the corrosion resistance of the steels.

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INTRODUCTION

As part of the Federal Bureau of Mines effort to conserve scarce mineral resources, the effect of utilizing the magnetic fraction of urban refuse in steel products was studied to determine changes in resistance to atmospheric corrosion. An estimated 10 x 10^9 kg of ferrous scrap is included annually in the urban refuse of the United States (13).[3] Roughly half of the ferrous scrap is tin-coated steel cans ("tin cans"); the balance includes small appliances and other small items from households and businesses (15). About 1.3 x 10^9 kg of this ferrous scrap is present in the residue concentrate from municipal incinerators, based on a processing rate for incinerators of 15 x 10^9 kg waste per year containing 8.2 pct ferrous metal (13), but the largest amount by far is disposed of directly in landfills. A small but increasing amount of this scrap is recovered through resource recovery efforts. Ferrous scrap recovery is being incorporated into nearly all of the more recently designed resource recovery facilities (2, 13). Markets for the recovered ferrous scrap range from the detinning industry to the copper industry (30-31), with the iron and steel industry being the largest potential market for the ferrous scrap recovered in the expanding effort to recycle urban refuse.

Interest in utilizing the magnetic fraction of urban refuse in the production of industrial goods has increased proportionately. Ostrowski (31) has shown that incinerated and nonincinerated tin-coated steel can scrap can be used in steel making, and that the residual elements (18), particularly tin and copper, and their concentrations determine use limits for the scrap. The establishment of specifications was recommended to reduce uncertainty in the quality of tin-coated steel can scrap supplies (1, 31). By extension, similar specifications should be established for the ferrous scrap supplies produced from urban refuse. Hunter (19) described the melting and casting of steels prepared from tin-coated steel can scrap, including the steels used in the present study. Hunter concluded that the magnetic separation of ferrous scrap prior to incineration of urban refuse, followed by detinning and then physical consolidation such as briquetting, bundling, or fragmenting, yielded the best product for steelmaking. The tensile properties of experimental carbon steels made by Hunter from this material were found to exceed those of the corresponding commercial product, while their impact strength met or exceeded typical values for hot-rolled commercial steels (6, 20).

The present study is a continuation of earlier work at the Bureau of Mines. Beginning in the 1960's, the Bureau of Mines developed and operated two pilot plants for the recovery of mineral values from incinerated and raw (nonincinerated) urban refuse (32-34). In 1972, the magnetic fraction of urban refuse, conditioned in various ways, was used as melting stock for steelmaking (19). Since the magnetic fraction of urban refuse has a potentially wide and varying content of residual elements, one objective of this work was to determine the effect of the residual elements on the rolling

[3] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

characteristics and the mechanical (20) and atmospheric corrosion properties of the resulting product steels. Two alloys were made from the ferrous scrap, a carbon steel and a high-strength, low-alloy (HSLA) steel. As commercial products, the first is free of all but traces of the residual elements present in ferrous scrap, while the second contains some of these elements as alloy additions. Atmospheric corrosion test panels, fabricated from the product steels, are currently being tested by the Bureau of Mines at rural, industrial, and marine sites for test periods up to 15 years. Results for exposures of 1.5 years showed that the atmospheric corrosion resistance of carbon steel, prepared from incinerated and from nonincinerated-nondetinned steel scrap, was equal to or better than that of the corresponding commercial product (6). Summarized here are the atmospheric corrosion results for exposures up to 3.8 years. This work has implications extending beyond the use of supplemental metallics, namely, the use of lower quality obsolete scrap in steelmaking when demand for scrap is high.

A second objective was to examine the corrosion film, that is, rust, formed on the weathered steels for evidence of the complex interaction between the atmosphere and the corroding alloy. The cumulative effect of this interaction determines the growth and development of the corrosion film, hence, the atmospheric corrosion resistance of the steels. In view of this, the growth kinetics and the composition of the corrosion film were investigated. Of particular interest were time-dependent changes in the composition of the corrosion film that reflect underlying processes affecting the protective nature of the film. Detailed analyses of the corrosion film chemistry were conducted, including determinations of the concentration, distribution, bonding, and structural arrangement of constituents in the corrosion films. This report presents results on the kinetics of corrosion film growth and the effect of sulfur in the corrosion film on the growth kinetics. In addition, limited data characterizing the concentration and distribution of several elements in the corrosion film are presented. The chemistry of the atmospheric corrosion films will be described more fully in a subsequent Report of Investigation.

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EXPERIMENTAL PROCEDURES

Melting and Casting Practice

In 1972, three types of scrap representing fractions magnetically recovered from urban refuse were used at the Albany (Oreg.) Research Center to make nine experimental heats of steel (19). The three types of scrap

were incinerated steel cans (IS), nonincinerated-detinned steel cans (NDS), and nonincinerated-nondetinned steel cans (NNS). No. 1 heavy melting scrap (HMS) was used to make dilutions of these scraps and to make two additional experimental heats of steel that served as controls for the steel melting and casting practice.

Electric-arc furnace melts of 900 kg each were used in making the 11 heats. The target compositions of the melts were 1030 carbon steel and a HSLA steel fitting the Cor-Ten B[4] specification. Alloy additions were made during melting to yield product steels of the desired composition. The melts were deoxidized with aluminum and cast into 22.7- and 362.9-kg (50- and 800-lb) ingots. A detailed description of the melting and casting practice is given by Hunter (19).

Forging and Rolling Practice

Following casting of the heats, the 22.7-kg ingots were shipped to the National Steel Corp. Research Center in Weirton, W. Va., to be hot-forged and rolled into 12.7-mm-thick plate and 3.2-mm sheet. The rolling temperature of these products was 925° C (1,700° F) for the final pass and they were then air-cooled. Commercially produced Cor-Ten B and 1030 carbon steel were purchased to provide samples for comparison with the experimental steels in subsequent studies. The commercial 1030 carbon steel was obtained in final form (3.2 mm thick). The commercial Cor-Ten B was obtained as 15.9-mm-thick plate and rolled to the final 12.7- and 3.2-mm thicknesses using the practice followed for the experimental heats. The 3.2-mm-thick sheet was to be used in the atmospheric corrosion studies described here, and both the 12.7- and 3.2-mm-thick products were to be used in mechanical property studies (6, 20). A detailed description of the forging and rolling practice is given by Kaplan and Makar (20).

Steel Chemistries

The compositions of the experimental heats and the two purchased (commercial) steels are shown in table 1. Experimental steels corresponding to Cor-Ten B were made from heavy melting scrap and incinerated steel can scrap. Manganese and silicon contents of these two heats were below the specification for Cor-Ten B. Experimental 1030 carbon steels were made from incinerated, nonincinerated-detinned, and nonincinerated-nondetinned steel can scrap and from dilutions of these scraps with heavy melting scrap. Carbon contents of several of these heats were outside the 1030 carbon steel specification. The high aluminum levels in all of the experimental heats were due to the way the steels were deoxidized rather than to input from bimetal cans in the scrap. Approximately 95 pct of this aluminum was soluble in a 1:1 solution of HCl in water and presumed to be present in the heats as metallic aluminum rather than as an oxide.

[4]Use of trade names is for identification purposes only and does not imply endorsement by the Bureau of Mines.

TABLE 1. - Composition of steel ingots[1]

Type of scrap	Element concentration, wt-pct									
	C	Mn	Si	Cu	Sn	Cr	V	Ni	Pb	Al
STARTING MATERIAL FOR COR-TEN B STEELS										
Purchased[2]	0.14	1.13	0.23	0.31	<0.01	0.40	0.04	0.03	<0.02	0.05
Heavy melting scrap (HMS).	.14	.83	.08	.38	<.01	.97	.09	.04	<.02	.19
Incinerated scrap (IS)	.18	.75	.08	.23	.15	.43	.02	.07	<.02	.24
STARTING MATERIAL FOR CARBON STEELS										
Purchased[3]	0.31	0.70	0.20	0.03	<0.01	0.03	<0.01	0.02	<0.02	0.01
Heavy melting scrap (HMS).	.36	.88	.08	.06	.01	.09	<.01	.03	<.02	.21
Incinerated scrap (IS)	.21	.65	.08	.18	.19	.10	<.01	.06	<.02	.25
50 wt-pct IS-50 wt-pct HMS	.26	.31	.05	.15	.08	.06	<.01	.06	<.02	.25
25 wt-pct IS-75 wt-pct HMS	.48	.65	.05	.14	.04	.12	<.01	.21	<.02	.20
Nonincinerated-nondetinned scrap (NNS).	.34	.50	.04	.07	.37	.12	<.01	.04	.11	.23
25 wt-pct NNS-75 wt-pct HMS	.30	.79	.08	.21	.12	.19	<.01	.10	<.02	.23
Nonincinerated-detinned scrap (NDS).	.19	.67	.12	.06	.06	.08	<.01	.04	.09	.23
HEAVY MELTING SCRAP										
"As-received" HMS	0.06	0.19	0.03	0.05	<0.01	[4]0.02-.05	([5])	[4]0.05-.13	([5])	([5])

[1] P <0.02, S <0.05, Zn <0.001
[2] United States Steel (0.10-.19C, 0.90-1.25 Mn, 0.04 P max, 0.15-.30 Si, 0.25-.40 Cu, 0.40-.65 Cr, 0.02-.10 V).
[3] National Steel (0.28-.34 C, 0.60-.90 Mn, 0.04 P max, 0.05 S max).
[4] Reference 21.
[5] Not measured.

The residual elements present in the magnetic fraction of urban refuse are listed in table 2, showing typical origins of the elements and their effect on the steelmaking process. The total content of the residual elements in the product steels is given in table 3. For purposes of computing total residuals, only the elements contributed by the scrap and not present in the steel specification were considered; that is, Sn for Cor-Ten B and Cr, Cu, Ni, Pb, and Sn for carbon steel.

TABLE 2. - Residual elements in magnetic fraction of urban refuse

Element	Origin	Effect on steelmaking[1]	References
Al	Bimetal cans	Lowers impact strength; brittle fracture.	20
Cr	Electroplate; low-alloy steel	Makes control of oxygen level in steel difficult.	15
Cu	Electrical wiring	Hot shortness	15
Ni	Electroplate; low-alloy steel	Reduces hot shortness due to Cu.	15, 18
Pb	Solder; machine bearings	Suspected cause of furnace bottom breaks.	15
Si	Enamel finishes	High furnace wear	15
Sn	Solder; tinplate	Hot shortness; lowers impact strength.	6

[1] All residual elements increase rate of work hardening of steel (18).

Comparison of tables 1 and 3 shows that the composition of the experimental heats was related to the source of the melting stock. For example, the copper and tin content of the carbon steel made from incinerated scrap was high while the lead content was low. This was due to separation of solder from the scrap during incineration, alloying of tinplate with iron during incineration, and cementation of copper on iron when the incinerator residue was water quenched. Conversely, the residuals content of carbon steel made from nonincinerated-detinned scrap was low since there was no thermal treatment and subsequent quenching of the scrap, and since tin plate and solder were chemically removed in a caustic solution. The residuals content of the purchased 1030 carbon steel shown in table 3 is typical for the commercial product (21).

