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# ATMOSPHERIC FACTORS AFFECTING THE CORROSION OF STEEL

BY

P. J. SEREDA

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# Atmospheric Factors Affecting the Corrosion of Steel

Measurement of temperature, sulfur dioxide, and surface moisture has resulted in systematic evaluation of the atmospheric corrosion of steel and should provide a basis for the rating of inland exposure sites

THE major factors in atmospheric corrosion recognized in the literature are moisture, sulfur dioxide, and temperature. Many studies have been concerned with their correlation with the corrosion rate of steel, but work with field exposures has always been complicated by the difficulty of recording simultaneously over long periods of exposure the variable factors involved.

Recently there has been developed a simple and reliable device for measuring the time-of-wetness on the surface of a corroding sample (12, 13). With this development it is possible to measure all the major factors during the field ex-

posure of samples. A program was planned, therefore, to measure time-of-wetness, sulfur dioxide, and temperature along with rate of corrosion of exposed steel samples to investigate the possibility of correlation. The results of this work are now reported.

The effect of moisture upon corrosion of steel has been demonstrated by many workers (1, 2, 3, 15). Moisture in the form of rain accounts for only part of the observed corrosion of steel in the atmosphere (3) and high humidity accounts for the remainder (3, 17). Experimental work has shown that in the presence of sulfur dioxide and dust particles, steel

will begin to corrode at a high rate when the relative humidity exceeds 80% (15).

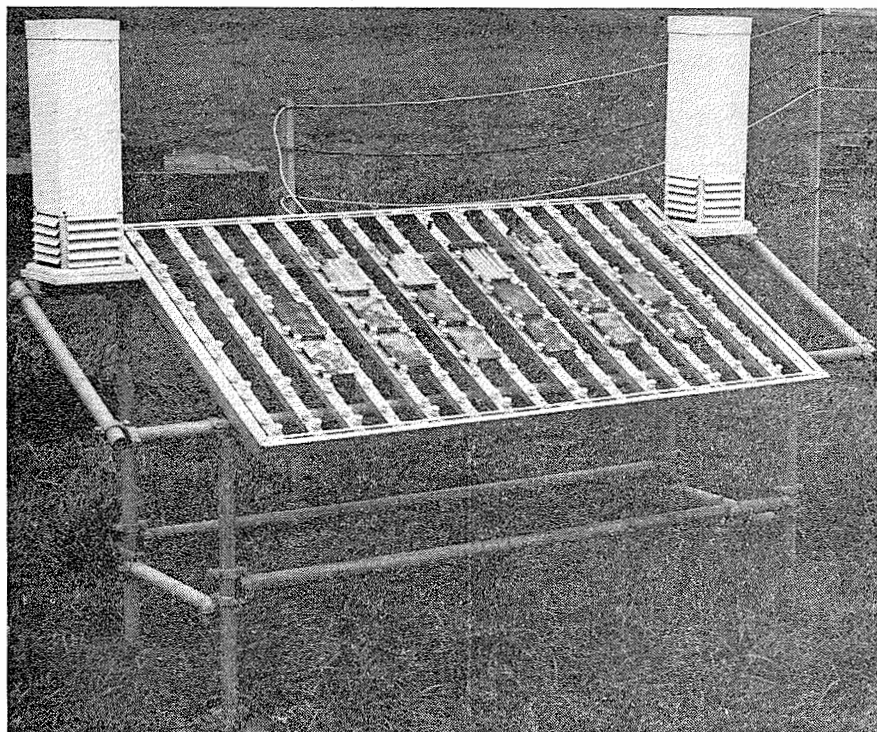
The effect of increased temperature in increasing corrosion rate has been demonstrated in the laboratory (10). As yet, no relationship has been established between the temperature of an exposed test panel and its corrosion rate although at a temperature of  $-25^{\circ}\text{C}$ . the corrosion rate decreases to a low value (4). Some of the difficulties in doing this are apparent from the field evidence which shows that corrosion rate of steel based on total time of exposure can be higher in winter than in summer (17).

Studies have been made which show that orientation of the sample affects the rate of corrosion (9, 14).

A direct relationship between sulfur dioxide pollution rate and rate of corrosion has been found (8, 17, 15). The lead peroxide method of measuring deposition rate of sulfur dioxide has been in use for some time at Canadian exposure sites (7). Determinations made by this method have been shown to relate directly to those obtained from a volumetric apparatus such as the autometer (5). More recently, however, a device has been developed to expose the lead peroxide cylinders only during the time-of-wetness. Details of this device will be reported separately.

