PREDICTION OF CORROSION BEHAVIOUR OF MILD STEEL IN DIFFERENT SRI LANKAN ATMOSPHERIC CONDITONS

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Thesis submitted in partial fulfilment of the requirement for the
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Declaration

I declare that this is my own work and this thesis does not incorporate without acknowledgement any material previously submitted for a Degree or Diploma in any other University or institute of higher learning and to the best of my knowledge and belief it does not contain any material previously published or written by another person except where the acknowledgement is made in the text.

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Abstract

Corrosion is defined as the deterioration of materials due to the reaction with its environment. According to the physical nature of environment, corrosion can be categorized as 'corrosion in atmosphere', 'corrosion in water', 'corrosion in sea', 'corrosion in soil' etc. Among them, corrosion of steel in atmosphere is identified as one of most important type of corrosion. Because studies show that corrosion cost of a country may vary between 1 to5% of their GDP and about one half of that cost is due to atmospheric corrosion.

Corrosion problem cannot be completely eliminated but it is possible to control by methods known as 'corrosion management systems'. Corrosion model is a one of the best tool that can be used for atmospheric corrosion management. Use of a corrosion model as a tool for corrosion prevention is the common practice in many other countries, but using this method is not a popular practice in Sri Lanka due to non availability of such model. Therefore, this project was carried out for the formulation of an atmospheric corrosion model that can be applicable in Sri Lankan atmosphere.

For this purpose, by reviewing internationally published literature a model structure was proposed. Then field exposure programs were conducted to obtain data required for model calibration. The model was calibrated with the obtained data and test has been done for goodness of fit and the model shows considerably acceptable goodness of fit with more than 80% of data are within the ±10% deviation from actual value. Finally, a completely different set of samples were placed in different locations and data gathered were used to find out the validity and forecasting capability of the model,. The model shows a good performance in forecasting capability with acceptable deviations.

Keywords: Prediction of Corrosion, Atmospheric Corrosion, Carbon Steel Corrosion

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1. INTRODUCTION

Corrosion is commonly known as the deterioration or loss of functions of materials due to the reaction with its environment. Always materials differently interact with different environmental conditions and these interactions will negatively affect the materials' usefulness [1]. This means that operational environment is the one of most important factor that determines the corrosive nature of a material.

According to the physical nature of the environment, corrosion can be classified as corrosion in atmosphere, corrosion in water, corrosion in sea, corrosion in soil etc. Among them, corrosion of steel in atmosphere can be considered as one of the most important type of corrosion Because studies show that corrosion cost of a country may vary between 1 to5% of their GDP and it is a well known factor that about one half of that cost is due to the corrosion of steel in the atmosphere [2].Mainly these corrosion cost has been calculated on the basis of financial loss and the actual cost to the society is much more than the calculated amount, Sometimes corrosion can be considered as a kind of a natural disaster. Similar to the other natural disasters such as severe weather disturbances, earth quarks, landslides etc., corrosion damage can affect everything from land vehicles, ships, aircrafts, pipe lines, and metallic structures even home appliances.

Unlike weather-related disasters, corrosion has advantage that corrosion is predictable and quantifiable. Therefore, although corrosion damage cannot be eliminated it is possible to minimize by having corrosion preventive strategies which is known as 'Corrosion Management'.

For an effective implementation of corrosion management strategy, it is required to identify the corrosive nature (aggressiveness) of the service environment of a material or a component. Therefore, for this purpose availability of method to identify the environmental corrosivity help for the timely implementation of corrosion prevention method. A wide Varity of methods are available for the determination of environmental corrosivity and among them environmental classification method, corrosion map, corrosion modeling are some of commonly used methods. Corrosion modeling is predicting or indirect measuring of corrosivity with the aid of equation which has relation between corrosivity and atmospheric factors which effect the corrosion process. Models of material degradation processes have been developed worldwide for a multitude of situations using many varieties of methodologies [4, 5, 6, 7, 8, 9, 10, 11, 12, 13,14, and 15]. For Scientists and Engineers who are involving in corrosion technology, those models have become an essential tool for the selection and life prediction associated with the introduction of new materials or processes. In fact, models are, in this context, should be an accepted method of representing current understandings of reality.

When the infrastructure development in Sri Lanka is considered, there was an increase in use of steel for the construction of bridges, towers, power plants etc. When steel is used as a construction material in normal atmosphere it is a good practice to have a corrosion management plan throughout its lifetime. For these purposes several environmental assessments were conducted in local regions for specific purposes since there was no readily available data or method for environmental assessment. Therefore, in future, availability of methods for environmental corrosivity assessment will be a great advantage for the design and maintenance of metallic structures. Therefore, this project was started with the intension of developing a corrosion model as a corrosivity assessment tool that can be used to assess the corrosivity level of atmospheres in different areas in Sri Lanka.

It is well known fact that the consituents in atmosphere and climatic conditions are directly effect the atmospheric corrosivity. Among them climatic factors like Relative Humidity (RH), Rain Fall (RF) Temperature (T), and atmospheric constituents such as Sulphur compounds (SO_X), Salinity (Cl^-), Time of Wetness (TOW) are considered as main factors and the presence of air born particles, nitrogen compounds (NO_X),Ozone concentration, Carbon Dioxide etc, are also have some minor effect on corrosivity[3]. This means that there is a relationship between above-mentioned atmospheric variables and corrosivity and there is a possibility to find out an equation or model for determination of the corrosivity level as dependent variable and other atmospheric factors as independent variables.

This report gives details of the project carried out to develop an equation for atmospheric corrosion which can be used for the prediction of atmospheric corrosion of low carbon steel in Sri Lankan atmosphere. This research project involves firstly an comprehensive study of the previously developed models and their approaches to find out a suitable method for Sri Lankan condition and a new model structure was proposed referring to the well known 'Power Equation'. The constants of power equation are functions of atmospheric variables such as Temperature, Relative Humidity, and Salinity etc.

Secondly, field exposure tests were conducted in different areas of the countries and data gathered from those exposure tests were fitted to the model structure using computer based mathematical iteration process based on the theory 'Minimizing Percentage Least Square'. Finally, the goodness of fit of the data has been determined and then the proposed model was validated using a different set of data obtained by placing steel samples in different three locations in Sri Lanka..

2. LITERATURE SURVEY

2.1 Methods use to identify corrosive atmospheres.

This chapter describes the different type of techniques use for the determination of corrosive nature of atmosphere such as environmental classification method, corrosion mapping and corrosion modeling.

2.1.1 Environmental classification method.

According to the atmospheric constituents the atmosphere has been categorized in to different groups. The European standard and ISO standards classifications are two examples.

