

A GENERAL CORROSION FUNCTION IN TERMS OF ATMOSPHERIC POLLUTANT CONCENTRATIONS AND RAIN pH

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Abstract—The process of atmospheric corrosion of metals can be represented by the well-known exponential expression

$$M = at^b$$

where M is the metal loss during the exposure time (M : g m^{-2} ; t : years) and a and b are described below. The critical review of the available corrosion test programs yielded a data basis for the statistical analysis of the parameters a and b . If the multiplicative factor a is expressed in terms of t_w , the time-of-wetness, which is a fraction of the total exposure time t , e.g. $t_w = f \cdot t$, then $a = f^b A$, and A may be approximated as a linear function of the SO_2 and Cl^- deposition per unit surface. For example, for zinc, the following relationship holds:

$$A = 4.8 + 0.53 [\text{SO}_2 + \text{Cl}^- \text{ surface deposition, mg m}^{-2} \text{ d}^{-1}]$$

Units of A : weight loss per 1 wetness year, g m^{-2} .

The above relationship is highly significant and represents, in conjunction with the exponential expression, a general formula for all atmospheric zinc corrosion tests, i.e. it is an effective reconciliation of corrosion results. Its predictive error is less than $\pm 50\%$ for one-half of the cases and less than $\pm 20\%$ in the other half. Similar expressions have been obtained for carbon steel and for copper. In the instance of carbon steel, the predictive accuracy is less than for zinc because 'carbon steel' was not exactly the same alloy on all test programs. For copper the relationship holds quite well, but the data base is yet small.

The exponent b , which characterizes the diffusivity of the corrosion product layer, can be expressed as a function of the average rain pH. For zinc, this relationship is:

$$b = 1.55 - 0.142 (\text{average rain pH}).$$

The correlation is very highly significant.

The physical concept explaining the parameters a and b is strongly supported by observations about the skyward and groundward exposed corrosion samples. Tests at sheltered sites (inside louvered cabin) also fit into the general pattern.

INTRODUCTION

During the last two decades, at least 20 damage functions have been proposed to represent the corrosion behavior of zinc, galvanized steel and steel in the atmosphere. Most of them use an a priori statistical approach, meaning that a number of variables (like time-of-wetness, atmospheric corrosivity, perhaps H^+ concentration etc.) which a priori seem pertinent for the process, are selected first. Then a best-fit regression equation is sought. The form of this equation is determined by best fit, not through physico-chemical considerations.

A simple physico-chemical rationale, taking into consideration the diffusive behavior of the corrosion product layer, has already been proposed by

Tammann in 1923. The present approach uses this concept and attempts to go one step further: to link the two constants of the exponential (called also linear bi-logarithmic) relationship to the most salient environmental factors. As both corrosion and environmental measurements are loaded with large random and systematic errors, the link of the data with the constants must use some method of optimal fitting, i.e. statistics. To be valid, the statistics must be on a wide basis. Results obtained within one country only seldom show enough range either in corrosion or in environmental parameters (perhaps continent-size countries excepted) to obliterate the inevitable noise. Therefore, it seems logical to base such an attempt on worldwide data.

Several major atmospheric corrosion projects have

been accomplished during the last 10 years. Some of them are still ongoing. Standardization notwithstanding, their results have been expressed in almost as many ways as the number of projects. Almost every project resulted in one or more damage equations, best fitted to the basic data, but differing from project to project.

To accomplish the statistical task of linking environmental corrosive factors to the meaningful constants of the linear bi-logarithmic level, a first requisite was to reconcile all available experimental material.

1. THEORETICAL BACKGROUND

During the last 50 years, several authors observed that the exponential expression

$$M = at^b, \quad (1)$$

where M is the metal loss in g m^{-2} , t is the exposure time in years, and a and b are constants, represents with good approximation the time dependence of the atmospheric corrosion of many metals. As most data points lie close to the line

$$\log M = \log a + b \log t, \quad (1a)$$

the name 'bilogarithmic law' has also been applied (Schwenk and Ternes, 1968; Haynie and Upham, 1971; Legault and Preban, 1975; Pourbaix, 1982).

Equation (1) was in fact developed by Tammann (1923) to represent growth of scale and tarnish layers on metallic surfaces.

For a diffusion-controlled mechanism, the mass of reactant arriving into contact and reacting with the surface must be inversely proportional to the thickness x of the film covering the surface

$$\frac{dx}{dt} = \frac{k}{x} \text{ or } x^2 = 2kt \quad (1a)$$

where

x = thickness of the film covering the surface

t = time.