## Experimental

Steel panels were exposed at each of two sites 800 yards apart, for a period of eight months during 1957-58. One of these sites was very close to the powerhouse on the property of the National Research Council where the sulfur dioxide pollution rate was as much as four times that at the other site, which is one of the eight Canadian corrosion sites used by the NRC Associate Committee on Corrosion Research and Prevention (ACCRP). As the sites



This field exposure rack was used for mounting corrosion samples and instrumentation for measuring factors affecting the corrosion of steel

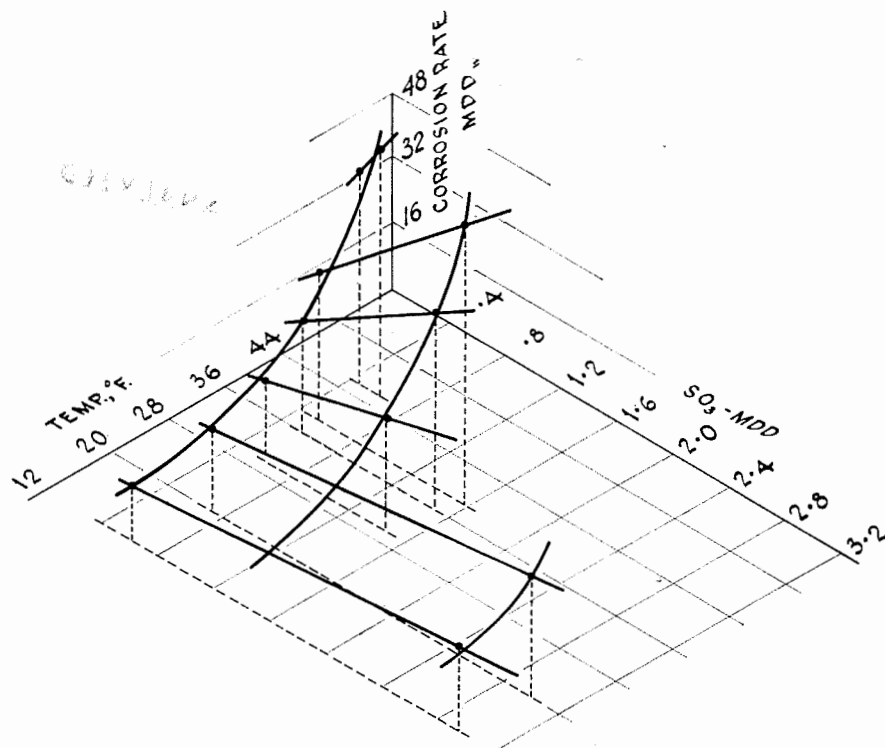


Figure 1. Graph shows how the rate of corrosion of steel based on a day of wetness is affected by the temperature and sulfur dioxide pollution rate (from Table I)

were very close together it is probable that the major variation between them was in sulfur dioxide pollution rate. It was, in fact, necessary to assume in analyzing results that temperature and time-of-wetness were identical at the two sites because electric power for complete instrumentation was available only at the first site.

During the exposure of the test samples, the period when moisture was present on the surface, defined as the time-of-wetness, was obtained from the record of the moisture-sensing element which was exposed in the same manner and location as the test samples. The method (12, 13) involves measurement of the potential developed by closely spaced electrodes of platinum and zinc when the surface film moisture provides the electrolyte. The time-of-wetness was obtained for both the skyward and the groundward exposures and the total time-of-wetness for any test sample was the average of the two values giving the corroding time as days of wetness,  $D_w$ .

The temperature of a corroding sample of steel was measured continuously by means of a copper constantan thermocouple and a Leeds and Northrup Speedomax recorder. Thirty-gage wire was looped on the groundward side of the panel and held to the metal surface with Scotch electrical tape No. 56. Thus each month the average hourly temperature of the test sample was obtained for the periods when wetness occurred. This average temperature was used in

relating the effect of temperature to the rate of corrosion.

Sulfur dioxide was measured separately at each of the two sites, using the lead peroxide method (7). The sulfur dioxide pollution rate thus obtained was based on a monthly collection and expressed as an average daily rate. For purposes of correlation with corrosion rate, it was assumed that the rate during periods when wetness occurred was the same as the average rate, including both wet and dry periods. Instrumentation was not at that time available for exposure of the lead peroxide cylinder only during wet periods. It was also

necessary to assume that the sulfur dioxide deposition rates shown by the lead peroxide cylinder were directly related to those for the exposed samples.