2.1.1.1 European standard classification

The European standard EN 12500-2000 [16] defines five categories of outdoor environment namely,

(a) *Rural atmosphere:* countryside and small towns, minor contamination of corrosive agents (carbon dioxide, chlorides, artificial fertilizers).

(b) Urban atmosphere: densely populated areas, few industrial activities, medium contamination of corrosive agents (sulfur dioxides).

(c) *Industrial atmosphere:* intensive industrial activities, high corrosive agent contamination (sulfur dioxides).

(d) *Marine atmosphere:* areas close to the sea, or internal zones strongly affected by airborne salinity. Corrosion effects are influenced by topographic conditions, prevailing wind direction.

(e) *Marine Industrial atmosphere:* complex environment, areas close to both the sea and industrial districts, or internal zones located in the prevalent wind direction, Medium and/ or high corrosive agent contamination (sulfur dioxides, chlorides). Due to its simplicity this has been the most commonly used method to classify the corrosive environment but the main drawback of this method is there is no clear boundary to distinguish each environment.

2.1.1.2 ISO Classification of atmospheric corrosivity

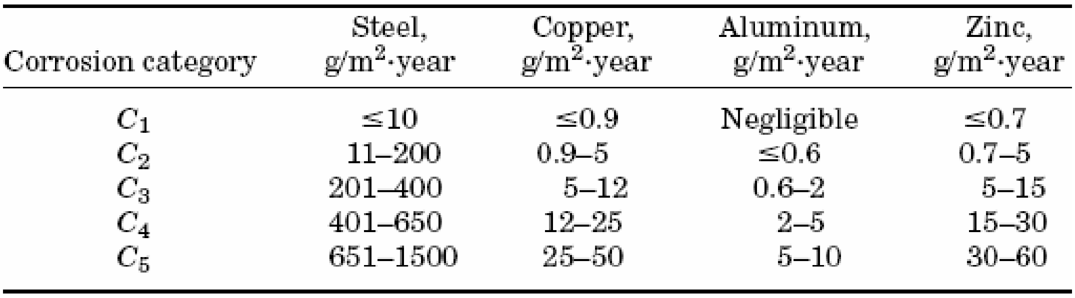
A classification method has been introduced by International Standard Organization to assess the atmospheric corrosivity based on atmospheric variables. The methods given in the standards describe to determine each of variables and respective rate of corrosion. These variables and corrosive atmospheres are categorized in different groups [17, 18, and 19].

(a) The classification of corrosive environments is present in Table 2.1.
(b) Categorization of sulphur dioxide and chloride according to their deposition rate Table 2.2.
(c) Time of wetness (TOW) in Table 2.3. TOW is defined as the time duration of relative humidity is more than 80 % and the temperature is higher than the 0^0C[1].
(d) Following the categorization of these three key variables, the applicable ISO rate of corrosion (g/m^2.year) can be determined using the ISO chart (Table 2.4.).

As an example in a particular atmospheric condition with sulphur dioxide deposition rate of 11-35 mg/m^2.day (P_1 in Table 2.2) and chloride deposition rate of 61-300 mg/m^2.day (S_2 in Table 2.3) with a time of wetness category (T_4 in Table 1.3) the metal steel comes under corrosion category C_4 (Table 2.1) which corrode with the rate of 401-650 g/m^2.year The table 2.5 shows relevant standards for this classification and measurements for rate of corrosion.

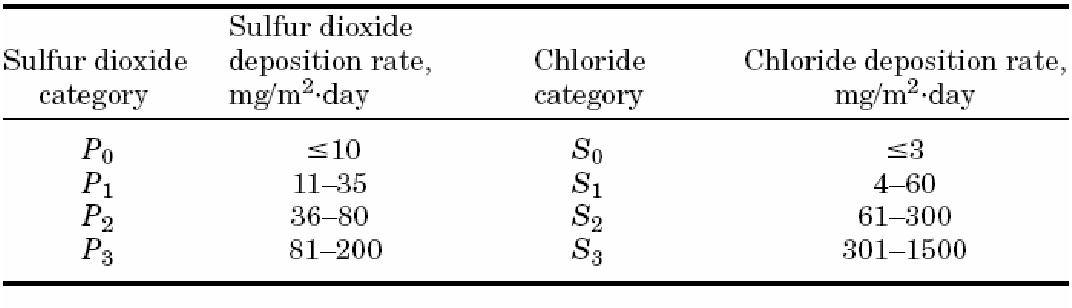
Although the ISO methodology represents a simple approach to corrosivity classification it has considered only three atmospheric variables, sulphur dioxide deposition rate chloride deposition rate and time of wetness (TOW). Therefore, it is limited in its accuracy and precision. Since the atmospheric parameters determining the corrosivity classification do not include the effects of potentially important corrosive pollutants and impurities such as nitrogen compound, hydrogen sulfide, carbon dioxide, as well as temperature, rainfall, wind speed etc..

Table 2.1: ISO Classification of corrosion rate after one year exposure predicted for different corrosivity classes



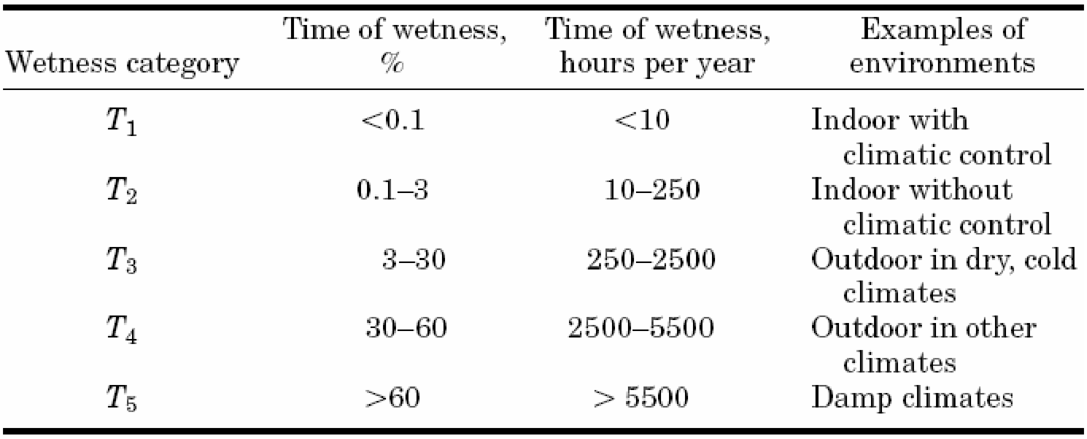
Corrosion category	Steel, g/m^2·year	Copper, g/m^2·year	Aluminum, g/m^2·year	Zinc, g/m^2·year
C_1	≤10	≤0.9	Negligible	≤0.7
C_2	11–200	0.9–5	≤0.6	0.7–5
C_3	201–400	5–12	0.6–2	5–15
C_4	401–650	12–25	2–5	15–30
C_5	651–1500	25–50	5–10	30–60