TABLE 3. - Total content of residual elements in steel

Steel	Total residuals, wt-pct
Cor-Ten B (Sn):[1]	
Purchased	0
Heavy melting scrap (HMS)	0
Incinerated scrap (IS)	.15
1030 carbon steel (Cr, Cu, Ni, Pb, Sn):[1]	
Purchased	.08
Heavy melting scrap (HMS)	.18
Incinerated scrap (IS)	.53
50 wt-pct IS-50 wt-pct HMS	.35
25 wt-pct IS-75 wt-pct HMS	.51
Nonincinerated-nondetinned scrap (NNS)	.71
25 wt-pct NNS-75 wt-pct HMS	.62
Nonincinerated-detinned scrap (NDS)	.33

[1]Elements included in total residuals.

Atmospheric Corrosion Tests

The 3.2-mm-thick sheet was sheared into standard 101.6 by 152.4-mm (4 by 6-inch) panels at the Avondale (Md.) Research Center for mounting in racks provided at the atmospheric corrosion test sites. All panels were notched for identification and then edge-ground to a 320-grit finish to remove machining burrs. Most of the panels were rough owing to mill scale embedded in their surface during rolling (20). To remove this mill scale the panels were pickled at 90° C in 20 vol-pct sulfuric acid containing 0.1 vol-pct Rhodine 95 inhibitor. The panels were then rinsed with distilled water, dried, weighed to ±0.5 mg, and stored in a desiccator prior to exposure.

The initial exposure of the panels was in July 1973 at three sites used extensively for ASTM and industry atmospheric corrosion studies (24). These were the industrial site at Kearny, N. J., the rural site at State College, Pa., and the 800-foot (245-meter) marine site at Kure Beach, N. C. Twelve panels and, in several cases, 24 panels of the individual steels listed in table 1 were exposed at each site for weight-loss corrosion tests. They represented from two to four samples for six exposure times extending up to 15 years. Eighteen additional panels from selected heats also were exposed

at each site for corrosion film studies that required destroying the original panel. A total of about 500 panels were exposed at the 3 test sites. These were mounted between porcelain insulators, inclined at an angle of 30° with the horizontal, and faced due south (24).

The panels for the weight-loss tests were removed from the test sites at scheduled intervals beginning at 0.5 year following initial exposures. The weight loss due to corrosion was measured by stripping the corrosion film from the panels in concentrated HCl inhibited with 20 grams of Sb_2O_3 per liter at 25° C. Approximately 375 ml of fresh acid was used to strip the film from each panel. There was no outgassing of the film at any time during stripping nor was any odor of hydrogen sulfide detected. The immersion time required to completely remove the corrosion films from the panels increased with the time panels had been exposed to the atmosphere and with panel surface roughness. Typically, the corrosion film was completely removed in 4 to 7 min. for panels exposed 0.5 year. The immersion time increased to 27 min. for panels exposed 3.8 years. After the corrosion films were removed, the panels were rinsed in distilled water, dried, and reweighed to ±0.5 mg. To establish the maximum amount of metal lost from the panels while the corrosion film was being removed, bare metal samples were exposed to the stripping solution for times up to 30 min. The average loss rate for six panels of Cor-Ten B and 1030 carbon steel in the inhibited acid was 1.87 mg/dm^2/min, or 0.058 gram of metal lost from a 101.6- by 152.4-mm panel in a 10-min. immersion. This rate was equivalent to no more than 1 pct of the total weight lost by any of the panels due to atmospheric corrosion.

Analysis of Corrosion Films

The bulk, or average, composition of the corrosion films was determined by chemical analysis of the stripping solutions.[5] First, the stripping solutions for duplicate panels (each 375 ml in volume) were combined and approximately 10 ml concentrated HNO_3 was added to oxidize ions in solution to their highest oxidation state. For some of the stripping solutions, violent gassing occurred when the HNO_3 was added, indicating that an appreciable amount of material in a reduced state was present in the corrosion film. The gas produced by this oxidation was nitrogen dioxide. No hydrogen sulfide was produced. The solutions were then evaporated to dryness to yield a solid product that was a mixture of oxides of the elements to be analyzed and the Sb_2O_3 inhibitor. In general, the mixture consisted of roughly 70 wt-pct oxides from the corrosion film and 30 wt-pct Sb_2O_3. The solid product was ground and mixed in preparation for subsequent analyses.

Copper and iron were determined using wet chemical techniques. A sample of the solid product was first redisolved in HCl. The concentration of copper was then determined in this solution by atomic absorption spectrophotometry using matrix matched standards. The concentration of iron was determined using a stannous chloride reduction followed by potassium dichromate titration.

[5] The analyses were conducted by Wayne F. Lowry, David L. Neylan, and James B. Zink, Avondale Research Center, Bureau of Mines, Avondale, Md.

The elements Sn, Ni, Cr, Si, Al, Pb, and V were determined quantitatively by optical emission spectrographic analysis. Samples were prepared for analysis by mixing 1 part (by weight) of the solid product with 3 parts pure Fe_2O_3 and 6 parts graphite. Standards were prepared using National Bureau of Standards (NBS) and British low-alloy steel reference materials containing the elements of interest. These steels were converted to oxides, primarily Fe_2O_3, by dissolving them in HNO_3, evaporating the solutions to dryness, and baking the residues at 550° C. A mixture of 70 wt-pct pure Fe_2O_3 and 30 wt-pct Sb_2O_3 was made to approximate the composition of the solid product. Standards were then prepared by mixing 1 part mixture (70 pct Fe_2O_3-30 pct Sb_2O_3) with 2 parts pure Fe_2O_3, 1 part oxide prepared from the low-alloy steel reference materials, and 6 parts graphite.

Sulfur was determined by X-ray fluorescence analysis using a molybdenum X-ray tube at 40-kv and a flow proportional counter. Sample preparation consisted of mixing 1 part solid product with 1 part organic binder (Somar) and pressing into 1-inch-diameter disk-shaped pellets. Standards were prepared by mixing known amounts of Na_2SO_4 into the 70 wt-pct pure Fe_2O_3 - 30 wt-pct Sb_2O_3 mixture. These were then combined in a 1-to-1 ratio with the organic binder and pressed into pellets

The results of the wet chemical, optical emission spectrographic, and X-ray fluorescence analyses were originally reported as weight-percent, x_i, in the solid product formed from the stripping solutions. However, since the solid product contained Sb_2O_3 and only the 10 elements (Fe, Cu, Sn, Cr, Ni, Al, Si, Pb, V, and S) present in the corrosion film were of interest, the normalization procedure shown in equation 1

$$y_i = 100x_i / \Sigma x_i . \qquad (1)$$

was used to convert the results to concentrations, y_i, in the corrosion film. Summation over these 10 elements effectively removed the Sb_2O_3 from the final results. In addition, by considering only metallic constituents (with the exception of silicon and sulfur) the oxygen present in the corrosion film was also removed from the final results. Thus, for purposes of computing y_i, the basis for the results was a corrosion film consisting of metallic species, silicon, and sulfur. Moreover, this was essentially the same basis used in reporting composition of the steels, table 1. Thus, the two sets of analytical results are comparable and they can be examined to determine the effect of residual elements in the steels and atmospheric pollutants on the composition of the corrosion films.

Corrosion films were analyzed by X-ray fluorescence while the films remained attached to samples cut from a select group of 18 panels included in the study for destructive testing. These analyses examined differences in the corrosion film chemistry on the skyward and groundward sides of the panels. Squares 2.5 by 2.5 cm were cut from the panels with a band saw while carefully protecting the corrosion film from physical damage or contamination. A molybdenum X-ray tube operated at voltages from 30 to 50 kv was used in the analyses, with a flow proportional counter for the elements Cr, Al, Si, S, and Cl, and a NaI (Tl) scintillation detector for the elements Sn, Pb, Cu, Ni, and Mn. Approximate sampling depths based on normal incidence of the X-ray beam on

a Fe_2O_3 matrix were (in micrometers): Sn-860, Pb-80, Cr-95, Mn-120, Ni-30, Cu-45, Al-3.5, S-10, Si-5, and Cl-15. NBS low-alloy steels were used as standards in the analyses for Sn, Pb, Cr, Mn, Cu, and Ni. Artificial standards for Al, Si, S, and Cl were prepared from pure Fe_2O_3 and compounds of these elements.

From the same group of 18 panels, samples were cut for depth profiling the distribution of selected elements in the corrosion film with an electron microprobe[6] (Materials Analysis Company, model 400). The cut samples were mounted in epoxy and the sample cross sections were ground and polished. The final polish was with 6-μm diamond abrasive. The electron microprobe was operated at 15 kv and the detector was a wavelength dispersive spectrometer fitted with appropriate crystals for the different elements. The electron microprobe beam was approximately 1 μm in diameter and the analysis volume, because of electron scattering and fluorescence, was 3 μm in diameter. Scans of the polished cross sections were begun in the alloy and traversed outwards through the corrosion film and into the epoxy mount in a direction normal to the edge of the sample. Multiple scans were made to determine the distribution of Cu, Sn, Cr, S, Si, Al, and Pb in the corrosion film. Successive scans were made as close to the path of the original scan as possible. Lateral displacement of the scan line occasionally occurred and, in such cases, the distances between the metal-film and film-mount interfaces were not always the same. Dips in the signal on the strip chart record below the background occurred because the background for holes, cracks, and the epoxy mount was less than that for the polished sample surface. Pure elements were used as standards for Cu, Sn, Cr, Si, and Al, while pure FeS_2 was used for sulfur.

RESULTS

Atmospheric Corrosion

The weight-loss results are summarized in tables 4, 5, and 6 for exposures of 0.5, 1.0, 1.5, and 3.8 years at the marine, rural, and industrial sites, respectively. Individual results are the average for duplicate panels. Also included in these tables are the mean weight loss, $\bar{X}$, for the panels from all of the heats of each alloy and the standard deviation, σ, describing the distribution of the weight-loss values about this mean. The standard deviation is used later to assess the effect of residual elements on the atmospheric corrosion resistance of the alloys in much the same way it has been used to examine the effect of annual variations in the weather (3). Atmospheric corrosion continues on two remaining sets of panels that are scheduled for removal after 8 and 15 years exposure.

[6]Electron microprobe analyses were conducted by Marion P. Krug and Peter A. Romans, Albany Research Center, Bureau of Mines, Albany, Oreg.

TABLE 4. - Weight-loss results at 800-foot marine test site, mg/dm^2 [1]

Steel	0.5 year	1.0 year	1.5 years	3.8 years
Cor-Ten B:				
Purchased	2,090	3,120	3,581	6,731
HMS	2,210	3,010	3,471	6,793
IS, heat 1	2,060	3,370	3,878	6,263
IS, heat 2	2,260	3,240	3,514	6,451
$\bar{X} \pm \sigma$	2,155± 95	3,185±155	3,611±184	6,559±247
1030 carbon steel:				
Purchased	1,190	2,960	3,373	7,610
HMS	2,220	3,350	4,182	8,284
IS, heat 1	1,745	3,015	3,426	6,436
IS, heat 2	2,570	3,110	3,888	7,184
50 wt-pct IS-50 wt-pct HMS	2,320	3,500	4,299	8,058
25 wt-pct IS-75 wt-pct HMS	2,220	3,470	4,183	7,286
NNS	1,570	2,550	3,098	6,533
25 wt-pct NNS-75 wt-pct HMS	2,200	3,350	3,799	6,614
NDS	2,070	4,210	4,395	8,705
$\bar{X} \pm \sigma$	2,012±429	3,279±461	3,829±461	7,412±826

[1] To convert milligrams per square decimeter to mil (0.001 inch) for carbon and HSLA steels divide milligrams per square decimeter by 1,989.