With $(2k)^{1/2} = a$, one obtains Equation (1a) in the special case $b = 1/2$, i.e. the ideal diffusion-controlled mechanism when all corrosion products remain on the surface as an unperturbed layer. However, if the diffusion coefficient decreases with time, e.g. due to a decrease in porosity of the rust layer (recrystallization, agglomeration, filling up of pores etc.), then b will have a lower value than 0.5. Alternatively, if the diffusion process is accelerated by removal of the layer by erosion, dissolution, flaking, cracking, or other similar processes, the exponent b will be higher than 0.5, attaining the limiting value of 1.0. Thus b is an index of the presence and of the physico-chemical behavior of the corrosion product layer, including the reactions of this layer with such environmental factors as rain acidity.

In deriving Equation (1a) no hypothesis has been advanced about the nature of the reactants or about what is diffusing through which kind of layer.

Equation (1a) is a mass-balance equation showing that the diffusional process is rate-determining and this rate depends upon the diffusive properties of the layer separating the reactants.

The accuracy of Equation (1a) and its reliability to predict long term ($> 2y$) corrosion behavior from short-term tests have been demonstrated, among others, by Legault and Preban (1975) and Pourbaix (1982).

From (1a) it is clear that the exponent b is independent of the units in which M and t are measured. If instead of t , the total exposure time, t_w , the time during which wetness is present is introduced, then as $t_w = ft$ ($0 \leq f \leq 1$)

$$M = a \left(\frac{t_w}{f} \right)^b = At_w^b. \quad (1b)$$

A is the corrosion loss in the same units as M (e.g. in g m^{-2}) in one year of wetness; $A = af^{-b}$.

One essential step distinguishing this approach from all former uses of the bilogarithmic law consists in the use of t_w instead of t as time variable. It has been stressed previously by almost all authors dealing with metallic corrosion that the process stands still in the absence of a wet film (see also Section 2.2.1). Therefore t and a cannot be related to the progress of the corrosion, while t_w and A can be used as explanatory variables. As Section 3 demonstrates, the statistical analysis of A allows pollutants to be taken into account, thus leading to the reconciliation of results.

The instantaneous corrosion rate dM/dt_w follows from Equation (1b) through differentiation:

$$\frac{dM}{dt_w} = Abt_w^{b-1} \quad (2a)$$

or

$$\log \frac{dM}{dt_w} = \log A + \log b + (b-1) \log t_w. \quad (2b)$$

Finite time intervals Δt_w a month, in longer series even one year, may approximate dt_w (i.e. the chord taken for the tangent) and (Ab) and $b-1$ can be computed from successive monthly corrosion rates.

The mean corrosion rate M/t_w ($t_w = 1$) for a one-year exposure (respectively for one year of wetness, $t_w = 1$) is:

$$\frac{M}{t_w} = \frac{At_w^b}{t_w} = At_w^{b-1}. \quad (3)$$

In the special case when $b = 1$, the mean corrosion rate of the one-year exposure is equal to A , the intersection of the line on the bi-logarithmic plot with the abscissa $t_w = 1$ y. There is no physical sense in $b > 1$, as $b = 1$ is the limit for unimpeded diffusion (highly permeable corrosion products or no layer at all). Values of $b > 1$ occur practically as exceptions, due to outliers in the weight loss determinations, for example.

As a rule, $b < 1$ (see also Table 2). It follows from

Equations (2a) and (3) that, in this case, $dM/dt_w < M/t_w$.

2. THE LIMITS OF RECONCILIATION

The limits of the reconciliation of damage functions (or of corrosion data) are set by the acquired data quality. Here is a brief reminder of the main sources of divergence.

2.1. Metallurgical definition

The metals submitted to corrosion testing by different investigators are not of the same batch. LaQue (1951) has already pointed out that different sections of the same steel ingot may show weight losses in the ratio of 1 to 2 under identical atmospheric testing conditions.

As for 'pure' zinc and 'pure' aluminum, mostly reported as containing > 99.9% of the main component, one might be slightly more optimistic concerning their corrosion behavior in various testing programs. Nevertheless, an ideally coincident corrosion behavior can scarcely be expected. Impurities well below the 0.1% limit may fundamentally alter the corrosion process and/or the adherence and the diffusivity of the corrosion products which determine the progress of the corrosion process.

2.2. Environmental variables

2.2.1. Time-of-wetness. Metallic corrosion progresses only in the presence of wetness on the surface. In some instances, the presence of the water film has been monitored through a galvanic or conductivity cell on an identical surface placed nearby (Guttman, 1968; Barton and Czerny, 1980; Atteraa and Haagenrud, 1982, etc.). Such records not being available everywhere, several authors (e.g. Guttman, 1968; Sereda, 1977; Haynie, 1980) have proposed formulae linking the average relative humidity of the test site with time-of-wetness. Average relative humidity is a parameter

which can quite readily be obtained from climatological records.

As some of these attempts have been criticized as not having a wide enough experimental basis, a radically new approach has been attempted herewith.