Table 2.2: ISO Classification of sulfur dioxide and chloride



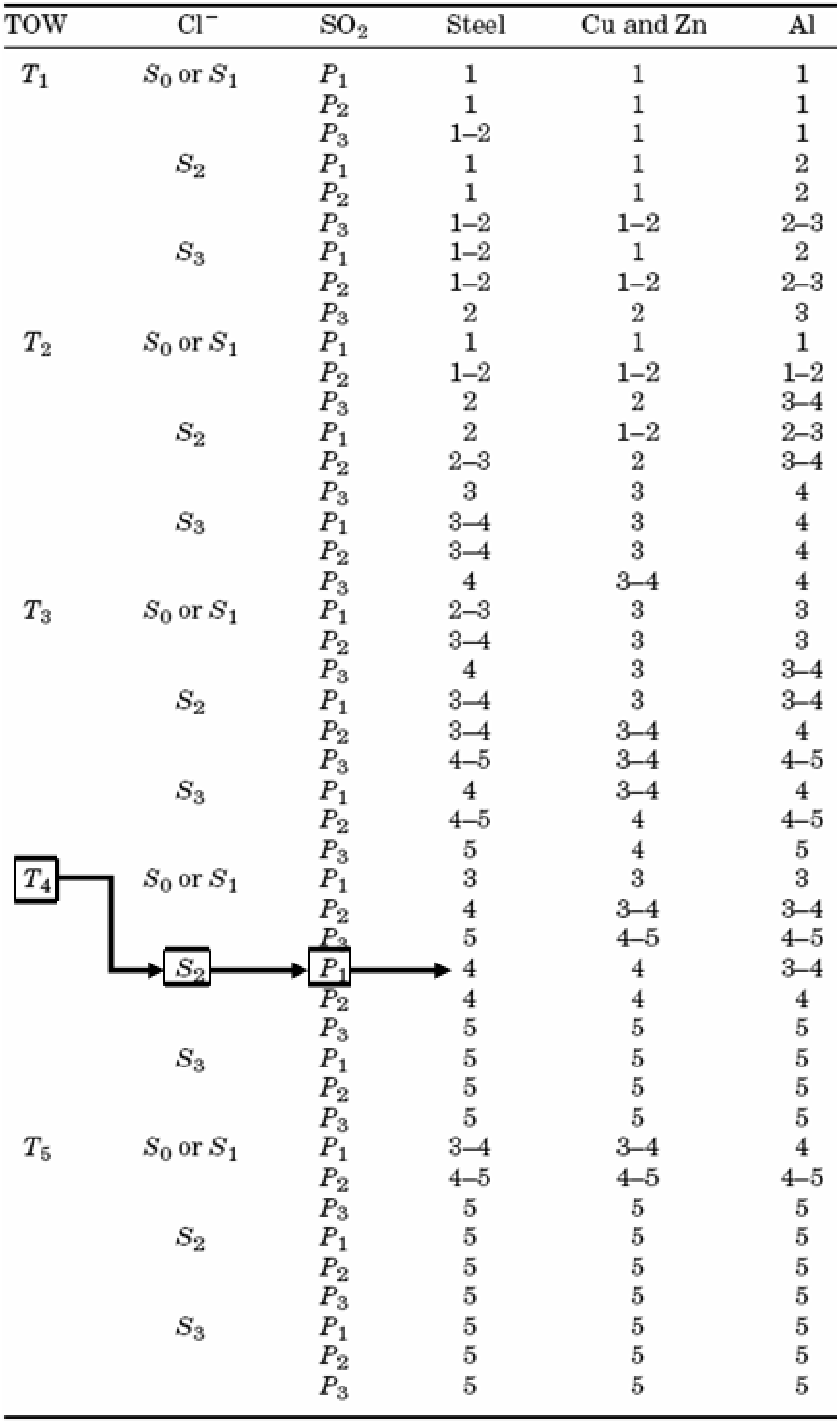
Sulfur dioxide category	Sulfur dioxide deposition rate, mg/m^2·day	Chloride category	Chloride deposition rate, mg/m^2·day
P_0	≤10	S_0	≤3
P_1	11–35	S_1	4–60
P_2	36–80	S_2	61–300
P_3	81–200	S_3	301–1500

Table 2.3: ISO Classification of time of wetness



Wetness category	Time of wetness, %	Time of wetness, hours per year	Examples of environments
T_1	<0.1	<10	Indoor with climatic control
T_2	0.1–3	10–250	Indoor without climatic control
T_3	3–30	250–2500	Outdoor in dry, cold climates
T_4	30–60	2500–5500	Outdoor in other climates
T_5	>60	> 5500	Damp climates

Table 2.4: ISO Classification of corrosivity and pollutions levels



TOW	Cl^-	SO_2	Steel	Cu and Zn	Al
T_1	S_0 or S_1	P_1	1	1	1
		P_2	1	1	1
		P_3	1–2	1	1
	S_2	P_1	1	1	2
		P_2	1	1	2
		P_3	1–2	1–2	2–3
	S_3	P_1	1–2	1	2
		P_2	1–2	1–2	2–3
		P_3	2	2	3
T_2	S_0 or S_1	P_1	1	1	1
		P_2	1–2	1–2	1–2
		P_3	2	2	3–4
	S_2	P_1	2	1–2	2–3
		P_2	2–3	2	3–4
		P_3	3	3	4
	S_3	P_1	3–4	3	4
		P_2	3–4	3	4
		P_3	4	3–4	4
T_3	S_0 or S_1	P_1	2–3	3	3
		P_2	3–4	3	3
		P_3	4	3	3–4
	S_2	P_1	3–4	3	3–4
		P_2	3–4	3–4	4
		P_3	4–5	3–4	4–5
	S_3	P_1	4	3–4	4
		P_2	4–5	4	4–5
		P_3	5	4	5
T_4	S_0 or S_1	P_1	3	3	3
		P_2	4	3–4	3–4
		P_3	5	4–5	4–5
	S_2	P_1	4	4	3–4
		P_2	4	4	4
		P_3	5	5	5
	S_3	P_1	5	5	5
		P_2	5	5	5
		P_3	5	5	5
T_5	S_0 or S_1	P_1	3–4	3–4	4
		P_2	4–5	4–5	4–5
		P_3	5	5	5
	S_2	P_1	5	5	5
		P_2	5	5	5
		P_3	5	5	5
	S_3	P_1	5	5	5
		P_2	5	5	5
		P_3	5	5	5

Numerical 1,2,3,4 & 5 shown in table 2.4 represent the corrosivity categories C_1, C_2, C_3, C_4 & C_5 respectively.