TABLE 5. - Weight-loss results at rural test site, mg/dm^2

Steel	0.5 year	1.0 year	1.5 years	3.8 years
Cor-Ten B:				
Purchased	1,570	2,340	2,969	4,462
HMS	2,172	2,341	2,816	3,927
IS, heat 1	1,540	2,170	2,823	3,799
IS, heat 2	1,510	1,940	2,793	4,661
$\bar{X} \pm \sigma$	1,698±317	2,197±190	2,850± 80	4,212±415
1030 carbon steel:				
Purchased	1,300	2,130	2,957	4,832
HMS	2,080	2,550	3,210	5,440
IS, heat 1	1,490	2,440	3,039	4,616
IS, heat 2	1,270	2,160	2,799	4,597
50 wt-pct IS-50 wt-pct HMS	1,930	1,980	3,254	5,207
25 wt-pct IS-75 wt-pct HMS	1,920	2,710	3,567	5,087
NNS	1,270	1,820	2,618	4,053
25 wt-pct NNS-75 wt-pct HMS	2,060	2,560	3,307	4,316
NDS	1,530	2,280	3,219	5,350
$\bar{X} \pm \sigma$	1,650±346	2,292±296	3,107±287	4,833±477

TABLE 6. - Weight-loss results at industrial test site, mg/dm^2

Steel	0.5 year	1.0 year	1.5 years	3.8 years
Cor-Ten B:				
Purchased	1,540	2,080	2,525	3,223
HMS	1,590	2,000	2,434	3,151
IS, heat 1	1,470	2,000	2,277	3,043
IS, heat 2	1,440	1,700	2,034	2,810
$\bar{X} \pm \sigma$	1,510± 68	1,945±168	2,317±215	3,056±180
1030 carbon steel:				
Purchased	1,450	2,150	2,632	4,035
HMS	2,210	2,290	3,021	4,155
IS, heat 1	1,300	1,750	2,212	3,083
IS, heat 2	1,640	1,910	2,250	3,207
50 wt-pct IS-50 wt-pct HMS	1,950	2,030	2,417	3,548
25 wt-pct IS-75 wt-pct HMS	2,020	2,390	2,720	3,673
NNS	1,330	1,780	2,041	2,870
25 wt-pct NNS-75 wt-pct HMS	2,070	2,380	2,501	3,332
NDS	1,520	2,360	2,643	3,897
$\bar{X} \pm \sigma$	1,721±345	2,115±258	2,493±300	3,533±444

Corrosion Film Chemistry

The atmospheric pollutant sulfur dioxide potentially has the most damaging effect on the corrosion of steels exposed to weathering conditions in rural and industrial environments. In the past several decades SO_2 levels in the atmosphere of heavily industrialized sections of the country and in areas downwind from these sections have risen substantially, leading to the peculiar phenomenon of "acid rains" (26). The primary cause of these low pH rains is the presence of sulfurous acid formed by the combination of SO_2 and rainwater, although other oxides, notably nitrogen oxides, also contribute to this phenomenon (26). If SO_2 has a significant effect on the atmospheric corrosion of the steels one would expect to find substantial levels of sulfur in the resulting corrosion product.

Reported in tables 7, 8, and 9 are the average concentrations of sulfur, determined by X-ray fluorescence analyses, in the corrosion films removed (by stripping in inhibited HCl) from panels exposed at the marine, rural, and industrial sites, respectively. The substantial differences in the concentration of sulfur in the corrosion films formed during 0.5 year exposure, particularly on the carbon steels, cannot presently be explained. However, the sulfur concentrations for longer exposures appear to be approaching well-defined limits. The data for 3.8 years exposure have been plotted in figure 1 for carbon steel (open symbols) and Cor-Ten B (closed symbols). These data show a linear dependence on the sum of the copper and tin (Cu + Sn) in the steel similar to the trend observed earlier in the 1 year exposure data (5-6). This trend is satisfied without distinguishing between the data from carbon steel panels and from Cor-Ten B panels. Insofar as there is a dependence on (Cu + Sn), the sulfur concentration data from the two alloys are indistinguishable.

TABLE 7. - Concentration of sulfur (wt-pct) in corrosion films from 800-foot marine test site

Steel	0.5 year	1.0 year	1.5 years	3.8 years
Cor-Ten B:				
Purchased	0.38	0.34	0.34	0.52
HMS	.19	.35	.36	.41
IS, heat 1	.21	.42	.35	.46
IS, heat 2	3.44	.41	.35	.51
1030 carbon steel:				
Purchased	.21	.30	.33	.30
HMS	.20	.28	.33	.25
IS, heat 1	.21	.28	.37	.41
IS, heat 2	1.40	.42	.36	.43
50 wt-pct IS-50 wt-pct HMS	.22	.34	.32	.38
25 wt-pct IS-75 wt-pct HMS	.21	.23	.36	.38
NNS	.21	.29	.37	.39
25 wt-pct NNS-75 wt-pct HMS	.18	.35	.33	.43
NDS	.20	.32	.25	.29

TABLE 8. - Concentration of sulfur (wt-pct) in corrosion films from rural test site

Steel	0.5 year	1.0 year	1.5 years	3.8 years
Cor-Ten B:				
Purchased	0.81	0.65	0.49	0.76
HMS	.60	.42	.70	.84
IS, heat 1	.81	.62	.62	.84
IS, heat 2	.70	.55	.58	.62
1030 carbon steel:				
Purchased	1.20	.80	.57	.68
HMS	2.11	.51	.51	.70
IS, heat 1	.83	.65	.63	.80
IS, heat 2	1.11	.76	.72	.81
50 wt-pct IS-50 wt-pct HMS	2.42	.43	.53	.69
25 wt-pct IS-75 wt-pct HMS	.21	.48	.60	.74
NNS	1.23	.57	.52	.77
25 wt-pct NNS-75 wt-pct HMS	2.18	.54	.59	.76
NDS	.85	.51	.60	.70

TABLE 9. - Concentration of sulfur (wt-pct) in corrosion films from industrial test site

Steel	0.5 year	1.0 year	1.5 years	3.8 years
Cor-Ten B:				
Purchased	0.90	1.01	0.80	1.07
HMS	1.22	.92	1.04	1.08
IS, heat 1	1.77	1.00	.96	1.00
IS, heat 2	1.08	1.11	1.33	1.11
1030 carbon steel:				
Purchased	1.04	.96	.79	.86
HMS	2.13	.74	.64	.97
IS, heat 1	.94	1.29	.99	1.04
IS, heat 2	2.66	1.20	1.00	1.03
50 wt-pct IS-50 wt-pct HMS	3.10	1.05	1.31	1.14
25 wt-pct IS-75 wt-pct HMS	3.49	1.08	.86	.90
NNS	1.25	1.11	.96	1.11
25 wt-pct NNS-75 wt-pct HMS	2.76	.89	.97	1.02
NDS	.83	.76	.80	.95

There is a striking dependence of the sulfur concentration on the type of environment. For example, intercepts of the curves in figure 1 are (sulfur in weight-percent): marine-0.27; rural-0.67; and industrial-0.90. These values are clearly related to the amount of SO_2 in the atmosphere at the three sites. Typical values reported by the Environmental Protection Agency (7-12) near the test sites for the period 1972-77 are (in micrograms of SO_2 per cubic meter): Marine (Cape Hatteras, N.C.)--3 to 10; rural (Indiana County, Pa.)--14; and industrial (Newark, N.J.)--49 to 57.

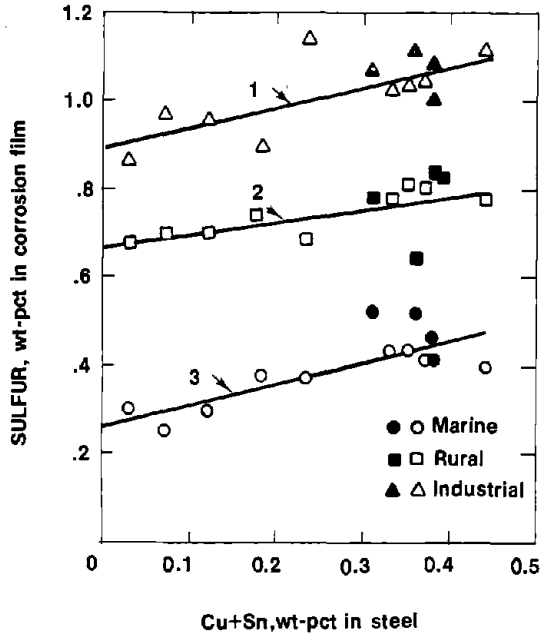

FIGURE 1. - Concentration of sulfur in the corrosion film formed on Cor-Ten B and 1030 carbon steel following 3.1 years exposure: 1, industrial site (Δ); 2, rural site (□); and 3, marine site (○). (Cor-Ten B—solid symbols; 1030 carbon steel—open symbols.)

Comparison of the corrosion film composition with that of the alloy can aid in identifying the origin of certain film constituents and in determining whether alloying elements from the steel are retained in the film. Treated in terms of an enrichment factor, that is, the ratio of the average concentration in the film to that in the alloy, such a comparison is made in table 10 for carbon steel and Cor-Ten B panels exposed 3.8 years at the industrial site. The enrichment factor for sulfur was exceptionally high, ranging from 34 to 108. Since the alloys contained less than 0.05

wt-pct sulfur, it is evident that nearly all of the sulfur in the corrosion film originated in the atmosphere. Only a small fraction of the sulfur (less than 5 pct) in the corrosion film was sulfide as determined by wet chemical analysis of films removed by wire brushing of corrosion test panels. It is presumed, therefore, that the sulfur was present primarily as a sulfate. The enrichment factor for aluminum was 2 to 7.2, with a higher value computed for purchased carbon steel because of the low aluminum content in that alloy compared with the other product steels. The enrichment factor for silicon was 4.4 to 13.9. The high values for aluminum and silicon also suggest an atmospheric origin for these elements with particulate matter such as fly ash and dust the likely sources. Horton (16) has shown that particulate matter appears primarily in the outer region of the corrosion film. Chromium data suggest that there is no chromium enrichment in the corrosion films, particularly for those on carbon steels. On the other hand, copper, which must originate solely in the alloy, appears to be somewhat more concentrated in the corrosion film on both the carbon steel and Cor-Ten B alloys. This would suggest that copper is present in the film in a less soluble form than that of other constituents, particularly iron.

TABLE 10. - Enrichment factor for corrosion films from 3.8 years exposure at industrial test site (expressed as ratio of average film concentration to metal concentration)

Steel	Cu	Cr	Si	Al	S
Cor-Ten B:					
Purchased	1.1	1.9	4.4	7.2	63
HMS	1.7	.8	8.1	3.0	108
IS	1.7	1.4	10.6	3.3	50
1030 carbon steel:					
Purchased	3.0	0.0	4.8	29.0	86
HMS	2.5	.8	8.3	2.9	97
IS	1.4	.5	13.9	2.0	34

The effect of panel orientation on the corrosion film composition is shown in table 11 by X-ray fluorescence results for the skyward and groundward side of panels exposed 3.8 years at the industrial site. Clearly, dense atmospheric particulate matter, indicated by the data for aluminum and silicon, is more readily incorporated into the corrosion film on the skyward side where it has a greater chance of settling. It would appear from the data for sulfur that the SO_2 exposure of the panels is independent of orientation. However, examination of all data for panels exposed 3.8 years at the three sites showed somewhat greater concentrations of sulfur in the corrosion film on the groundward side. This may be due to the greater washing action of rainfall on the skyward side or may indicate that the SO_2 exposure of the groundward side is increased by the slower drying time of the groundward side and by increased time-of-wetness from dew accumulations.