Statistical analysis of worldwide climatological data has shown that instrumentally recorded time-of-wetness (galvanic or conductivity, see above) is strongly correlated to the number of days with precipitation and average temperature above freezing. These data are of easy availability from national or from WMO climatological tables. The relation thus found is:

$$t_w = 1.686 \times 10^{-3} + 3.66 \times 10^{-3} D \approx 3.65 \times 10^{-3} D \quad (4)$$

where D = number of days per year with precipitation and average temperature > 0°C. This relation is significant beyond the 0.001 level (see Column 4 of Table 1). The predictive skill of Equation (4) may be judged from Table 1.

2.2.2. The aggressivity of the atmosphere. As a starting point, we may accept that some atmospheric trace-substances, SO₂, chlorides etc. are corrosion-promoting factors. To act as such, they must arrive in contact with the surface.

The flux to a surface has recently been described by Haynie (1980, the case of a logarithmic wind velocity vs height distribution) or by Benarie (1984, arbitrary wind vs height distribution). The essential conclusion of these theoretical considerations is that the friction velocity above the surface is the decisive factor which characterizes the deposition process. A concentration measurement alone is not enough. Concentration plus wind velocity may give a better approximation, mainly because wind velocity (provided it varies logarithmically with the height) is more or less proportional to friction velocity. However, wind velocity measured at the nearest airport is not necessarily the wind velocity above the sample rack.

There are deposition velocity dependent pollutant

Table 1. Comparison of the number of days with precipitation (column 2) with the instrumentally (galvanic or conductivity cell) recorded time-of-wetness t_w (column 3) and with computed t_w (columns 4 and 5)

	$D_{\text{precipitation}}$ with > 0°C	t_w experimental	t_w computed:	
			Equation (4)	Formula of Haynie (1980)
Prague (Letnany)	79	0.25	0.29	
Oslo (Lillestrom)	75	0.26	0.275	
Madrid	73	0.29	0.27	
Bilbao	126	0.55	0.46	
Vietnam (Hanoi)	175	0.66	0.64	
Saint Louis, MO	74	0.246	0.27	0.246
Boston, MA	57		0.21	0.214
Denver, CO	47		0.17	0.146
Kansas City, KS	57		0.21	0.199
Las Vegas-Boulder Cy, NE	18		0.067	0.070
New York, NY	74		0.27	0.206
Seattle, WA	110		0.40	0.345

measuring devices in existence, and this has been so for a long time: lead peroxide coated surfaces and 'candles,' the IRMA-method (VDI, 1982), the 'wet surface' chloride determinations, etc.

The pollutant measurements obtained by such deposition velocity sensitive methods relate much better to corrosion damage than concentration measurements. Whenever available, this kind of information has been used here. The transformation of concentration data into mass per surface time units is rather uncertain, even if (airport) wind velocity measurements are available. Except when otherwise indicated, the following relationship has been used

$$\text{Sulphation (mg m}^{-2} \text{ d}^{-1}) \cong \text{SO}_2 (\mu\text{g m}^{-3}) \quad (5)$$

knowing that this is a very rough approximation and deviations of $\pm 50\%$ may be rather frequent. This linear relationship is certainly not valid above $100 \mu\text{g m}^{-3} \text{SO}_2$. Arguments in favor of the sulphation for corrosion studies have also been developed earlier (Benarie, 1980). The highly significant correlations between zinc and steel corrosion on one hand, and sulphation plate and lead candle on the other, found during the Interstate Surveillance Project by Cavender *et al.* (1971), bear out the same point. The correlations between the corrosion rates of zinc and steel were even more significant. Thus, it is possible, in a statistical sense, to use the corrosion rate of one metal as proxy for the effective deposition velocity on the others, when adequate data for atmospheric aggressivity are not available.

The comparison of the open air/louvered cabin ambient pollutant concentration measurements is another argument in favor of the deposition velocity sensitive pollutant measuring methods. As Barton and Czerny's (1980) results show, the concentrations are the same outside and inside the cabin. Mechanical forces cannot change the composition of a gaseous mixture. But sulphation (and adsorption of chloride ions also) is only one-half to one-third in the cabin than outdoors, because friction velocity is less inside than outside and because of the impaction loss of NaCl-containing aerosols on the louvers before attaining the exposed surface.

For the determination of the chloride ion concentrations, which are of great importance in marine atmospheres, the dry (GOST, 1974) or wet (IRMA) deposition methods are to be preferred, for the same reasons as for the SO_2 exposed above.

In the instances where wet candle or wet cloth chlorine ion measurements were available next to the sample (this is the case with the COMECON and Scandinavian results) 1 g of chloride was equated with 1 g of sulfur dioxide to obtain the 'sulfur dioxide' entry of the reconciliation equation. This is an obvious oversimplification, but the general quality of the data scarcely justifies a more exact calculation by the equivalent weights, which would yield the factor of $1.11 \text{SO}_2 = \text{Cl}^-$.

2.2.3. *Initial conditions.* Initial conditions have great

influence on metallic corrosion. Vernon (1931), Ellis (1949) and Guttman (1968) demonstrated the initial condition effect for zinc.