Table 2.5: Relevant ISO standard for atmospheric corrosion

Standard	Title
ISO 9223: 1992	Corrosivity of atmospheres – Classification
ISO 9224:1992	Corrosivity of atmospheres - Guiding values for the Corrosivity categories
ISO 9225:1992	Corrosivity of atmospheres - Measurement of pollution
ISO 9226:1992	Determination of corrosion rate of standard specimens
ISO 8407: 1991	Corrosion of metals and alloys - Removal of corrosion products from corrosion test specimens

2.1.1.3 Environmental Severity Index (ESI)

Environmental severity index which is based on atmospheric parameters has been developed by Michigan state university of USA for the maintenance management of aircraft structures. A Corrosion Damage Algorithm (CDA) has been proposed as a guide for anticipating extent of corrosion damage for planning maintenance operations. This classification scheme was developed primarily for uncoated aluminum, steel, titanium, and magnesium alloys exposed to the external atmosphere at ground level and it is applicable for other metals with appropriate modifications. The CDA algorithm is presented in Fig.1 and considers the distance to sea, leading either to the very severe “AA” rating for close distance to seashore or a consideration of moisture factors. Following the moisture factors, pollutant concentrations are compared with values of working environmental Corrosion Standards (WECS). For example, a severe A rating would be given if any of the three pollutants considered in this scheme, that is, sulfur dioxide, total suspended particles (TSP), and ozone levels, would exceed the WECS values in combination with a high moisture factor. Considering the simplicity of the algorithms and simplifying assumptions in obtaining relevant environmental and maintenance data, the environmental corrosivity predicted from the CDA algorithm, was considered to be reasonable. However in this case also it is limited in its accuracy and precision since it has not considered other atmospheric parameters that determine the rate of corrosion.

Subsequent attempts to enhance the CDA algorithm using the results obtained from broad based corrosion testing programs have failed to provide enough differentiation between moderately corrosive environments. [20]

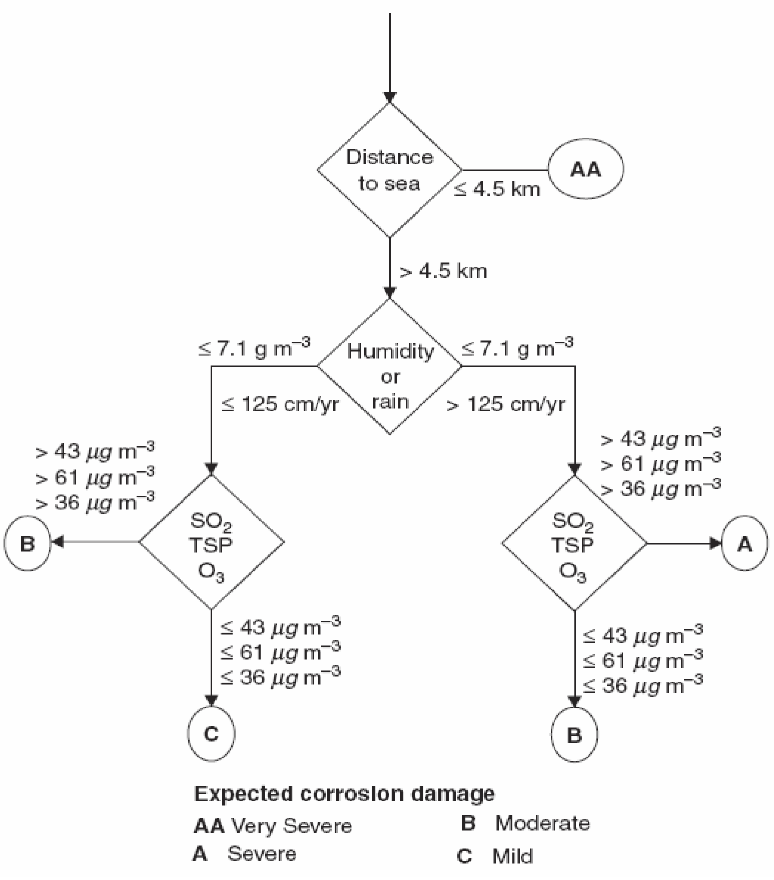


Figure 2.1: The CDA algorithm for determining the corrosion severity for a given location

2.1.2 Corrosion mapping

Corrosion map is a powerful tools use in the field of Corrosion Engineering. A diagram that shows regional corrosion behavior is called as a corrosion map and it helps to understand the period of maintenance of major structures and measures to prevent corrosion.

Development of a corrosion map can be done with direct measurement of corrosion loss (rate of corrosion) by exposure test and prediction of corrosivity by atmospheric variables. Exposure of standard metal specimens at a grid of sites and the generation of computer contoured corrosion maps has been shown to be a sensitive and cost-effective means of differentiating geographical variations in corrosivity, which is a measure of the aggressiveness of the environment [21]. Various countries have already developed their corrosion maps. Few examples are shown in Japan (Figure 2) Mexico (Figure 3) India (Figure 4).