TABLE 11. - Effect of panel orientation on corrosion film composition for 3.8 years exposure at industrial test site (expressed as concentration ratio of skyward to groundward side)

Steel	Si	Al	S
Cor-Ten B:			
Purchased	4.0	4.5	1.0
IS	3.0	4.5	.7
1030 carbon steel:			
Purchased	7.0	11.0	.7
IS	2.5	4.0	1.4

Depth profiles for Cu, Sn, Cr, S, and Pb, obtained using the electron microprobe, are shown in figures 2 and 3 for the skyward and groundward sides, respectively, of a 1030 carbon steel panel prepared from nonincinerated-nondetinned scrap (NNS) and exposed 3.8 years at the industrial site. This steel contains high levels of tin and lead, table 1. The figures show the variation in concentration of the elements with respect to position in the corrosion film cross section. As noted at the top of each figure, to the left lies the metal-film interface, to the right the film-mount interface. The distance scale indicates position with respect to the metal-film interface. The figures show that the thickness of the film on the skyward side is 73 μm, that on the groundward side is 90 μm. In both films the sulfur concentration increases near the outer edge of the film (film-mount interface). Copper profiles are relatively flat, the concentration decreasing slightly with increasing distance from the metal-film interface. Lead shows a very small rise in concentration near the outer edge for both the groundward and skyward sides of the panel. However, for the skyward side near the metal-film interface there is a substantial lead peak. Chromium has a broad peak near the outer edge for the skyward side of the panel; it has two inner peaks for the skyward side, but only a single inner peak for the groundward side. Tin exhibits one large peak and a second smaller one near the metal-film interface for the groundward side. For the skyward side, tin has three large peaks near the metal-film interface and a fourth smaller one. There is a good correlation between the location of the tin peaks, the "inner" chromium peaks, and several sulfur peaks in the films on both the groundward and skyward sides. The large lead peak for the skyward side lines up with peaks for S, Cr, and Sn. It would appear from these results that Cu, Sn, Cr and Pb in conjunction with S form a barrier within the corrosion film that retards the corrosion of the alloy. Improved corrosion resistance due to this barrier may result from diminished access to the metal surface by water, oxygen, and other corrosive agents.

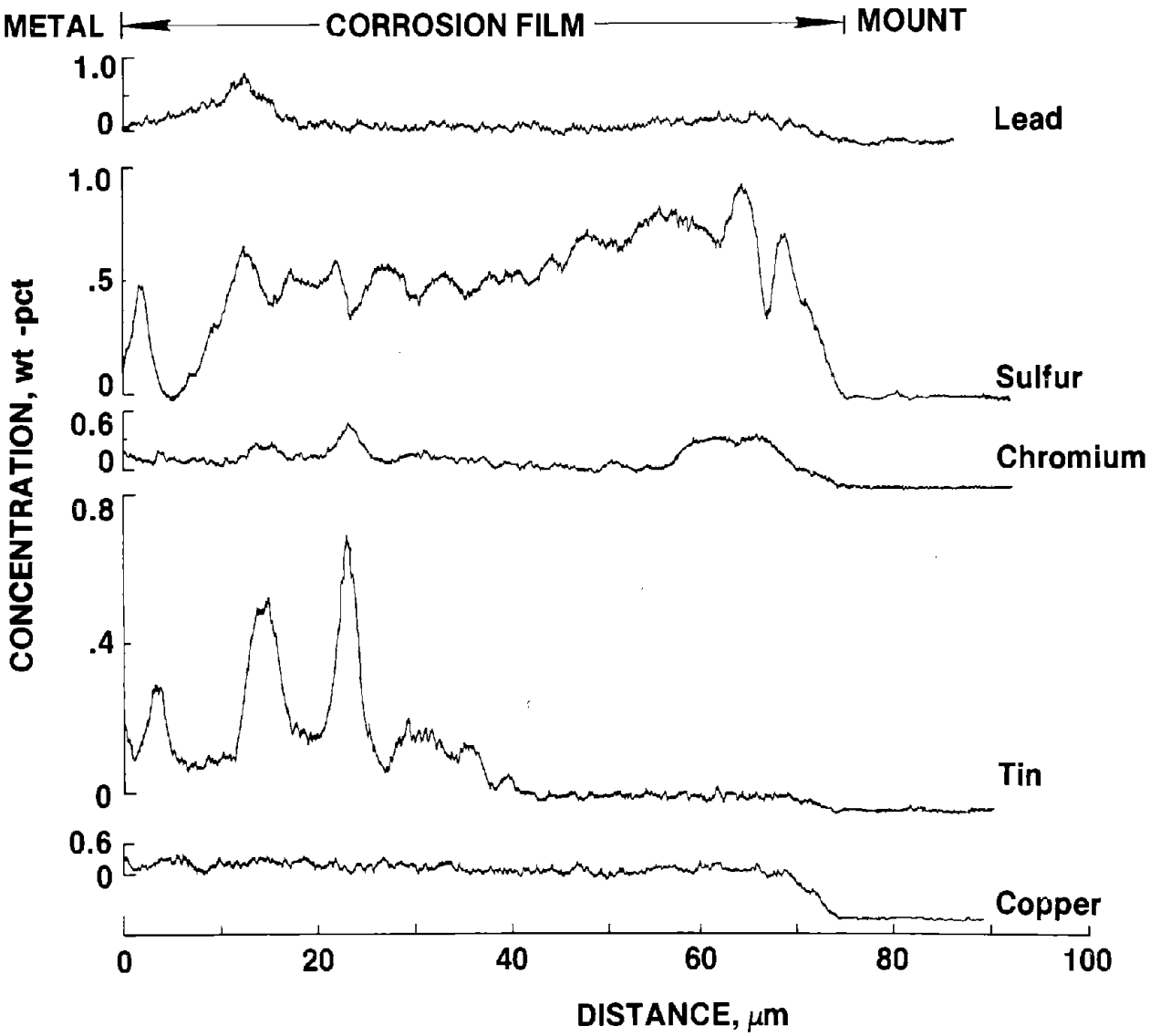

FIGURE 2. - Elemental depth profiles for corrosion film formed on skyward side of 1030 carbon steel panel prepared from nonincinerated-nondetinned scrap following 3.8 years exposure at industrial site. Location of metal-film and film-air interfaces indicated by "metal" and "mount," respectively.

DISCUSSION OF RESULTS

Atmospheric Factors

By exposing all of the panels at a site at the same time under identical weather conditions, comparisons of the weight-loss results for that site are not complicated by the daily, seasonal, and yearly variations in climate that have been shown to affect the atmospheric corrosion of test panels (3, 14, 23). However, since work of a similar nature was largely completed 20 or more years ago (23), there is interest in whether the climatic conditions presently affecting corrosion at the three test sites are similar to those in the past.

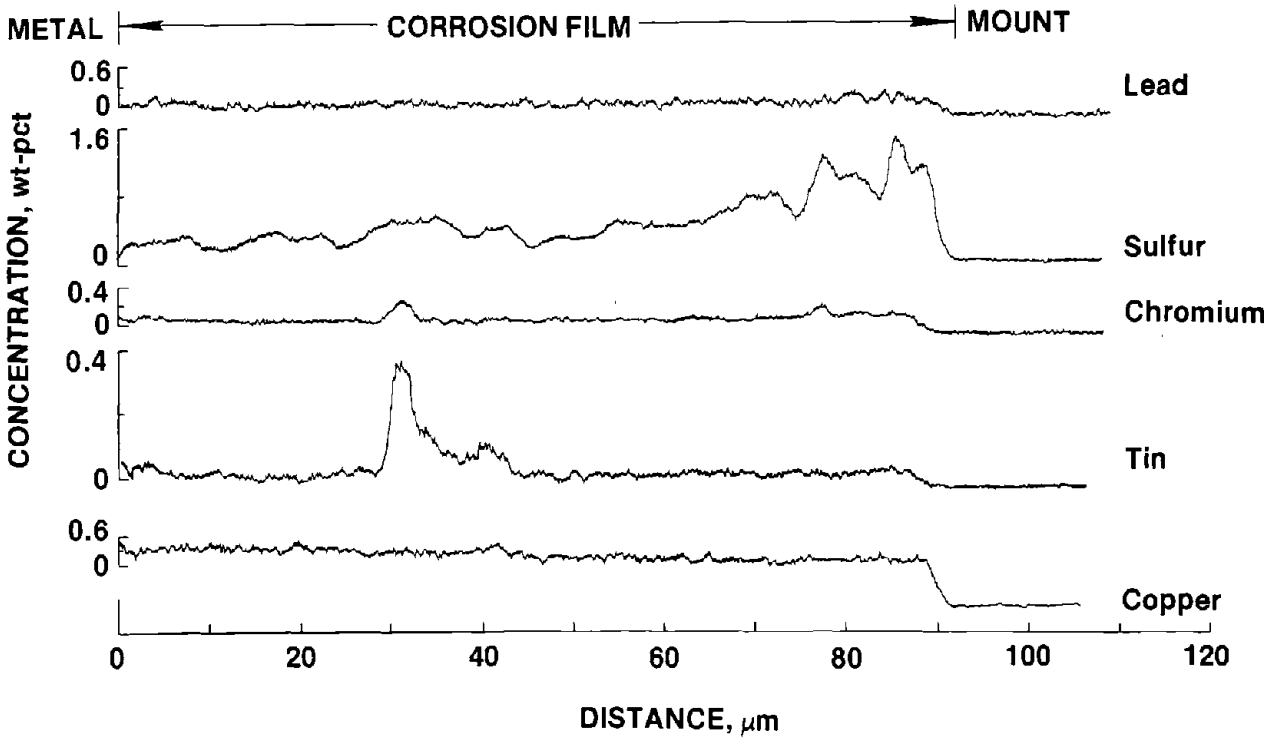

FIGURE 3. - Elemental depth profiles for corrosion film formed on groundward side of 1030 carbon steel panel prepared from nonincinerated-nondetinned scrap following 3.8 years exposure at industrial site. Location of metal-film and film-air interfaces indicated by "metal" and "mount," respectively.

The purchased Cor-Ten B and 1030 carbon steel were included here to provide a basis for comparison with the past work and with possible future studies.

The most corrosive environment for purchased 1030 carbon steel was the marine site, followed, in decreasing order, by the rural and the industrial sites (fig. 4). The results for purchased Cor-Ten B steel were similar. This is in sharp contrast to the corrosivity of the atmospheres at the three sites that has been reported in the past, where the rural site was rated as least corrosive and, depending upon time of exposure, the industrial and marine sites were rated as more corrosive (3). First, consider the weight-loss results as they pertain to the rural and marine sites. The present values for purchased 1030 carbon steel fall within the range of values reported for 1- and 2-year exposures of mild steel during the years 1948 through 1955 at the marine and rural sites (3). The present values, though smaller, also are similar to those reported for 1020 carbon steel[7] exposed at the rural site (28). Furthermore, the values for purchased Cor-Ten B steel are close to those reported for HSLA steels at the rural site (28). Of course, such comparisons are not exact, but the conclusion is that there have been no major changes in climatic factors affecting corrosion at the rural and marine sites during the last 20 years.