Steel behaves in a similar manner. It is well known that the porosity and the composition of the summer rust and winter rust are different (Chandler and Stanners, 1966; Mayne, 1959; Schikorr, 1964; Ross and Callaghan, 1966). They differ in their diffusive and/or protective properties. Wetting and drying cycles influence the structure of the rust layer and its protective properties (Clark *et al.*, 1969; Horton, 1964; Misawa *et al.*, 1974; Kunze, 1974; Schwitter and Bohni, 1980).

Rust formed on steel freely exposed to rain shows a dense and laminated structure as compared to the powder-like grainy structure of the rust formed on sheltered surfaces. Using capacitance and conductivity measurements the outdoor-formed rust layers were found to be less porous. Diffusion to the steel-rust interface is less than with cabin-formed rust; the latter is less protective (Clark *et al.*, 1969).

The enhanced corrosion resistance of steel surfaces exposed to rain is further confirmed by the differences in the skyward-groundward behavior (see Section 2.2.5).

There are no reports in the literature about initial effect on copper and aluminum, although with the latter it seems likely and some data suggest that it might occur.

More often than not, in any one corrosion monitoring program, the outset of the exposure is simultaneous for all samples. Due to this reason, the initial effect differences are automatically eliminated. They do not appear, e.g. on the multiple regression equations describing the results. Therefore, the fit of these equations to the one set of results at their base is mostly good. The surprises arrive only when an attempt is made to use such a formula to a different set of results.

2.2.4. *Temperature.* Theoretically, temperature must influence the corrosion process. It is likely, however, that due to antagonistic effects such as enhanced diffusivity and increasing dryness with rising temperature, the apparent effect is not a large one, in the usual range of temperatures. There is no convincing evidence in most outdoor studies (contrasting with some chamber studies) about a temperature effect. Therefore, no attempt has been made to include temperature in the reconciliation equation.

2.2.5. *The cumulative effect of uncertainties.* Due to the cumulative effect of the uncertainties in reporting metallurgical and environmental variables, the often unreported start of exposure etc., it can hardly be expected that a prediction should be more a priori accurate than $\pm 50\%$ for about one-half of the time and perhaps $\pm 20\%$ for the other half.

3. EXPLOITATION OF THE AVAILABLE EXPERIMENTS

3.1. *Synopsis of the corrosion tests*

There are quite a number of atmospheric corrosion measurements reported in the literature. Only a frac-

tion of them contain all the information which is the prerequisite to solve Equation (1b). These prerequisites are:

- At least three corrosion weight loss data must be known to interpolate the straight line on bi-logarithmic coordinates by Equation (1b). To use the much more sensitive test for smoothness (absence of noise, random error, etc.) of Equation (2a) even more points must be available. There is no condition on the time or the intervals. Results from a few months can be used as well as those from many years.
- A reliable assessment of the time-of-wetness must be available. In Table 2 only experimentally measured t_w s (galvanic or conductivity) have been considered, as reported by the authors. Where such t_w was not available, the factor A has not been computed, in contrast to the exponent b . The invariance of the latter [see Equation (1b)] allows its computation even in absence of reliable t_w .
- A reliable assessment of the pollutant deposition, $\text{SO}_2 + \text{Cl}^-$ at the metallic surface, must also be available. This is necessary for the analysis of the factor A and may be relaxed if only exponent b is sought.
- To analyze the exponent b physically, information about the aggressivity of rain must be present.

After a thorough bibliographical search, the data presented in Table 5 were considered as satisfying these four conditions.

In Table 2, A_{exp} and b_{exp} are the respective parameters as obtained by best fit to the experimental data using Equation (1b). A calculation was obtained by substituting into Equation (1b) (see Sections 3.2.1.1 and 3.2.1.2) the pollutant deposition values as listed in

3.2.1.1. Zinc. The best fit to the complete data set is clearly obtained by a function of $A = g([\text{SO}_2])$ where $[\text{SO}_2]$ stands for the $\text{SO}_2 + \text{Cl}^-$ deposition, i.e. A is a linear function of $[\text{SO}_2]$. If the analysis is restricted to the $10\text{--}50 \text{ mg m}^{-2} \text{ d}^{-1}$ values of $[\text{SO}_2]$ only, then a $\tan \alpha = 0.55$ is the best fit, suggesting a relationship of $A = g([\text{SO}_2]^{1/2})$.

As neither theoretical considerations nor the available experimental evidence can clearly distinguish between these possibilities, for the present purpose it is enough to obtain a best linear fit to the whole data set (columns 2 and 7 of Table 2)

$$A = 4.795 + 0.529[\text{SO}_2] \quad r = 0.96 \quad (6)$$

31 degrees of freedom, significant beyond 0.001 level.

Units of A (the weight loss per 1 wetness year): g m^{-2} .