Figure 2.2 - Corrosion map of Japan

Figure 2.3 - Corrosion map of Mexico

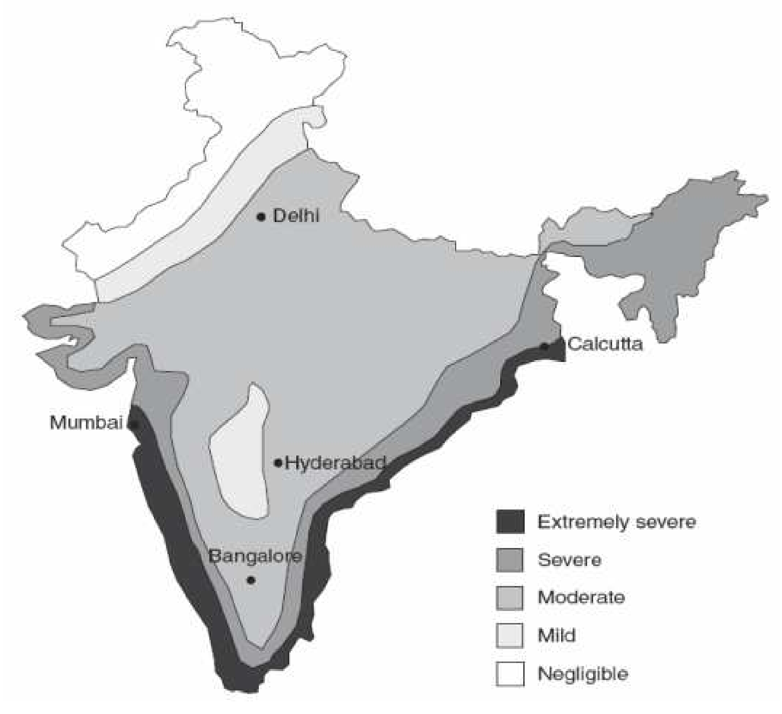


Figure 2.4 - Corrosion map of India

2.1.3 Corrosion modeling

Models of materials degradation processes have been developed for a multitude of situations using a great variety of methodologies. For Scientists and Engineers who are developing materials, models have become an essential benchmarking element for the selection and life prediction associated with the introduction of new materials or processes. In fact, models are, in this context, an accepted method of representing current understandings of reality. Traditional models can be divided into two main categories.

(1) Mathematical or theoretical models.
(2) Statistical or empirical models.

Mathematical models have the common characteristic that the response and predictor variables are assumed to be free of specification error and measurement uncertainty. Statistical models, on the other hand, are derived from data that are subject to various types of specification, observation, experimental, and/or measurement errors. In general terms, mathematical models can guide investigations, and statistical models are used to represent the results of these investigations.

2.2 Reviewing of existing models

In 1968, Guttman and Sereda [6] proposed a model for corrosion loss. This was a most primary level corrosion model expressed as follows.

$$k= 0.16\, TOW^{0.7}(SO_2 + 1.78) \qquad (2)$$

Where:
k : Corrosion loss (g/m^2. month)
TOW : Time of wetness (hours)
SO_2: Sulphur deposition rate in (mg/m^2.day)

In 1974, Haynie and Uphan [7] developed a model which describes the “Corrosion Depth” in terms of sulphur deposition rate and percentage of relative humidity.

$$K = 325t^{0.5}e^{\{0.00275SO2-\left(\frac{163.2}{RH}\right)\}} \tag{3}$$

Where:
K : Depth of Corrosion (μm)
RH : Percentage relative humidity
SO_2: Sulphur deposition rate in (mg/m^2.day)
t : time (year)

In 1980, Hakkarainen and Yladaari [8] developed a model to describe the corrosion depth (K in μm) as a function of time of wetness (TOW in hours) and sulphur dioxide (SO_2 in mg/m^2.day).

$$K = 1.17\mathrm{TOW}^{0.66}(SO_2 + 0.048) \tag{4}$$

In 1984, Knotkova et.al. [9] developed a model to describe the corrosion depth (K, μm) as a function of the time of wetness (TOW), Sulphur dioxide deposition rate (SO_2), Chloride deposition rate (Cal).

$$K = 1.327 + 0.4313SO_2 + 0.005TOW + 0.138Cl \tag{5}$$

In the corrosion model shown in equation 4 and 5, the corrosion loss was estimated as a function of time of wetness (TOW) and Sulphur dioxide (SO_2) deposition rate. The main disadvantage of these models is it could not be useful for the prediction of service life of a steel structure because this equation do not contain any component of time factor.

Japanese scientists analyzed the corrosion rate of carbon steel for one year in 43 exposure sites [10]. They have developed equations for each atmospheric condition.

(a) In urban or industrial sites,

Corrosion rate (mdd) = $4.15+0.88\times T$ (°C)–$0.073\times$RH (%)–$0.032\times$rainfall (mm/month)
$+2.913\times[Cal^-](\times10^{-6})+4.921\times[SO_2]$ (mdd). (6)
Where : mdd: mg per square decimeter per day

(b) In marine atmosphere,

Corrosion rate (mdd) = $5.61+2.754\times[Cal^-](\times10^{-6})+6.155\times[SO_2]$ (mdd). (7)

The corrosion model shown in equations 6 calculate the corrosion loss as a function of relative humidity, rain fall, salinity and sulphur dioxide. In this model when the RH becomes zero there is a value for corrosion rate but in real practice moisture (relative humidity) is the essential factor for the occurrence of electrochemical reaction and in absence of moisture there is no corrosion, but this model has failed to represent this phenomenon.

Equation 6.and 7 calculates corrosion loss as a function of chlorides, relative humidity, time of wetness, and sulphur dioxide. According to the equation the corrosion loss has a constant value even if all of environmental parameters equal to zero. Therefore this model structure is not an accurate representation of the corrosion process.

A model has been developed by International Cooperative Program ICP group (Equation 8, 9, 10and 11) with the aim to generalize the corrosion loss over time period for different environments, reporting the climate and pollutants variables as independent factors. These functions have been formulated for different metallic materials and are based on both long-term exposures and trend analysis based on repeated one-year measurements of exposure. The degradation of metal over time is expressed by means of mass loss (ML) as a function of climatic parameters (RH; T), gaseous pollutants (SO_2, O_3) and precipitation parameters (Rain, H^+ Cal^-) reported as fallows [11].

(a) Weathering Steel

$ML= 34[SO_2]^{0.33}exp\{0.020Rh+ f(T)\}^{t0.33}$ (8)

(b) Zinc

$ML=1.4[SO2]^{0.22}exp\{0.018Rh+ f(T)\}t^{0.85} + 0.029Rain[H+]t$ (9)

(c) Aluminum

$ML = 0.0021[SO2]^{0.23}.Rh\ exp\{f(T)\}t^{1.2} + 0.000023Rain[Cal^-]t$

(10)

(d) Copper

$ML=0.0027[SO2]^{0.32}[O3]^{0.79}Rh\ exp\{f(T)\}t^{0.78} + 0.050Rain[H+]t^{0.89}$

(11)

Where:

ML: Mass loss [g/m2],

t: Exposure time (years),

Rh: Relative humidity (%),

T: average annual temperature (°C),

$f(T) = a(T – 10)$ when $T< 10$ °C, otherwise $f(T) = b (T – 10)$,

a, b being constant values depending on the specific metal,

SO_2: Sulfur dioxide concentration (µg/m3),

O_3: ozone concentration (µg/m3);

Rain: Average annual rainfall precipitation (mm),

H^+: hydrogen ion concentration in precipitation (mg/L),

Cal^-: Chloride ion concentration in precipitation (mg/L).

The model shown in equation 8 calculate the corrosion loss as a function of sulphur , relative humidity and temperature although this model is applicable for weathering steel, this is not applicable for general structural steels due to there is no effect of chloride on corrosion rate of steel.