[7] The small difference in carbon content between 1020 and 1030 carbon steel should not affect the atmospheric corrosion results.

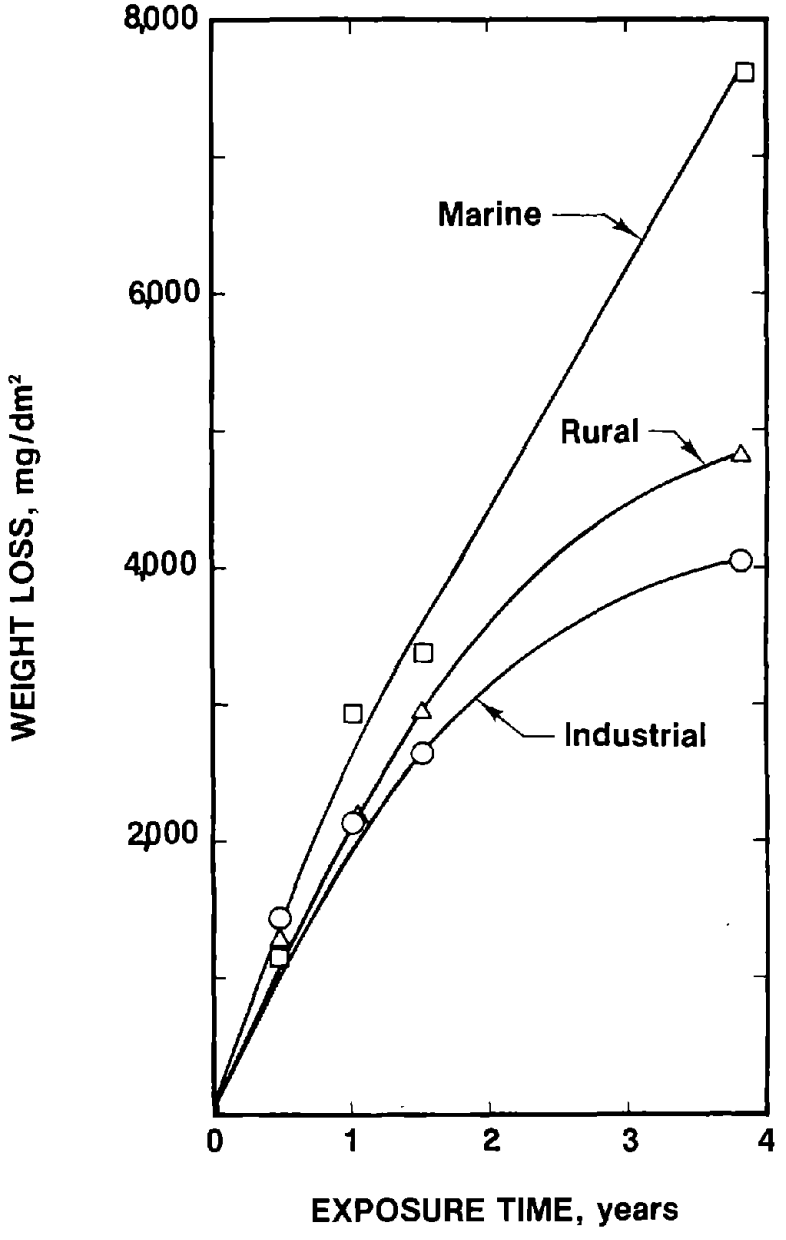

FIGURE 4. - Weight loss of purchased 1030 carbon steel exposed at three atmospheric corrosion test sites.

On the other hand, the weight-loss values for purchased 1030 carbon steel at the industrial site were a factor of 2 to 6 smaller than the values reported for 1- to 2-year exposures of mild steel during the years 1948 through 1955 (3). The weight-loss values for purchased 1030 carbon steel and purchased Cor-Ten B steel were also a factor of 2 to 3 smaller than the values obtained in another earlier study (28). Thus, there is evidence of a marked reduction in the corrosivity of the environment at the industrial site. Two factors that could have influenced this reduction are the time of initial exposure and the time of wetness. The panels were initially exposed during the summer at the hottest and driest time of the year. Atmospheric factors, rather than alloy chemistry, largely control the corrosion of the carbon and HSLA steels during this initial exposure (lasting a month or more) and can have a long-term effect on subsequent weight loss (14). For example, in exposures ranging from 1 to 4 years, the weight loss of mild steel exposed at an industrial site was nearly twice as great when the initial exposure occurred in the fall rather than the spring (3). Secondly, the weight loss of mild steel increases with the time of wetness (14), which is a function of atmospheric conditions such as humidity, rainfall, and temperature. The present results are not sufficient to determine whether these factors lead to the observed low weight-loss values for the industrial site. However, they do indicate that at this site a significant change has occurred in the factors affecting atmospheric corrosion.

Steels Prepared From the Magnetic Fraction of Urban Refuse

Weight-loss results for the 11 experimental steels and for the two purchased steels have been summarized in figures 5, 6, and 7 to show the range in values observed for (1) the 1030 carbon steels (shaded area) and (2) the Cor-Ten B steels, at the marine, rural, and industrial sites, respectively. With increasing exposure time, the trend for the Cor-Ten steels is towards lower weight loss than for the carbon steels, reflecting the more protective nature of the corrosion film on HSLA steels (16, 22-23). This trend was apparent at the industrial site within 1.5 years (fig. 7), and at the more corrosive marine site after a somewhat longer time (fig. 5).

The most important feature of these figures is the considerable overlap in the atmospheric corrosion behavior of the 1030 carbon steels and the Cor-Ten B steels. In effect, some of the carbon steels behaved as though they were Cor-Ten B steels. Of course, the extent of this overlapping behavior varied with the site. At the marine site, where chloride ions can critically affect the corrosion behavior of steel (14), the reportedly beneficial effect of more than 0.5 pct chromium (22, 24) clearly lead to a weight loss that was progressively lower for Cor-Ten B steels than for the carbon steels. On the other hand, at the industrial site (and to a lesser extent at the rural site) it was difficult to distinguish the corrosion behavior of some of the carbon steels and the Cor-Ten B steels. This overlap would appear to be solely attributable to the residual elements present in certain of the carbon steels.

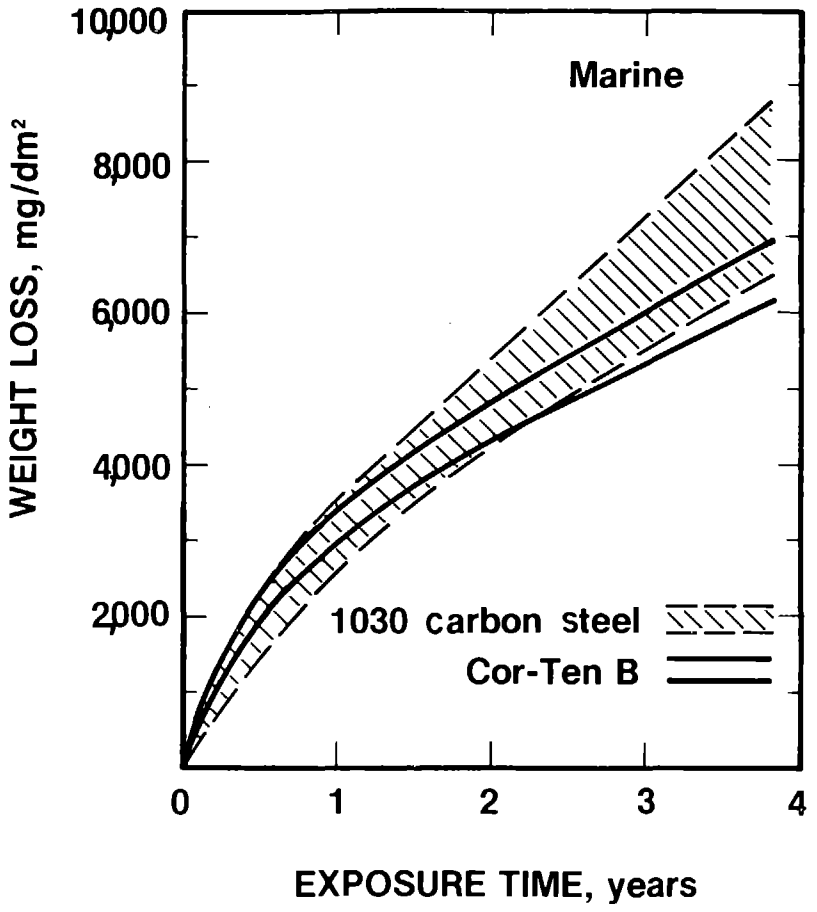

FIGURE 5. - Weight loss of Cor-Ten B and 1030 carbon steels exposed at marine test site.

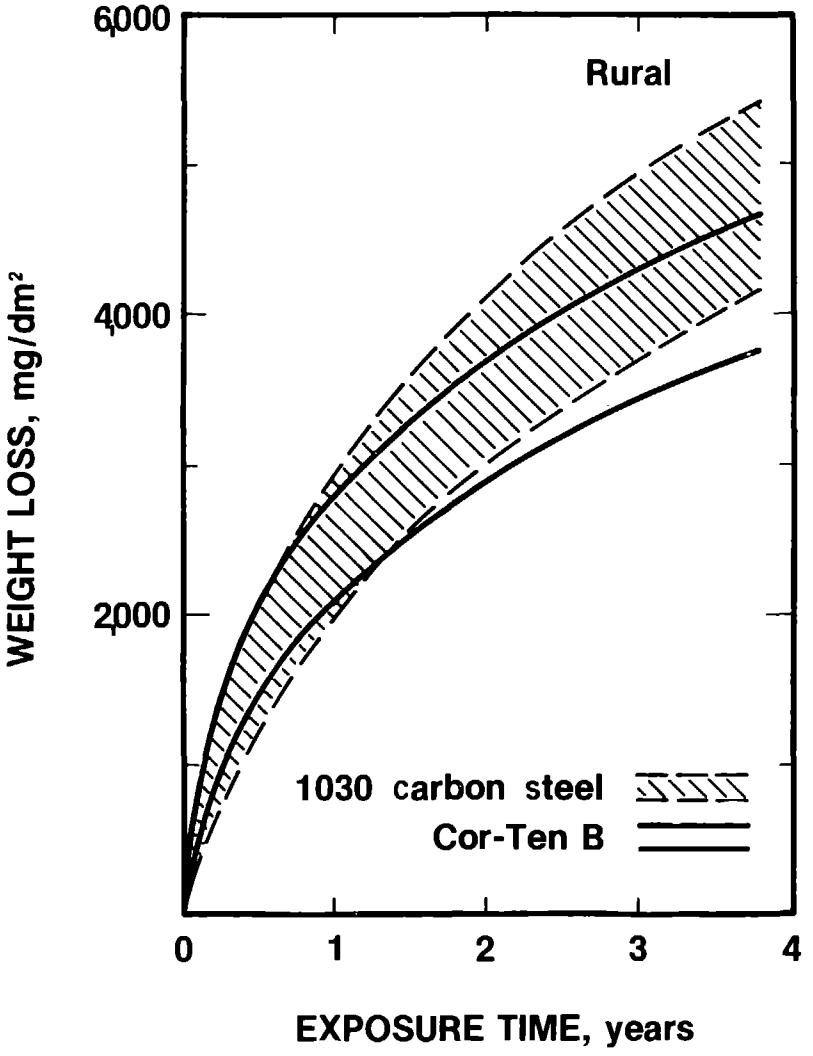

FIGURE 6. - Weight loss of Cor-Ten B and 1030 carbon steels exposed at rural test site.