$[\text{SO}_2] = \text{SO}_2 + \text{Cl}^-$ deposition in $\text{mg m}^{-2} \text{ d}^{-1}$ (see Section 2.2.2).

If only the results with $[\text{SO}_2] < 50 \text{ mg m}^{-2} \text{ d}^{-1}$ are taken into account, the linear best fit would be

$$A = 7.03 + 0.374[\text{SO}_2]; \quad r = 0.61, \quad 16 \text{ d.f.} \quad (7a)$$

significant at the 0.01 level.

The constant 4.795 in Equation (6) confirms the fact already known from chamber and indoor studies (Haynie *et al.*, 1976; Rice *et al.*, 1982) that corrosion progresses also in the absence of SO_2 or Cl^- .

With the exponent $b = 1$ (see Section 3.2.2) A is equal to the instantaneous corrosion rate dM/dt_w at time $t_w = 1 \text{ y}$ [Equation (2a)] and also to the mean corrosion rate M/t_w [see Equation (3)] for one year. Haagenrud (1984) gives for the 'corrosion rate' of Zn (from the context, 'corrosion rate' means M/t) the following relationship:

$$K_{\text{Zn}} \text{ (monthly corrosion rate } \text{g m}^{-2}) = 6.0 + 0.22[\text{SO}_2]. \quad (7b)$$

the column $\text{SO}_2 + \text{Cl}^-$. 'Noisy data' in the Remarks column flags the experimental series where at least one weight loss at t_2 was less than at t_1 ($t_1 < t_2$).

The comparison between A_{exp} and A_{calc} gives a summary about the predictive skill of Equation (1b) as used over all results, i.e. as a reconciliation equation. As expected (Section 2.2.5) about half of the calculated results are within $\pm 20\%$ of the experimental values and the other half within $\pm 50\%$, with a few outliers. The latter will be the object of further discussion in Sections 3.2.1.1 and 3.2.1.2.

3.2. Metallic corrosion as a function of the pollutant deposition

In want of any one compelling theoretical model linking pollutant deposition to the progress of metallic corrosion, i.e. to A and b , the available evidence of Table 2 will be submitted to empirical scrutiny to obtain a fitting parsimonious function.

3.2.1. The corrosivity of the atmosphere: analysis of factor A in Equation (1b).

Taking into account the relationship (see Section 1) $t_w = ft$ with $f = 0.4$ at the Scandinavian sites, Equation (7b) transformed in t_w terms yields:

$$A = 15 + 0.55 \text{ SO}_2 \quad (7c)$$

which, apart from the constant, is in fair agreement with Equation (6).

The magnitude of the added constant obviously depends on the data base to which the equation is fitted. Equation (6) is dominated by a few sites with high pollution (Chicago, Philadelphia, Detroit, etc.) with the effect that the dense cluster of low-polluted sites weighs relatively less. With a set of data containing overwhelmingly sites with low pollution (and at the same time, many low t_w values pertaining to arid sites, like the Interstate Surveillance Project, see Cavender *et al.*, 1971) an even higher constant, ~ 20 yields a somewhat better fit.

This non-universality of the additive constant points to the fact that the functional form $A = g([\text{SO}_2])$ is not yet fully settled. This inconsistency notwithstanding

Detroit	99	73	0.99	602	631	0.62	130	4.10	pH: Barrie <i>et al.</i> (1982)
Cincinnati	42	42	1.16	273	469	0.34	70	4.2	
Los Angeles	20	26	0.85	180	389	0.37	40	5.6	pH: Lipfert <i>et al.</i> (1984)
New Orleans	17.4	18.5	1.00	326	351	0.56	26	5.0	
Philadelphia	113	108	1.00	398	806	0.36	195	4.2	
San Francisco	18.2	20.7	0.92	363	362	0.60	30	5.6	
Washington	75	93	1.00	347	728	0.39	166	4.20	
Guttman (1968)									
Birchbank, B. C.	54.5	52	0.86	—	—	—	90		
Feliu (1977)									
Madrid	—	—	—	634	483	0.44	75		
Barcelona	—	—	—	1300	577	0.62	110		
Bilbao	—	—	—	1840	1035	0.43	280	5.6	
Cadiz	—	—	—	680	550	0.58	100		
Zaragoza	—	—	—	840	435	0.51	57		
Köhler and Heider (1976)									
Neuruppin	—	—	—	—	†	0.51	†	5.1	pH: Lahmann and Fett (1983)
Pourbaix (1982)									
Ruhr	—	—	—	—	†	0.7	†	4.05	
Strekalov <i>et al.</i> (1983)									
Hanoi	8.8	†	0.54	—	†	0.75	†	5.3	
Yasukawa <i>et al.</i> (1983)									
Niigata, industrial	—	—	—	1190	1224	0.57	350	4.35	
Niigata, rural	—	—	—	240	550	0.43	100	4.35	

* All following pH values without specific reference are best estimates from Georgii (1981), Georgii (1982), OECD (1977), and BapMon (WMO, 1975–1980) data.