Field exposure test conducted by a research group in Brazil [12] obtained values for parameter n and k of Power law $C=kt^n$ (Table 2.6) with the following equations. This model is a primary version of power model and it can be applicable only for the location where the field exposure was conducted.

$$\frac{dc}{dt} = nkt^{n-1} \tag{12}$$

$$n = 1 + 0.477[\log\left(\frac{dC}{dt}\right)_2 - \log\left(\frac{dC}{dt}\right)_1] \tag{13}$$

$$k=\frac{1}{n}\left(\frac{dC}{dt}\right)_1 \tag{14}$$

Where $(\frac{dC}{dt})_1$, $(\frac{dC}{dt})_2$ represent the first year and second year corrosion losses respectively.

Table 2.6 - Values of n and k

location	Low carbon steel		Copper		Aluminium	
	n	k	n	k	n	k
1	1.55	71.25	0.72	8.43	0.58	1.12
2	0.86	22.13	1.12	2.88	1.02	0.17

Research project conducted by group of Iberoamerican presented an Artificial Neural Network (ANN)-based solution methodology for modeling atmospheric corrosion processes from observed experimental values, and an ANN model developed using the cited methodology for the prediction of the corrosion rate of carbon steel in the context of the Iberoamerican Corrosion Map (MICAT) Project, [5] which includes seventy-two test sites in fourteen countries throughout Iberoamerica. Classical regression model also developed in the context of this study,

In this model when there is no presence of chloride and sulphur compounds the corrosion loss becomes constant.

$$Fe = b_0 + Cl^{-}(b_1 + b_2.P + b_3.RH) + b_4.TOW.SO_2 \tag{15}$$

With b_0=6.8124, b_1=1.6907, b_2=0.0004, b_3=0.0242, and b_4=2.2817.

Where:

Fe: Depth of corrosion (μm/month)

Cal^- : Chloride deposition rate (mg/m^2.day)

SO_2: Sulphur deposition rate (mg/m^2.day)

In the year 2007 by Dawn E Klinsmith develop a corrosion model by addressing the many of the problems mentioned above

$$Y = At^{B}\left(\frac{TOW}{C}\right)^{H}\left(1+\frac{\mathrm{SO2}}{E}\right)^{F}\left(1+\frac{Cl}{G}\right)^{H}e^{J(T+T0)}$$

(16)

In this model fallowing features of corrosion is described. It is well known fact that the rate of corrosion is increased by atmospheric salinity and sulphur compounds, but in absence of moisture in atmospere there is no effect of chloride or sulphur on corrosion rate. Therefore this phenominon was described by including this model. The corrosion can occur in absence of chloride or sulphur therefore to express this phenomina a separate TOW component was added in to the model. The temperature has effect on overall rate of corrosion. Therefore the temperaute component was also included as it effect on all component of the model .

Therefore among many of corrosion models reviewed it can be identified this model as a one of best corroison mode that describe the nature of atmospheric corrosion.

3. EXPERIMENTAL PROCEEDURE

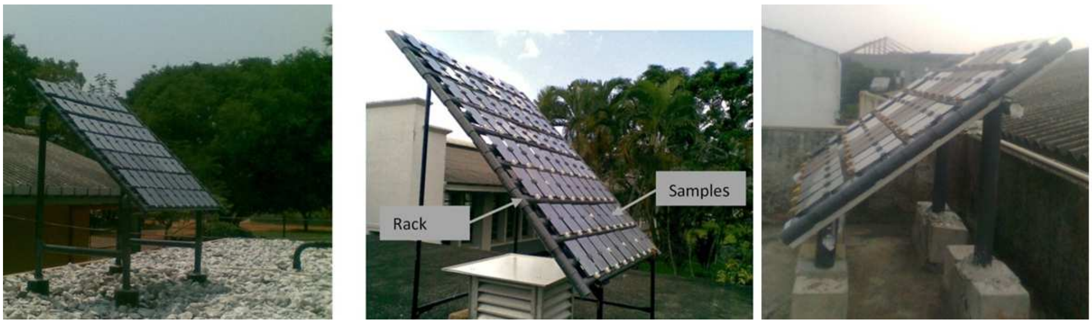
In this chapter the process involve in field exposure test , data collection and processing, model development, model calibration and validation of model will be described.

3.1 Field exposure test

The main part of the project is field exposure test that was conducted in different four locations, in Sri Lanka namely Peradeniya (Rural wet), Colombo (Urban) , Kolpetty (Marine) and Anuradhapura (Rural dry). The geographical locations of test sites are shown in the figure 3.1.

Specimens of mild steel plates having dimensions 150X100X2mm were used for this study. The atmospheric variables temperature, humidity and rain fall of each location were recorded by one month time intervals which were obtained from the data available at the Department of Meteorology. The sulphur dioxide deposition rate was measured by passive sampling method and chloride deposition rate was determined by wet candle method as per the method given in ISO 9225: 1992. [19]. The average mass loss of three specimens with same exposure condition was determined by two month time intervals for two years as per the method given in ISO 9226: 1992 [20].

Figure 3.1 Locations of field exposure program conducted.



(a)Anuradhapura (b) Peradeniya (c) Colombo ITI

Figure 3.2: Field exposure racks in diffferent locations

3.1.1 Preparation of corrosion test panel

3.1.1.1 Preparation of corrosion test specimen

Three type of materials (Mild steel : 45 specimens, Stainless steel grade 304 :15 specimens, Stainless steel grade 316: 12 specimens) with the dimension 150X100X2 mm and having chemical composition shown in table 3.1 were used for this study, the test specimens were prepared according to the method given in ISO 9226 [19] in Appendix A. The specimens were fixed on the exposure rack with the aid of plastic fixing elements as shown in the figure 3.1 and placed in the selected locations.