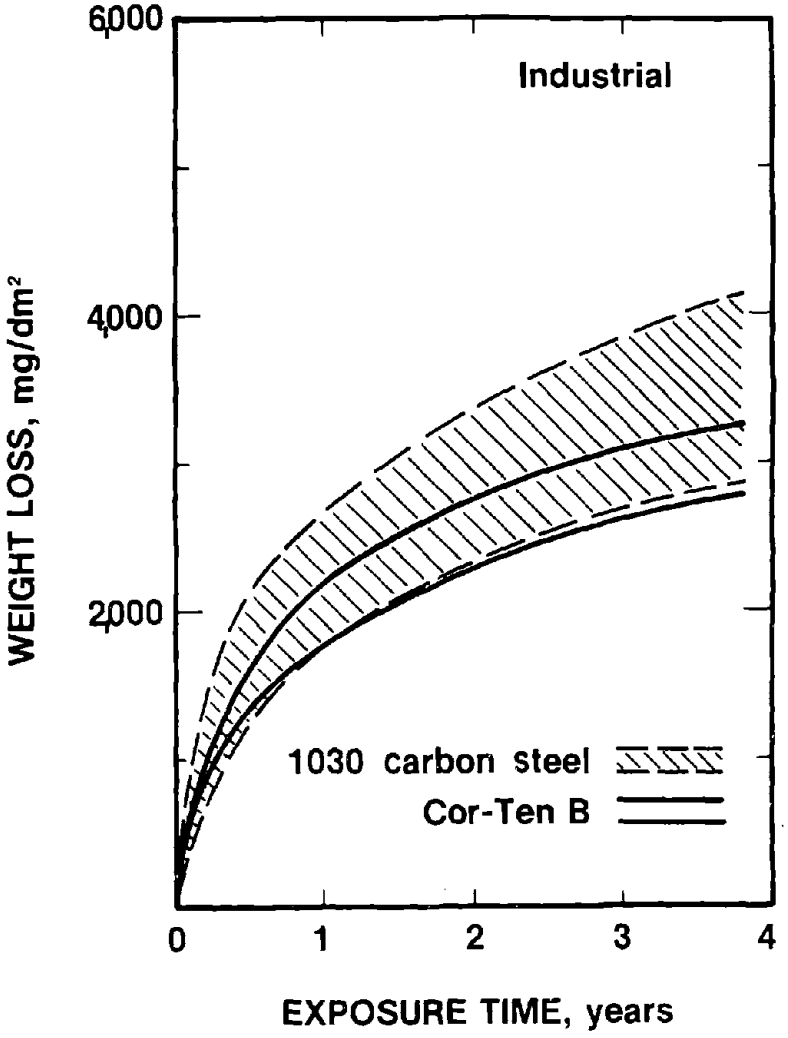

FIGURE 7. - Weight loss of Cor-Ten B and 1030 carbon steels exposed at industrial test site.

The standard deviation of the weight-loss results, tables 5, 6, and 7, can be used to show the effect of residual elements on atmospheric corrosion, just as in the past it has been used to demonstrate the effect of climate (3). Averaged over the four exposure times, the standard deviations for Cor-Ten steel and 1030 carbon steel are given in table 12 for the industrial, rural, and marine test sites. Since experimental errors in the weight-loss measurements would be similar for the two alloys, the markedly higher standard deviation for the carbon steel is evidence of the larger influence of the residual elements (table 3) on its corrosion behavior. Thus, the effect of the residual elements (Cu, Sn, Cr, Ni, and Pb) on the carbon steel, which contains no metallic alloy additions in the purchased steel, appears substantial and leads to the wide variations in corrosion behavior shown in figures 5 through 7. Conversely, the effect of residual elements (mainly tin) on the corrosion behavior of the HSLA steel, which contains relatively high levels of alloy additions, is small. Variations in the concentration of C, Si, Al, and Mn should not, at the levels present, affect the corrosion properties of either steel (24, 29) .

TABLE 12. - Average standard deviation for weight-loss results, mg/dm² (average of 4 exposures during the 3.8-year period)

Steel	Industrial	Rural	Marine
Cor-Ten B.....	158	250	170
1030 carbon steel.....	337	351	545

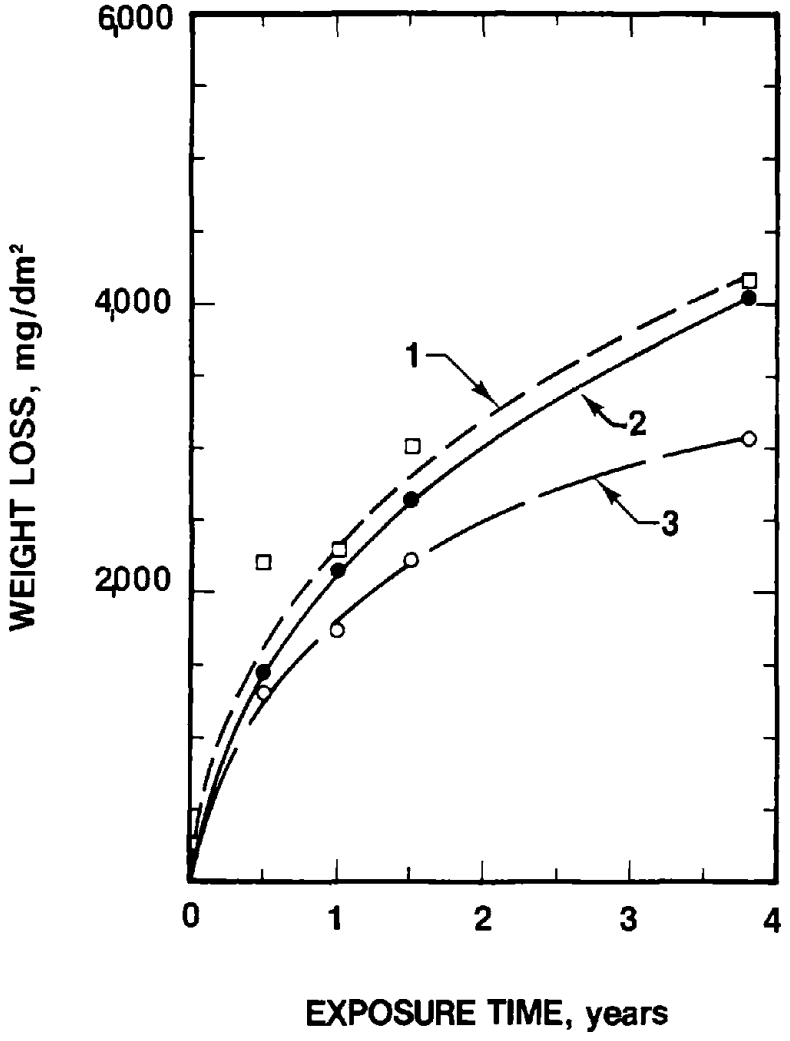

FIGURE 8. - Weight loss of 1030 carbon steel exposed at industrial test site: 1, No. 1 heavy melting scrap; 2, purchased steel; and 3, incinerated scrap.

Detailed examination of the weight-loss results for 1030 carbon steel showed that certain of the experimental steels had markedly better atmospheric corrosion resistance than either the purchased steel or some of the other experimental carbon steels. While only the results from the industrial site will be discussed, the observations that are to be made are applicable to the results from the rural and marine sites as well. Figure 8 shows that the purchased steel (curve 2) and steel made from heavy melting scrap (curve 1), both low in residuals, lost weight at nearly identical rates. The small amount of chromium and nickel present in the heavy melting scrap product had an insignificant effect on the corrosion. Much higher levels are reportedly necessary to improve corrosion performance (22, 24). On the other hand, following 3.8 years exposure, the weight loss of the steel made from incinerated scrap (curve 3) was 25 pct less than that of the purchased steel. The incinerated scrap product contained substantial copper, one of the more important elements for improving the atmospheric corrosion resistance of low-alloy steels (17, 24), and tin.

The weight-loss results for two additional experimental heats of 1030 carbon steel are shown in figure 9. Results for the incinerated scrap product are included for reference. Following 3.8 years exposure, the weight loss for the nonincinerated-nondetinned product (curve 3) was 7 pct lower than that for the incinerated product (curve 2). While the copper content of the nonincinerated-nondetinned product was less than half that for the incinerated product, the tin content was twice as great and there was a higher level of lead. It is possible, therefore, that either tin or lead compensated for the lower copper level in the nonincinerated-nondetinned product and is responsible

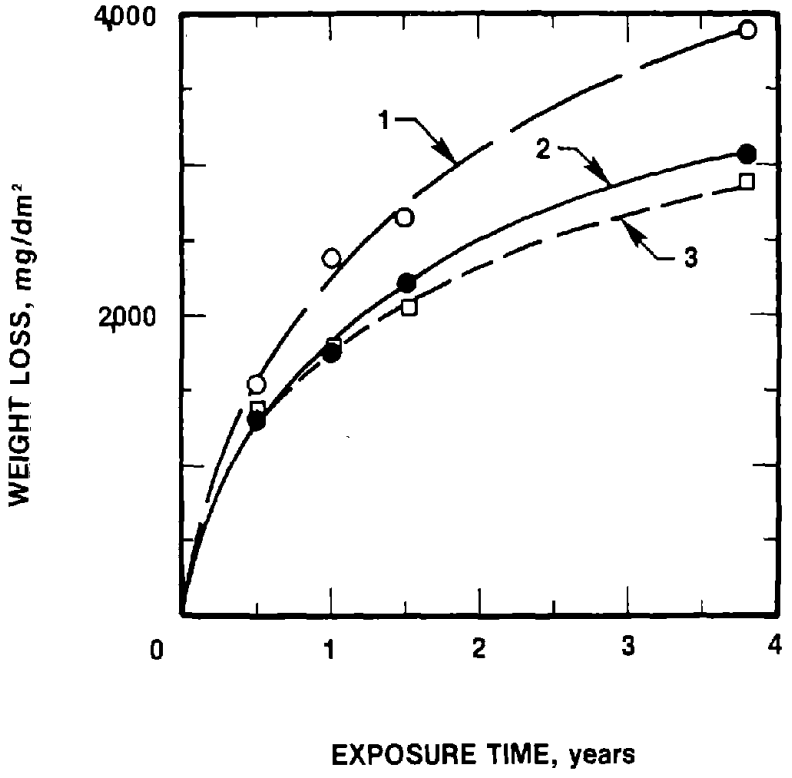

FIGURE 9. - Weight loss of 1030 carbon steel exposed at industrial test site: 1, Nonincinerated; detinned scrap; 2, incinerated scrap; and 3, nonincinerated-nondetinned scrap.

in part for its greater atmospheric corrosion resistance. The effect of lead in the alloys can be determined by examining the results for the nonincinerated-detinned product (curve 1). This product had a high lead content and low tin content, and yet the weight loss was only slighly less than that of the purchased steel. Thus, lead appears to have had little or no effect on the atmospheric corrosion resistance of the steels. Evidently the improved corrosion resistance of the nonincinerated-nondetinned product was due to the tin.