† No calculation was possible due to lacking $\text{SO}_2 + \text{Cl}^-$ data.

— Indicates that the metal in question has not been tested at that site.

ing, it is quite remarkable how Equation (6) covers widely different environmental conditions, as open air and cabin exposures. Thus, when $[\text{SO}_2 + \text{Cl}^-]$ and t_w are known, Equation (6) introduced into Equation (1b) is a very satisfactory reconciliation equation. The unexplained outliers (here Borregard alone) are few.

3.2.1.2. Steel. The least-square linear best fit to the data in columns 4 and 7 in Table 2 is: $A = 281 + 2.66 [\text{SO}_2]$; [Equation (8)], $r = 0.67$ with 40 d.f. significant beyond the 0.001 level, units and symbols as in Equation (6).

The most prominent outliers are Washington, Philadelphia, Chicago and Cincinnati, clearly below the regression line which may probably be explained by the somewhat more corrosion-resistant alloy used. A metallurgical reason might be the cause of the systematic above-the-line situation of the Spanish tests. As yet unexplained outliers remain Moscow-cabin, Borregard and Niigata-rural.

The conclusions to be drawn here are the same as those for zinc at the end of Section 3.2.1.1 and need not be repeated.

3.2.1.3. Copper. Similar analysis as in 3.2.1.1 and 3.2.1.2 of the copper data from the COMECOM sites yielded the following equation: $A = 0.38 [\text{SO}_2]$; [Equation (9)], $r = 0.98$ and 10 d.f., significant much beyond the 0.001 level, units and symbols as in Equation (6). For copper, no additive constant has been found, apparently meaning that in the absence of SO_2 or Cl^- , there is no corrosion. That agrees with what is already known about the behavior of this metal.

3.2.2. *The effect of rain acidity on corrosion: analysis of the exponent b in Equation (1b).* The H^+ concentration in rainwater is but one of the rain-connected factors affecting corrosion. A strongly acidic solution directly attacks some metallic surfaces as the more electropositive metal replaces the H^+ ion. Rain carries a load of sulfates, chlorides, etc. which enhance corrosion. By providing a liquid film, it also enhances electrolytic intergranular corrosion, but it may also slow down the corrosion process, by washing out deposited corrosion accelerators. The final effect depends largely upon the ratio of deposited accelerators to those contained in the rainwater and upon rain duration and intensity. The final effect, nevertheless is that, in most cases (at least with steel), the rain-exposed surface corrodes less than the sheltered side. The rain-exposed rust is more protective: see more details about this effect in Section 4.

Atteraa and Haagenrud (1982), and Haagenrud (1984) represented $\Delta M/\Delta t_w$ for carbon steel as a function of the SO_2 concentration, days with precipitation and H^+ concentration in the precipitation, but independently of the time. This approximation may represent the results at $t = \text{const}$ and $b = 1$ [see Equation (2a)] but lacks general validity.

Here an attempt will be made to correlate b with the average rain pH. The latter is certainly not the only governing variable; it is a proxy for the ones we are

looking for, the specific effect of H^+ . Ideally, only the acidity below some pH limit, depending on the metal, and the frequency of occurrence of the low pH events should be counted. This information is only exceptionally available for the time being, although in a few years' time, more data will be collected. It is known, however (OECD, 1977), that the distribution of H^+ precipitation events is log-normal. Therefore, the pH must be really normally distributed around the mean. Information about the standard deviation is mostly lacking, for the time being. Thus the use of the average pH is a first approximation, a proxy, as it was called at the beginning of this paragraph.

3.2.2.1. Zinc. The regression of the exponent b pertaining to zinc (column 4 in Table 2) upon the best estimate of the average local rain pH (column 9 in Table 2) yields:

$$b = 1.5496 - 0.1423 \text{ pH (nondimensional)} \quad (10)$$

with $r = -0.68$ and 23 d.f., significant beyond the 0.001 level. Range of validity covered by the data is between pH 3.5 and 7.7.

The statistical relationship makes sense also from the physico-chemical point of view. Thus, for example with pH = 4, Equation (10) gives $b = 0.98$, meaning the absence of any layer hindering diffusion. This is in agreement with what is known about the solubility of zinc corrosion products (basic zinc carbonates and sulfates, Strekalov *et al.*, 1983) in acidic media. It also agrees with observations of Haagenrud (1984) in chamber studies. In media of weaker acidity, some corrosion products stay on the surface and the access of corrosion accelerators becomes diffusive. As a consequence, the exponent tends towards 0.5.

It is especially gratifying to observe that besides the generally fair fit of Equation (10), a few sites which have outlying pH values have their b values correctly predicted, as shown in Table 3.