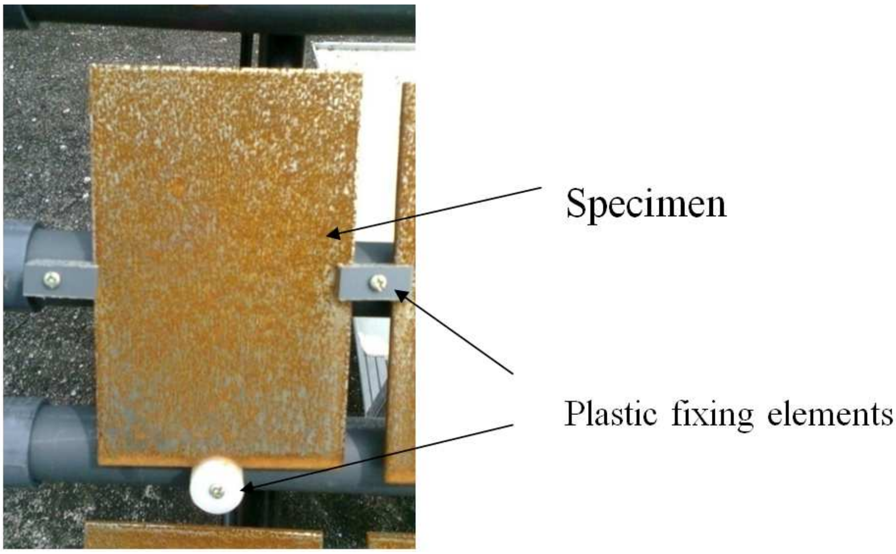


Figure: 3.3 fixing of test specimen to panel

Table:3.1 Chemical compositions of the materials used for the experiments

Material	**Chemical Composition**							
	C	S	Mn	Si	P	Cr	Ni	Mo
Carbon Steel	0.14	0.02	0.50	0.25	0.01	-	-	-
SS 304	0.06	0.01	1.01	0.40	0.02	18.2	9.5	-
SS316	0.06	0.02	1.00	0.24	0.02	17.25	12.45	2.45

Table 3.2. Test method

Test parameters	**Test method**
SO2	ISO 9225 :1992
Cal-	ISO 9225 :1992
Relative humidity	Department of meteorology Sri Lanka
Temperature	Department of meteorology Sri Lanka
Weight loss	ISO: 9226 :1992
Strength loss	BS 18. 1996

3.1.2 Measurement of atmospheric variables and corrosion loss

3.1.2.1 Measurement of sulphur deposition rate:

For the measurement of sulphur deposition rate the passive sampling method that was given in ISO 9225 was used. (Appendix B). Three passive samplers were located in each location and the sulphur deposition rate was measured by two month time intervals

Figure 3.4: Passive sampler for SO_x deposition

Figure 3.5: Wet candle for Cl^- Deposition

3.1.2.2 Measurement of chloride deposition rate:

For the measurement of chloride deposition rate the wet candle method that was given in ISO 9225 was used. (Appendix C). Three wet candles were located in each location and the chloride deposition rate was measured by two month time intervals.

3.1.2.3 Measurement of temperature and relative humidity:

The meteorological data such as temperature, rain fall and relative humidity were obtained from the Department of Meteorology, Sri Lanka.

3.1.2.4 Measurement of corrosion loss (Mass loss):

Three specimen from each location were removed by two months periods and the corrosion loss was determined according to the method given in ISO 9226 (Appendix D)

3.2 Data processing

The average result of each parameter of data collected from exposure test was determined by the to the equation given below and tabulated. As an example, Average chloride deposition during the period of 't months' was determined as follows.

$$(Cl)_t = \frac{\sum_{n=1}^{t}(Cl_n)}{t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (18)$$

Where: Cl_n: Average chloride deposition of the nth month

$(Cl)_t$: Average chloride deposition during the period of t months

t: Duration

Similarly results of Temperature $(T)_t$ Chloride deposition rate $(Cl)_t$, Sulphur deposition rate $(S)_t$, and rainfall $(RF)_t$ during the period of t months were determined.

3.3 Development of corrosion model.

3.3.1 Development of model structure

It is well established fact that the rate of atmospheric corrosion follows the power equation shown in equation 19.

$$C = Kt^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (19)$$

Where C is the loss of weight due to corrosion and *t* is the exposure time which is the primary factor that determines the basic rate of corrosion. The initial corrosion loss observed during the first unit time of exposure is described by K, while n is a measure of the long-term decrease in corrosion rate or pasivation of materials which is directly dependent on the metal, the physical–chemical atmospheric conditions and the exposure conditions [3].

Therefore, power equation can be applicable for any location by appropriately defining constant K and n as a function of atmospheric variables in particular location.

$$n=F\ (TOW, Cl^-, RF, SO_2, T, etc.) \ldots\ldots\ldots\ldots \quad (20)$$

$$K=F\ (TOW, Cl^-, RF\ SO_2, T, etc.) \ldots\ldots\ldots\ldots \quad (21)$$

Therefore based on the above concept a model structure was proposed that can be applicable in for Sri Lankan atmospheric conditon.. Based on this, two type of corrosion models were selected.

in model formulation fitting of data to a linear model is a more common practice. Therefore, firstly the most basic type of model that represent the multy variable linear equation shown in equation 22 and 23 were considered.

$$n = \alpha_1(RH) + \alpha_2(T) + \alpha_3(S0_2) + \alpha_4(Cl^-) + \alpha_5(RF) \qquad (22)$$

$$k = \beta_1(RH) + \beta_2(T) + \beta_3(S0_2) + \beta_4(Cl^-) + \beta_5(RF) \qquad (23)$$

The symbols "α_1 ,α_2 ,α_3, α_4 ,α_5 , β_1 , β_2 , β_3, β_4 , β_5 " represent the model constant which has to be determined by environmental and corrosion data of field exposure test.

Secondly, by reviewing published literature on corroion modeling it was identified few corrosion models can be applicable in sri lankan condiiotns. Among those models the corrosion model published by Dawn E. Klinsmith [4] (Shown in equation 24) was identified as a one of best corrosion model which suitable to Sri Lankan conditions. This corrosion model shows basic features of power equation and it do not show many of disadvantages in other published models.

$$Y = At^{B}\left(\frac{TOW}{C}\right)^{D}\left(1+\frac{SO_2}{E}\right)^{F}\left(1+\frac{Cl}{G}\right)^{H}e^{J(T+T_0)} \qquad (24)$$

Where,

Y - Mass loss due to corrosion
t -Time
TOW -Time of wetness
SO_2 -Sulphur deposition rate
Cal -Chloride deposition rate
T -Temperature
A, B, C, D, E, F, G, H, J and T_0 – Constant

Although this model has shown good performances in many cases, when consider the Sri Lankan atmospheric conditions the rain fall is one of main factor that can be influenced the outdoor atmospheric metal corrosion according to the meteorological data it is shown that comparatively high rainfall even in dry zone of the country throughout the year and the effect of rain on atmospheric corrosion damage are somewhat ambiguous. While providing electrolyte effect for corrosion and rain can influence in beneficial manner by diluting harmful corrosive surface species [3]. Therefore, when consider the Sri Lankan atmospheric condition parameter of Rain fall (RF) has to be added to the model. In addition to that relative humidity is the main factor that determine the time of wetness (TOW). In general practice TOW is defined as the *time duration in which relative humidity more than80 % and the temperature is higher than the* $0^{0}C$*[1]*. When the Sri Lankan atmospheric condition is considered the relative humidity everywhere in the country is always nearly 80%

or more. Therefore, whole exposure time of metals in atmosphere is equal to time of wetness. Further, the value of relative humidity determines the amount of moisture deposit on the metal surface and it has a significant effect on the corrosion rate. Therefore, the authors have decided that it is reasonable to replace TOW by RH in the equation no.5 and the constants A and C in equation 5 has been reduced to constant A in equation 6 {(A/C^D) =A}.Then the modified equation of the proposed corrosion model will be as follows;

$$Y = At^B (RH)^D \left(1+\frac{SO2}{E}\right)^F \left(1+\frac{Cl}{G}\right)^H \left(1+\frac{RF}{K}\right)^L e^{J(T+T0)} \qquad (25)$$

Where : RF is rain fall and K,L are constants.