Samples of low-carbon plain steel measuring  $4 \times 6 \times \frac{1}{8}$  inch were used. The composition of the steel, determined by the Steel Co. of Canada, was as follows:

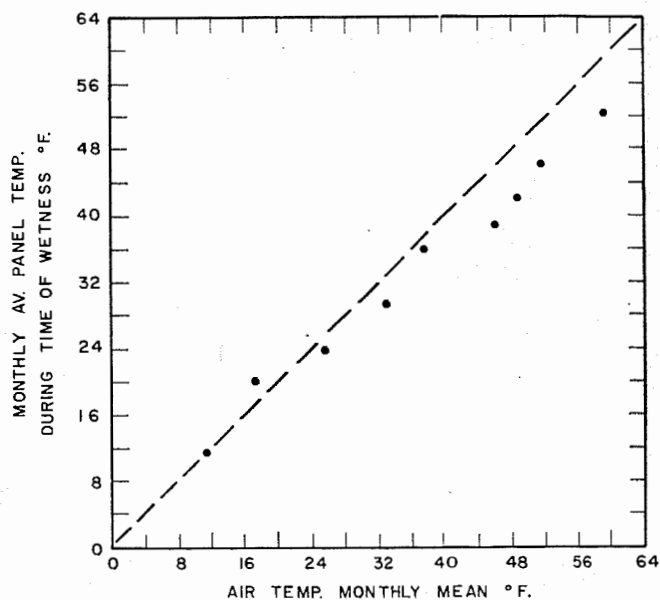
	%
Carbon	0.052
Phosphorus	0.014
Sulfur	0.039
Manganese	0.350
Silicon	0.002
Aluminum	0.008
Copper	0.066
Molybdenum	0.007
Tin	0.011
Nickel	0.048

The surface of the samples was grit-blasted using No. 30 aluminum oxide, then degreased with carbon tetrachloride.

The samples were exposed for one month at a time at  $30^\circ$  to the horizontal on standard corrosion racks facing south (photograph). At the end of each month, samples were taken to the laboratory and the corrosion products were removed by 50% hydrochloric acid solution containing 2% rodimine. A blank was run to check the amount of steel removed. The blank correction was never more than 1% of the total monthly weight loss. Samples were exposed in triplicate and agreement between samples was good, with differences between weight losses being less than 2%.

The weight loss was reduced to the corrosion rate in terms of milligrams per square decimeter per day of wetness by combining the weight loss for the month with the time-of-wetness for the same month. This corrosion rate was then plotted against the average temperature values and the corresponding pollution rate in terms of milligrams of sulfur trioxide per square decimeter per day, on three-coordinate isometric graph paper (Figure 1).

Figure 2. This graph shows that the average panel temperature during time of wetness is similar to the mean air temperature



The rate of corrosion increased almost logarithmically with temperature and a replot of the values of log rate against temperature and sulfur trioxide gave a reasonable plane. The least-squares method was then used to determine the equation for the best fitting plane for the values. The equation for this relation is:

$$Y = 0.131X + 0.0180Z + 0.787$$

where:

$Y$  = log corrosion rate,  $MDD_w$  (mg. per sq. dm. per day of wetness)

$X$  = sulfur dioxide pollution rate,  $MDD$  (mg. sulfur trioxide per sq. dm. per day)

$Z$  = temperature ° F. (monthly average during the time-of-wetness)

The analysis of variance was carried out to determine whether a significant tendency existed for the points represented by the data to fall upon this plane. This analysis indicates that there is a definite regression of temperature and sulfur dioxide pollution rate with respect to the rate of corrosion.

## Discussion

A relationship has been established which shows how the rate of corrosion of low-carbon plain steel, in the presence of oxygen and water, is modified by the atmospheric factors of temperature and sulfur dioxide pollution rate. The particular relationship found applies only to one type of steel exposed on standard corrosion racks at Ottawa sites. Further, these two sites differed mainly only in sulfur dioxide pollution rate. Nevertheless the fit of points and the orderliness of the curves shows promise that some such representation may be applicable to a wider range of data and to other sites.