3.2.2.2. Steel. In the case of Zn, the dissolution of the corrosion products and the unimpeded access of pollutants to the surface explain much of the observed behavior. The case of carbon steel is more complicated. The antagonistic effects of rain are combined with the behavior of the adherent rust layer, which is more coherent, contains more Fe_3O_4 grains, relatively coarse and less soluble on the rain-exposed surface (more information about this topic is given by the skyward-groundward differences in Table 5 and Section 4). Moreover, the steel samples used for the corrosion tests were not all of the same composition (see Section 2.1). The result is a less clear-cut situation,

Table 3. Values of the exponent b from Equation (10) vs observed b for zinc for two stations with extreme pH

	pH observed	b observed	b calc. from Equation (10)
Borregard	3.5	0.94	1.05
Brevik	7.7	0.42	0.45

a weaker correlation between the exponent *b* characterizing diffusional behavior and rain pH.

$$b = 0.74 - 0.0298 \text{ pH}, r = -0.20, 33 \text{ d.f.} \quad (11)$$

Significance does not attain the 0.1 level.

With 5 outliers left out—Zvenigorod, Neuruppin, Borregard, Washington and Niigata rural—the relationship can be much improved:

$$b = 0.836 - 0.046 \text{ pH}, r = -0.66 \text{ 28 d.f.} \quad (11a)$$

This is significant beyond the 0.001 level, but the statistical soundness of leaving out five outliers, even when experimental grounds could be invoked, remains open to question.

Along with this uncertainty, there are also some reassuring aspects in scrutinizing the exponent *b* for steel. Thus, for example in the five stations near Bergen, with [SO₂ + Cl⁻] levels varying in the ratio approximately 1 to 2, the exponent remains within the 0.54–0.65 range as it is unlikely that rain pH did change within the limited area. Brevik is fairly well predicted as 0.48 by Equation (11a) (experimental: 0.35) from an exceptional local 7.7 pH, etc.

3.2.2.3. Galvanized steel. Until no exposed free steel surface appears, galvanized steel behaves very similarly to pure zinc.

During the Scandinavian corrosion test program (Atteraa and Haagenrud, 1982) galvanized steel and sheet zinc samples were exposed at the same sites. As Table 4 shows, the *b* values obtained are nearly the same. The difference between the weight losses (not shown here) is of the same order of magnitude as that between two simultaneously exposed samples of the same metal.

Table 4. Values of *b* in Equation (1b) for galvanized steel and for zinc. Computed from Atteraa and Haagenrud (1982)

	Galvanized steel	Zinc
Stord 50	0.78	0.73
Bergen Tidende	0.97	0.90
Bergen VERITAS	0.90	0.95
Alvim	0.94	1.02
Brevik	0.18	0.42
Porsgrunn	0.73	0.79
Lillestrom	0.66	0.65

The correlation coefficient is 0.95, significant beyond the 0.001 level, and would even be more significant if the values for Brevik were not very erratic (the weight loss at 3y was lower than the loss at 2y).

4. SKYWARD-GROUNDWARD DIFFERENCES

The discussion of the skyward-groundward differences buttresses the hitherto outlined physico-chemical explanation ascribed to the parameters *A* and *b* in Equation (1b).

4.1. Zinc

The weight loss of zinc on the skyward and groundward sides seems to be determined by the skyward-to-groundward wetness time alone. In the instance of Guttman's (1968) experiments, on the groundward side 1.35 times more wetness hours were recorded than on the skyward face. As the exponent *b* in Guttman's tests was 0.83 on the average (see below, Table 5) the factor 1.35^{0.83} [see Equation (1b)] must transform *A* groundward into *A* skyward. In fact the error is only +3.5%.

In Vietnam, where 1.17 times more wetness hours were recorded on the upper side than on the groundward side (Strekalov *et al.*, 1983), the corrosion loss of the skyward side of zinc sheets was on the average 1.33 times the groundward value.

As for the exponent *b*, the following skyward-groundward values are on record, as shown in Table 5. The groundward exponent is always the lower one, albeit slightly, indicating a somewhat more diffusive-protective behavior at the underside. At the groundward surface, more of a diffusive-protective layer builds up, the exponent is nearer to 0.5 while at the upper face 0.5 < *b* < 1.0.