The weight-loss results for the nine experimental heats of carbon steel and the purchased steels suggest by inspection that the tin is as important as the copper in determining the atmospheric corrosion properties of the steels. For instance, the sum of copper and tin (Cu + Sn) was somewhat greater for the nonincinerated-detinned product (0.12), than for either the heavy melting scrap product (0.07), or the purchased steel (0.03), and would seem to account for the slightly better corrosion resistance of the nonincinerated-detinned product indicated by a comparison of figures 8 and 9. Furthermore, (Cu + Sn) in the incinerated and the nonincinerated-nondetinned products was 0.37 and 0.44 wt-pct, respectively, and while the latter exhibited somewhat better corrosion resistance, the copper content was less than half that of the former.

To illustrate the combined beneficial effect of copper and tin, the weight-loss results for the industrial site have been plotted in figure 10 as a function of (Cu + Sn) for each exposure period. The open symbols represent 1030 carbon steels and the solid symbols the Cor-Ten B steels. These curves are similar in form to those originally reported by Buck (4). However, rather than plotting the weight loss as a function of the copper content of the steel, as done by Buck, the sum of the copper and tin contents was used in figure 10. Since all of the steels examined had copper contents of 0.03 wt-pct or greater, the sharp decrease in weight loss with increase in copper content up to 0.02 wt-pct observed by Buck was not observed here. For a 0.5-year exposure, the weight loss actually increased with (Cu + Sn) up to a value of about 0.2 wt-pct, and then decreased for higher values.

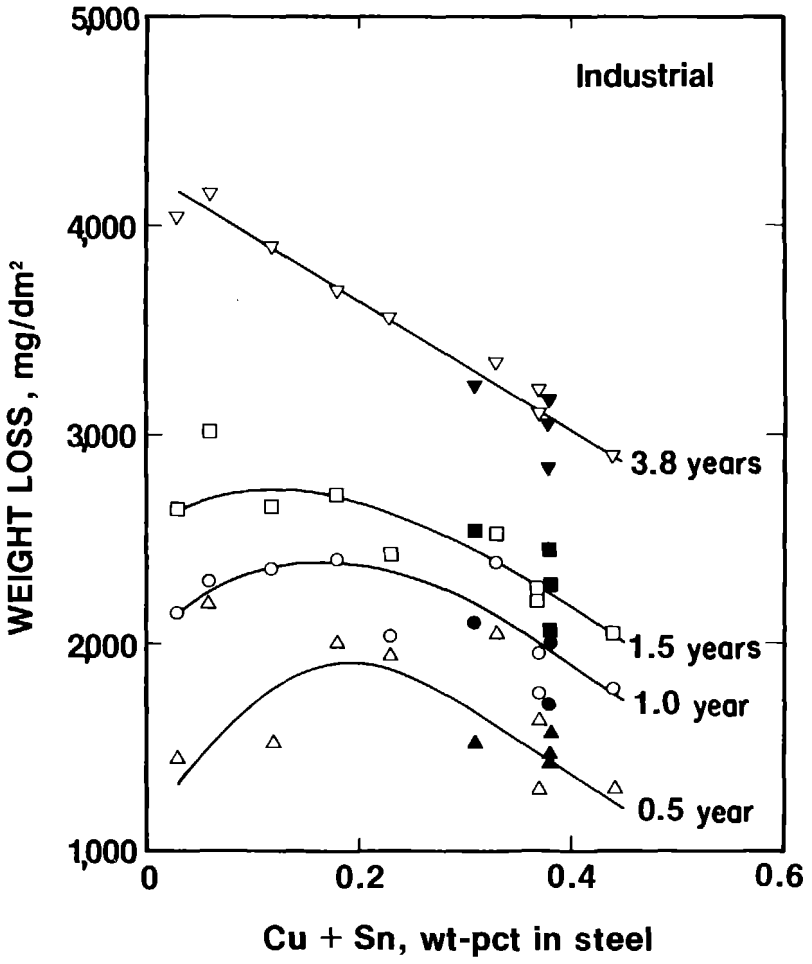

FIGURE 10. - Effect of copper and tin in steel (Cu + Sn) on weight loss of Cor-Ten B steel (solid symbols) and 1030 carbon steel (open symbols) exposed at industrial test site.

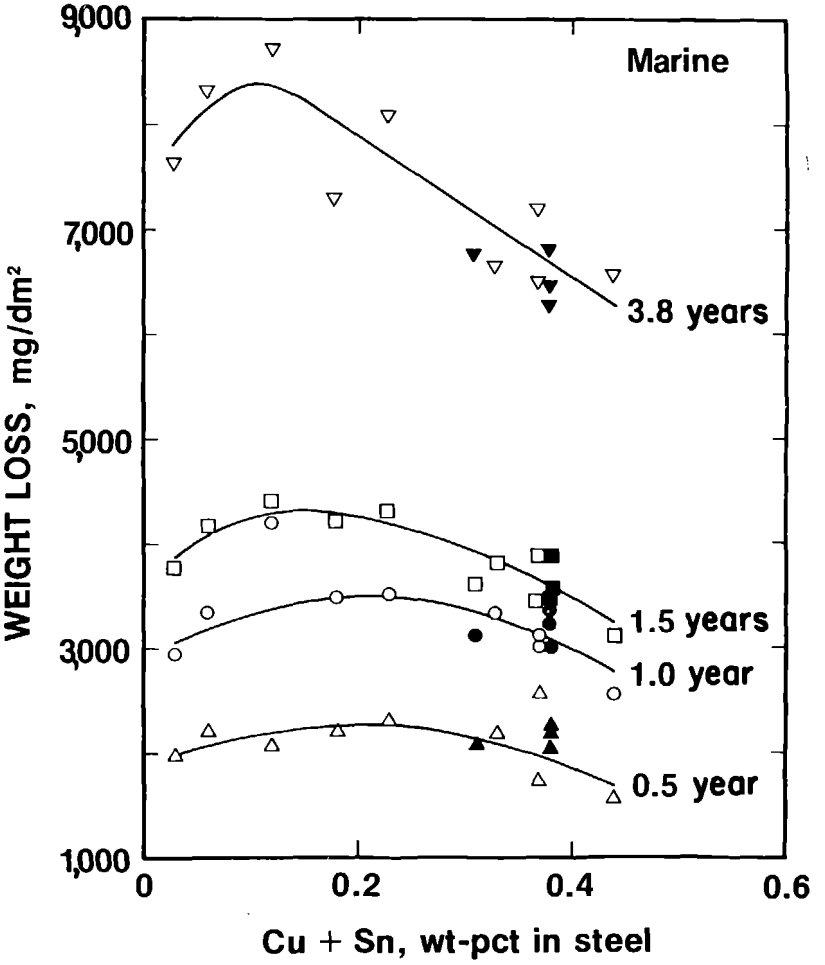

FIGURE 11. - Effect of copper and tin in steel (Cu + Sn) on weight loss of Cor-Ten B steel (solid symbols) and 1030 carbon steel (open symbols) exposed at marine test site.

For longer periods, the maximum in the curve steadily shifted to lower values of (Cu + Sn) as the corrosion film became more protective. This is perhaps associated with the gradual accumulation of tin near the metal-film interface illustrated by the depth profiles in figures 2 and 3. With 3.8 years exposure, the weight loss decreased linearly with increasing (Cu + Sn) content, and the experimental steels all showed a lower weight loss than the purchased carbon steel. Furthermore, the weight-loss values for the carbon steels prepared from incinerated scrap, nonincinerated-nondetinned scrap, and 25 wt-pct NNS-75 wt-pct HMS were clustered about the Cor-Ten B values, indicating equivalent atmospheric corrosion resistance. The fact that the Cor-Ten B values are similar to those for 1030 carbon steel of the same (Cu + Sn) content suggests that the chromium and nickel contribution to the atmospheric corrosion resistance of the Cor-Ten B steels is small compared with that of copper and tin. Figure 11 shows similar curves for the weight-loss results from the marine site. The presence of the maximum in the curve for the 3.8 years exposure is an indication that longer times are required for the formation of stable, protective corrosion films in this more corrosive environment.

Thus, in general, the atmospheric corrosion properties of all the experimental carbon steels prepared from the magnetic fraction of urban refuse were comparable to or better than those of the purchased steel. With low levels of residual copper and tin, as in the nonincinerated-detinned product or products made by dilution with heavy melting scrap, the corrosion resistance of the experimental steels were more like those of the purchased steel. Conversely, the atmospheric corrosion resistance of the carbon steels prepared from the incinerated scrap and nonincinerated-nondetinned scrap and containing high levels of copper and tin were markedly better than those of the purchased product and behaved much like the Cor-Ten B steel. There was no evidence that Cr, Ni, or Pb significantly affected the corrosion resistance of either the 1030 carbon steels or the Cor-Ten B steels. Copper and tin appear to be the critical residual elements in the carbon steels and responsible for improving their atmospheric corrosion properties.

Kinetics of Atmospheric Corrosion

For purposes of this discussion, the growth kinetics of the atmospheric corrosion film and the dissolution kinetics of the corroding steel are presumed to be equivalent since the corrosion products from the steel are added directly to the corrosion film. This analogy, of course, ignores several other processes that affect corrosion film growth, incorporation of atmospheric pollutants in the film and leaching of corrosion products from the film. However, these processes are less important to the actual thickening of the corrosion film. (Conversely, they can be quite important in modifications of the corrosion film that eventually determine its protective characteristics.) Because the principal measure of corrosion in this report is the weight loss of the exposed panels, the growth kinetics of the corrosion film will be analyzed in terms of the dissolution kinetics of the corroding steels.

Legault and Pearson (25) have shown that the rate law governing the atmospheric corrosion of steels in industrial and marine environments is an exponential function of time.

$$\frac{dm}{dt} = -kt^n . \qquad (2)$$

In this equation, m is the mass per unit area of the corroding panel in milligrams per square decimeter, t is time in years, and k is the rate constant. Values of the exponent, n, greater than zero represent autocatalytic reactions, and values less than zero correspond to the formation of protective corrosion films. MacDonald, Roberts, and Hyne (27) have successfully used this rate equation in studies of the corrosion of carbon steel in wet elemental sulfur. Integration of equation 2 shows that the weight loss of the panels, Δm, is

$$\Delta m = m_t - m_o = \frac{kt^{n+1}}{n+1} \qquad (3)$$

Equation 3 was fit by least squares to data for each steel and for each test site. These data were the eight weight-loss values representing duplicate panels for the four exposure periods. The curve fitting was performed to obtain the parameters k and n. The smoothed weight-loss values obtained by this procedure for the 13 steels differed from the experimental data by a mean error of 4.2 pct. This was higher than the mean error recorded by Legault and Pearson (25) of 2.0 pct for steels exposed to a marine environment.