A number of approximations have been made, some of which have already been noted. The sites have been assumed to be identical, apart from sulfur dioxide. The sulfur dioxide determination was taken over the whole month and not just over the hours of wetness. Finally, the data are based on averages for monthly periods. This ought to affect the temperature correlation particularly since corrosion rate is far from linear with respect to temperature.

Subsequent work has shown that sulfur dioxide pollution rates are different during wet periods than during dry periods. This is no doubt due in part to the different wind directions which may exist during rainy weather. The extent of these variations is related to various climatic conditions and it would be best to use the value obtained during

Table I. Hours of Wetness to Which Samples Were Exposed Show the Difference between Skyward and Groundward Exposures

Month	Hour Wetness					
	Total		From precipitation		From condensation	
	Groundward	Skyward	Groundward	Skyward	Groundward	Skyward
1957						
Oct.	428	348	154	126	274	222
Nov.	492	316	276	215	216	101
Dec.	594	457	322	291	272	166
1958						
Jan.	544	452	267	245	277	207
Feb.	614	553	416	430	198	123
March	432	346	109	104	323	242
April	311	247	149	120	162	127
May	266	138	175	100	91	38
June	285	185	135	103	150	82

the time-of-wetness for which instrumentation is now available.

The temperatures used were those measured directly during the periods of wetness, as obtained from the continuous record of temperature. However, a comparison of the temperature averages thus found with the monthly mean temperatures for Ottawa obtained by the Meteorological Division, Department of Transport, shows a remarkably close agreement (Figure 2). This suggests that regular meteorological records of mean monthly temperature may be suitable, thus eliminating the requirement for special measurement of temperature at a site during hours of wetness only.

Influence of temperature upon corrosion rate is clearly shown, once the observed corrosion rate is reduced to a basis of time-of-wetness. The increased

time-of-wetness during winter months (Table I) provides an explanation of the increased winter corrosion reported in the literature despite the lower mean temperatures.

Atmospheric pollution is an important factor especially when considered in relation to temperature. At 11° F. a fivefold increase in sulfur dioxide pollution rate increased the rate of corrosion by a factor of 1.6, whereas at 39° F. a threefold increase in the pollution rate increased the rate of corrosion by a factor of 1.9 (Table II). Also, sulfur dioxide which is deposited from the atmosphere cannot account for all of the corrosion of steel in the atmosphere and obviously oxygen and water are also significant factors.

These results provide a basis for interpreting other effects noted in the literature. The groundward exposure

Table II. Results from Measurement of Temperature, Sulfur Dioxide, and Surface Moisture as Related to Observed Corrosion of Steel

Date	Wt. Loss, G.	Time-of-Wetness, $D_w$ Days	Corrosion Rate, $MDD_w$	SO <sub>2</sub> , $MDD$	Av. Temp., ° F.
ACCRP Corrosion Site					
1957					
Nov.	1.420	16.8	26.4	0.55	36.0
Dec.	1.519	21.9	21.6	0.64	23.9
1958					
Jan.	1.318	20.8	19.8	0.71	20.0
Feb.	0.999	24.3	12.8	0.60	11.2
March	0.971	16.2	18.6	0.61	29.3
April	1.334	11.6	35.8	0.53	38.9
May	1.404	8.4	52.0	0.47	46.1
June	1.341	9.8	42.8	0.31	52.3
DBR Property Site					
1957					
Oct.	2.791	16.2	54.0	1.02	42.0
Nov.	2.589	16.8	48.0	1.49	36.0
Dec.	2.561	21.9	36.4	1.96	23.9
1958					
Jan.	2.044	20.8	30.7	3.02	20.0
Feb.	1.589	24.3	20.4	2.95	11.2
March	1.373	16.2	26.4	1.48	29.3
April	2.554	11.6	68.6	1.59	38.9
May	1.635	8.4	60.6	0.62	46.1
June	1.931	9.8	61.6	0.62	52.3

Table III. Corrosivity Rating of the ACCRP Corrosion Sites Across Canada

Location	Annual Mean Temp., ° F. (1954-56)	Pollution Rate SO <sub>2</sub> MDD av. (1955-56)	Calculated		Observed	
			Rate of corrosion of steel, MDD <sub>st</sub>	Corrosive rating relative to Ottawa	Wt. loss av. yearly (1954-56) for "standard" steel (G.) <sup>a</sup>	Corrosive rating relative to Ottawa
Ottawa	43.3	0.47	42.4	1.0	7.1	1.0
Saskatoon	34.5	0.24	27.4	0.47	4.1	0.6
Montreal	44.7	2.24	76.8	1.8	10.0	1.5
Halifax (Federal Building)	45.7	12.52	177.7	4.2	25.8	3.8
Halifax (York Redoubt)	45.7	0.48	47.0	1.1	10.3	1.5
Norman Wells	19.1	0.01	13.5	0.32	0.22	0.03
Esquimalt	48.7	0.05	46.8	1.1	3.3	0.5
Trail	46.2	0.98	55.8	1.3	9.8	1.4