4.2. Steel

The situation with carbon steel is different. The rust on the upper side is always more compact, thin and dense, without signs of layering. On the underside, a thickened rust layer is formed with a loose porous structure and reduced cohesion. The rust particles adhere less strongly to the back (groundward) surface. The corrosion products formed on the groundward

Table 5. Values of *b* in Equation (1b) for skyward and groundward exposed zinc samples

	Skyward	Groundward	
Birchbank B.C.	0.86	0.80	Guttman (1968)
Vinh Phu, rural	0.54	0.45	
Hanoi, industrial (?)	0.56	0.53	Strekalov <i>et al.</i>
Honsu Island, marine	0.55	0.55	(1983)
East Chicago	1.06	0.79	As quoted by
Porter County	0.79	0.76	Pourbaix (1982)
			for galvanized steel

Table 6. Values of b in Equation (1b) for skyward and groundward exposed carbon steel samples

	Skyward	Groundward	
Bergen-VERITAS	0.59	0.63	Atteraas and Haagenrud (1982)
Vinh Phu, rural St. 3	0.75	0.86	
Hanoi, urban			
Steel 3	0.71	0.79	Strekalov <i>et al.</i> (1983)
Steel 45	0.69	0.80	
Honsu Island, marine			
Steel 3	0.71	0.80	
Steel 45	0.73	0.85	
Cuxhaven	0.49	0.57	Pourbaix (1982) quoting the ESC2 program (Germany)
Mülheim-Ruhr	0.65	0.61	
Olpe	0.60	0.68	

side had lower anodic polarizability and ohmic resistance than those formed on the skyward side (see Strekalov *et al.*, 1983; Wou Din Wui *et al.*, 1983, for a full discussion). Carbon steel loses more weight at the groundward surface.

Table 6 summarizes the recorded skyward-groundward b values for steel. In all cases, with one exception only, the exponent b is higher at the groundward face, demonstrating higher porosity there. A higher b points towards an increased corrosion rate and to higher cumulative weight loss at the groundward face. Rust formed on steel in louvered cabin (i.e. without exposure to rain) is also of loose, porous structure. At the COMECON stations, where such exposures were made, b for the cabin experiments is always the higher one (see Table 2), on the average about 1.0, while the open exposure reflects rain-pH influence (see Section 3.2.2.2).

5. FLOWSHEET FOR THE COMPUTATION OF CORROSION DAMAGE TO METALS FROM ENVIRONMENTAL DATA

(1) Obtain the input parameters

The requested input parameters are: t_w , the time-of-wetness; ($\text{SO}_2 + \text{Cl}^-$), the pollutant surface deposition (units, see below) and the average rain pH. Ideally, these parameters should be observed at the site. As the full set of observed environmental data is not always present, the following steps should be used in view to obtain the reasonable surrogates.

1.1. *Time-of-wetness.* Obtain the number of days of precipitation per year. Use Equation (4), Section 2.2.1, to obtain an estimate of t_w .

1.2. *Pollutants.*

1.2.1. Sulphur dioxide. Use the surface deposition value: lead peroxide or IRMA. If this is unavailable, equate $1 \mu\text{g m}^{-3} \text{SO}_2$ with $1 \text{ mg m}^{-2} \text{d}^{-1} \text{SO}_2$ surface deposition only for free air exposure. This relationship does not hold for louvered cabin or other shelters, where direct measurement is essential.

1.2.2. Chloride ion. Use direct (wet) deposition values. If unavailable, data obtained at distances less

than 10 km from the seashore are suspect (too low). This may occur also in heavily chloride-polluted industrial areas.

1.3. *Average rain pH.* If direct, local observations are not available interpolate from world-wide or continent-wide iso-acidity maps (see references).

If even the rough estimates for sulphur dioxide, chloride and rain acidity are unavailable, then use for zinc $b = 1.0$ in general, with the exception of very remote sites from source areas, where $b = 0.6$ would give a better fit. For steel, use $b = 0.7$.

(2) Intermediate step: compute the factor A

For zinc (and for galvanized steel) use Equation (7); for steel Equation (8), and for copper Equation (9), all in Section 3.2.1.

(3) Compute the weight loss

Use Equation (1b) with the factor A as computed above (point 2) and the exponent b (point 1.3 above) for any t_w . Transform, if necessary, into real time by $f^{-1} t_w = t$ (note: $t_w/t = f$). As this computation has general validity within its limits of error, it effectively accomplishes reconciliation.

6. CONCLUSION

It has been known for a long time that the atmospheric corrosion of metals can be described by an exponential (called also bi-logarithmic) law. The multiplicative factor and the exponent to which the time of the active corrosion process (the so-called 'time-of-wetness') is to be raised, have been successfully explained in terms of pollutant concentration and rain acidity. The heuristic explanation is not a full theory of atmospheric corrosion of metals, although it represents a step towards such a theory.

In its present form, the bi-logarithmic law is a quite effective reconciliation function for results obtained by various investigators. As a reconciliation method, this procedure has several attractive features: it is fairly simple and it works well. It is, however, not the complete solution because it does not yet take into

account all the complexities of the corrosion process and accomplishes formal reconciliation through linear approximation to the available data.

The exponent in the bi-logarithmic law has been convincingly linked to the average rain pH in the instance of zinc. For steel, the correlation is less clear, in the first instance due to differences between the steel samples used by the various investigators, and last but not least, also to the much more complicated physico-chemistry of the iron rust layer, in contrast to zinc (and galvanized steel).

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