Computed values of the rate constant, k, are tabulated in table 13 and those of the power law constant, n, in table 14. The rate constants for purchased carbon steel and purchased Cor-Ten B at the marine site are similar to those reported (25) for mild steel and a HSLA (A-242) steel exposed at the 800-foot marine site at Kure Beach, N. C., and follow the same trend with respect to the composition of the alloys. The power law constants are, however, somewhat smaller but this is most likely due to different conditions of exposure during the period of the tests. The results for carbon steel show that the presence of the residual elements in product steels prepared from the incinerated scrap and the nonincinerated-nondetinned scrap lead to lower initial corrosion rates at all three sites, that is, smaller k. The results also show that the purchased Cor-Ten B has improved corrosion resistance compared with the purchased carbon steel. Ranking of the three sites shows that the marine environment is the most corrosive and the industrial environment is least corrosive (smaller k, large negative n). This latter fact is contrary to several earlier reports (3, 28) but is verified here by data from over 300 test panels.

TABLE 13. - Rate constant, k, for steels exposed at atmospheric test sites

Steel	Marine	Rural	Industrial
Cor-Ten B:			
Purchased	1,736	1,188	747
HMS	1,681	767	692
IS, heat 1	1,678	977	683
IS, heat 2	1,596	1,224	595
1030 carbon steel:			
Purchased	2,008	1,374	1,050
HMS	2,191	1,322	856
IS, heat 1	1,750	1,274	758
IS, heat 2	1,741	1,300	671
50 wt-pct IS-50 wt-pct HMS	2,133	1,299	685
25 wt-pct IS-75 wt-pct HMS	1,949	1,326	723
NNS	1,742	1,112	651
25 wt-pct NNS-75 wt-pct HMS	1,709	997	553
NDS	2,430	1,474	987

TABLE 14. - Power law constant, n, for steels exposed at atmospheric test sites

Steel	Marine	Rural	Industrial
Cor-Ten B:			
Purchased	-0.431	-0.485	-0.636
HMS	-.451	-.697	-.660
IS, heat 1	-.465	-.551	-.648
IS, heat 2	-.492	-.428	-.664
1030 carbon steel:			
Purchased	-.338	-.350	-.502
HMS	-.352	-.516	-.670
IS, heat 1	-.371	-.450	-.574
IS, heat 2	-.484	-.372	-.664
50 wt-pct IS-50 wt-pct HMS	-.389	-.476	-.693
25 wt-pct IS-75 wt-pct HMS	-.421	-.518	-.704
NNS	-.304	-.419	-.629
25 wt-pct NNS-75 wt-pct HMS	-.468	-.627	-.768
NDS	-.321	-.377	-.550

The rate constant, k, is plotted in figure 12 as a function of the average concentration of the sulfur in the corrosion film (3.8-year values in weight-percent) tables 7 through 9. The data from all three sites--marine, rural, and industrial--fall on a single smooth curve with k decreasing with increasing sulfur concentration. An exponential equation gave a better least squares fit to the data than a linear equation and showed that the rate constant varied with sulfur concentration as

$$k = \frac{811}{\lceil S \rceil^{.9}} \cdot \qquad (4)$$

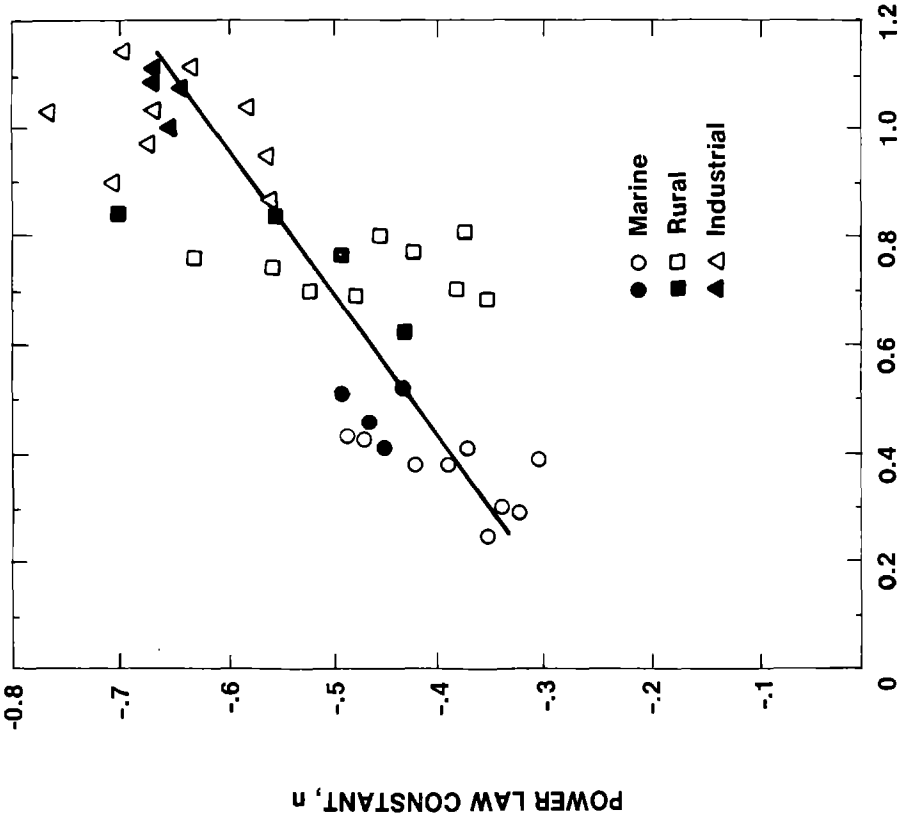

FIGURE 13. – Effect of sulfur in corrosion film on power law constant, n. (Cor-Ten B–solid symbols; 1030 carbon steel–open symbols.)

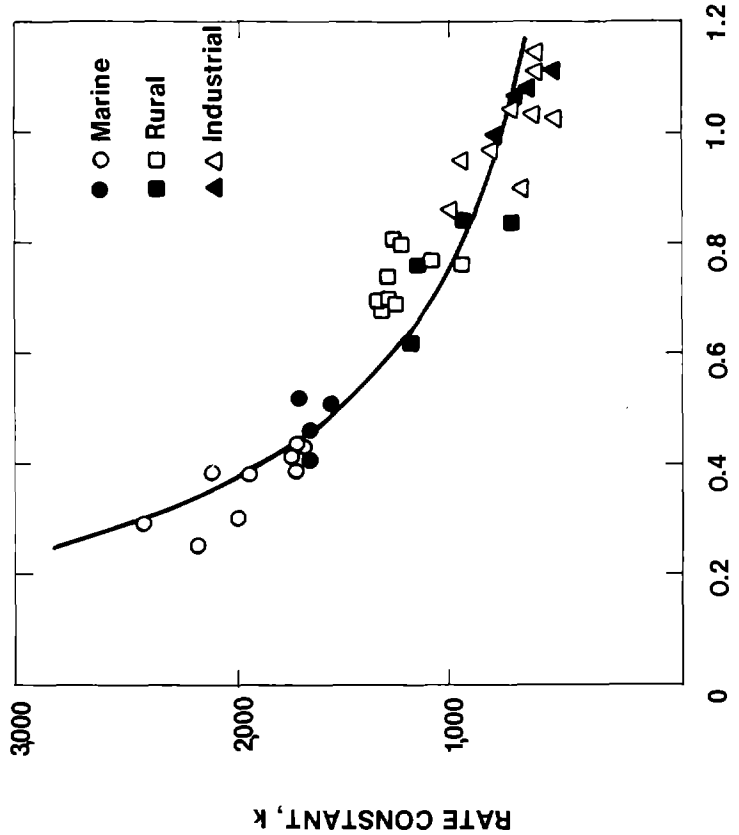

FIGURE 12. - Effect of sulfur in corrosion film on rate constant, k. (Cor-Ten B–solid symbols; 1030 carbon steel–open symbols.)

This result suggests an interesting experiment. Namely, in an SO_2 free environment, the results indicate that corrosion rates for carbon steels and HSLA steels would be substantially higher than those observed here or in past atmospheric corrosion studies.

A similar plot of the power law constant versus average sulfur concentration is shown in figure 13. The high degree of scatter suggests that other factors are also important in defining the protective characteristics of the corrosion film. Some of these factors will be explored in a later Report of Investigations dealing with the chemistry of atmospheric corrosion films. A least squares fit of the data to a linear equation gave

$$n = -0.235 - 0.382[S]. \quad (5)$$

The implication is that weight-loss curves, such as those shown in figure 4, will become increasingly linear and the atmospheric corrosion film less protective in environments containing lower amounts of SO_2. As noted earlier and shown in figure 4, this is the trend observed in going from the high-SO_2 industrial environments to the much lower SO_2 marine environments containing chlorides.

Referring back to figure 1, the connection between certain elements in the alloy, for example, copper and tin, is now clearer. These elements tend to increase the concentration of sulfur in the corrosion film. This apparently occurs by combination of these elements with the sulfur in some complex way within the corrosion film. In so doing, the rate constant for the corrosion reaction is reduced and the corrosion film formed is more protective. However, figure 1 shows that the most important factor leading to high sulfur concentrations in the corrosion film is the level of SO_2 in the environment. It would suggest that carbon steels and HSLA steels have experienced a decrease in their general corrosion rates as SO_2 levels in the atmosphere, over the past several decades, have increased.

CONCLUSIONS

Atmospheric corrosion properties of HSLA steels and of carbon steels exposed for 3.8 years to marine, rural, and industrial environments were not degraded by preparing these steels from the magnetic fraction of urban refuse. In fact, there was a marked improvement in the atmospheric corrosion resistance of 1030 carbon steel when incinerated scrap or nonincinerated-nondetinned scrap was used as melting stock. The critical residual elements responsible for the improved corrosion resistance were copper and tin. The beneficial effect of tin appears to be related to the accumulation of tin in the corrosion film near the film-metal interface. Chromium, nickel, and lead had no observable effect on the atmospheric corrosion resistance of either the HSLA steels or the carbon steels.

The presence of sulfur in the corrosion film was the most important factor affecting the corrosion resistance of the steels. The effect of copper and tin in the steels was to increase the concentration of sulfur in the corrosion films. With increasing sulfur concentration, the rate constant for the corrosion reaction was reduced and the corrosion film became more protective.

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16. Abstract (Limit: 200 words)

The Bureau of Mines conducted a study in which the magnetic fraction of urban refuse was used as melting stock in the preparation of high-strength, low-alloy and carbon steel. Product steels, made from incinerated steel can scrap, nonincinerated-nondetinned steel can scrap, nonincinerated-detinned steel can scrap, and dilutions of these scraps with No. 1 heavy melting scrap, were used in continuing tests in industrial, rural, and marine environments to determine the effect of residual elements and atmospheric pollutants on their atmospheric corrosion resistance. The respective commercial steels were exposed at the same time to establish baseline corrosion data for the test sites. Weight-loss data are reported for atmospheric exposures of 0.5, 1.0, 1.5, and 3.8 years. The marine environment was the most corrosive; the industrial environment was the least corrosive. The atmospheric corrosion resistance of the carbon steel was improved 25 pct by using incinerated scrap and nonincinerated-nondetinned scrap in the steelmaking process. In no case was the atmospheric corrosion resistance of carbon steel degraded by using the magnetic fraction of urban refuse as melting stock. The presence of sulfur in the corrosion film was the most important factor affecting the corrosion resistance of the steels. With increasing sulfur concentration, the rate of the corrosion reaction was reduced and the corrosion film became more protective. The residual elements in the product steels most responsible for improving corrosion resistance were copper and tin. These elements tended to increase the concentration of sulfur in the corrosion film. At the levels present in the product steels, Cr, Ni, and Pb had no observable effect on the corrosion resistance of the steels.

17. Document Analysis a. Descriptors
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