<sup>a</sup> Obtained by C. P. Larrabee for ASTM Committee B-3.

is shown to have been wet for a greater length of time than the skyward exposure for both rainy periods and condensation periods (Table I). This is the first direct evidence to explain at least in part why steel corrodes faster on the groundward side (9, 14). The reasons for the increased wetness of the groundward side are undoubtedly to be found in studies of radiant and convective heat transfer between the ground, panel, and sky (6). It may be noted that the temperature of the panel dropped as much as 8° F. below air temperature at night when the sky was clear and rose as much as 30° F. above air temperature when the sun was shining.

The excellent correlation of the rate of corrosion with atmosphere pollution in Great Britain (7) can be accounted for by considering that on a yearly basis the temperature during the times when wetness occurred might have been the same for all the exposure sites and also that the total time-of-wetness for the year might not have differed significantly from one site to another.

The sulfur dioxide pollution rate has been measured since 1954 at the eight corrosion sites in Canada maintained for the work of the ACCRP. An average yearly value was obtained and the mean yearly average temperature for the years 1954-56 was also available from meteorological data. If the equation for the rate of corrosion of steel is applicable for these other sites, they could be rated in terms of the corrosion rate per day of wetness (Table III).

The rating obtained by exposing "standard" steel samples as was carried out by Larrabee for ASTM Committee B-3 and reported to Subcommittee C of the ACCRP is also given.

A comparison of these two corrosive ratings implies that the hours of wetness are the same at all sites since one is related to a day of wetness while the other is based on actual corrosion rates on a full-time basis. The close agreement for a number of the sites suggests that this may well be so. Only at coastal and far northern sites where salt effects

and time-of-wetness are expected to be different from the Ottawa site does the rating differ significantly.

When corrosion in coastal areas is considered, it is certain that the effect of the salt carried as spray from the ocean must be included. The relationship given here would be modified to include the effect of salt and the measurement of salt concentration would have to be added to the observations.

The temperature of the sample appears to affect the process of corrosion directly and it is also important in altering the time-of-wetness due to the temperature difference between the sample and the ambient conditions. This involves the heat transfer by radiation and convection between the sample and its environment. In this regard the size, geometry, and orientation of the sample are important (6) and these factors should be studied.

Much work remains to be done to show the exact relationship of the concentration of sulfur dioxide in the air as determined by the lead peroxide method and the concentration of the reactants on the surface of the corroding metal. The effect of washing by rain must be assessed in this connection.

The correlation of the atmospheric factors affecting the corrosion of steel gives a new hope that atmospheric corrosion can be reproduced in the laboratory. This is of particular interest since conditions not conveniently provided by outdoor exposure can be explored as well and the study of the mechanism of the corrosion process facilitated.

Work on corrosion in the laboratory is now in progress. In planning a laboratory program to reproduce outdoor conditions it was realized that with reduced rate of air flow over the sample the concentration of the sulfur dioxide in the experimental atmosphere must be increased.

It has been found (5) that a concentration of 0.025 p.p.m. sulfur dioxide in the atmosphere results in a deposition rate of 1 MDD of sulfur trioxide by the

lead peroxide method. From this it can be concluded that a volume of over 25,000 liters of air per day must come in contact with the reacting surface if the complete removal of sulfur dioxide is assumed. This is not likely, and experiments to date have shown that the cylinder of lead peroxide used for determining the pollution rate removes less than 1% of sulfur dioxide from an air stream flowing at the rate of 700 liters per day having a sulfur dioxide concentration in the range 0.2 to 0.02%.

Thus, when the volume rate of air flow over the lead peroxide cylinder is reduced to 700 liters per day, the sulfur dioxide concentration has to be increased by a factor of 10,000 to give the same deposition rate as observed outdoors. This raises for further study the question whether the deposition of sulfur dioxide on the metal surface will bear the same relation as the deposition on the lead peroxide surface when the concentration of sulfur dioxide in the air is so drastically changed.

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