(In addition to the constant given in equation 24)

3.3.2 Calibration of Corrosion Model Structure.

For the determination of constant of model structure software based mathematical iteration method was used. (Refer Appendix .E method for Equation 25)

In this exercise the iteration involves the fallowing processes.

1. The systematic substitution of all possible combination of numerical values which are within the pre identified range to the model.
2. Determination of Root Mean Square Error (RMS Error) for each combination according to the equation 23 given below.
3. Select the combination which gives the minimum chi square value and meaningful value to the constants as the best combination.

$$\text{RMS Error } = \frac{\sum(C_{\text{actual}} - C_{\text{calculated}})^2}{C_{\text{Actual}}} \qquad (26)$$

Where:

$C_{\text{calculated}}$:	Corrosion loss calculated by Proposed equation. for a given combination of model constant.
C_{actual} :	Corrosion loss from field exposure data.

3.3.3 Validation of corrosion model

The field exposure test of Peradeniya and Colombo were continued for another few years to collect required data and also it was started another two exposure in Puttalum and Nawala . Then the actual test results collected by exposure test was compared by means of percentage with the results calculated by the proposed models to find out the prediction capability of models. In this process it was assumed that the pattern of variation of atmospheric variables throughout the year is same for all the years. Therefore for the calculation of forecasted mass loss the average values of atmospheric variables in first year were used.

4. Results

Table 4.1 shows the date of commencement and durations of exposure program in different location, the exposure program was continued in all locations for 24 month except in Anuradhapura. In Anuradhapura after the completion of 20 month the exposure rack has been destroyed by animals due to insufficient security. Therefore this incident is an important factor to be considered when the exposure racks are installed.

Table .4.1 Exposure program details (Date of commencement of the exposure)

Location	Exposure date	Exposed duration (Months)
Urban –ITI (Colombo 7)	2011/07/15	24
Rural (Wet) -Peradeniya	2011/08/25	24
Marine -Kolpetty	2011/10/28	24
Rural (Dry) –Anuradhapura	2012/03/09	20
Marine -Puttalum	2016/06/26	04

4.1 Atmospheric data

The Table 4.2, Table 4.3 and Table 4.4 show that the variation of relative humidity, temperature and rain fall respectively in each location and the graphical representation of the same data are shown in figure 4.1, figure 4.2, figure 4.3 . These data were obtained from the Department of Meteorology (DOM) Sri Lanka. The data measurement location is not the same location that exposure panel was set up but both locations are within the same region and assumed that has similar environmental conditions. Initially, it was measured the variation of temperature and relative humidity in exposure locations with the aid of a data logger for two month and compared with the data obtained from DOM . Then it was found that there is no considerable difference between these two values.

4.1.1 Variation of average relative humidity in exposure locations with the month

Table. 4.2: Average relative humidity (%) in testing locations

Year	Month	Colombo	Peradeniya	Kollupitiya	Anuradhapura
2011	July	81.5	-	-	-
	August	81	-	-	-
	September	79	84	-	-
	October	81.5	84	-	-
	November	81.5	86	81.5	-
	December	79	85.5	79	-
2012	January	75.5	80.5	75.5	-
	February	78.5	80	78.5	-
	March	78.5	77	78.5	75
	April	83.5	85.5	83.5	80.5
	May	77	78.5	77	76
	June	81.5	79.5	81.5	73.5
	July	80.5	80.5	80.5	74
	August	82.5	81.5	82.5	70.5
	September	83	81	83	72
	October	84	86.5	84	82
	November	82	88.5	82	84.5
	December	82.5	87	82.5	88
2013	January	74	83.5	74	84.5
	February	78.5	84	78.5	82.5
	March	80	83.5	80	79.5
	April	79.5	84	79.5	77
	May	83	85	83	79.5
	June	82.5	80	82	75
	July		82.5	82.5	74.5
	August		81	83	72
	September			82	69
	October			83.5	80.5

4.1.2 Variation of average temperature in exposure locations with the month

Table 4.3: Average temperature (^{0}C) in exposure locations

Year	Month	Colombo	Peradeniya	Kollupitiya	Anuradhapura
2011	July	28.2	-	-	-
	August	28.2	-	-	-
	September	28.3	24.8	-	-
	October	28.1	25.6	-	-
	November	27.55	24.7	27.6	-
	December	27.05	23.8	27.1	-
2012	January	26.8	23.9	26.8	-
	February	27.55	24.7	27.6	-
	March	28.2	25.8	28.2	29.1
	April	27.9	25.9	27.9	28.9
	May	29.2	26.0	29.2	29.9
	June	28.65	25.7	28.7	30.0
	July	28.55	25.3	28.6	29.9
	August	28.1	25.1	28.1	30.2
	September	28	25.4	28.0	30.3
	October	27.65	25.3	27.7	28.5
	November	27.5	24.7	27.5	27.1
	December	27.3	24.0	27.3	26.0
2013	January	27.265	23.1	27.3	25.8
	February	27.685	24.4	27.7	27.0
	March	28.51	26.1	28.5	28.7
	April	29.4	26.8	29.4	30.1
	May	28.97	26.5	29.0	29.6
	June	-	26.0	29.7	27.8
	July	-	25.3	27.2	30.5
	August	-	-	26.2	30.4
	Sept	-	-	26.1	29.7
	October	-	-	26.6	28.9

According to the above data it can be observed that comparatively there is no considerable variation of temperature and relative humidity in different locations in Sri Lanka throughout the year.

4.1.3 Variation of average rainfall in exposure locations with the month

Table 4.4: Rain fall (mm) in exposure locations

Year	**Month**	**Colombo**	**Peradeniya**	**kollupitiya**	**Anuradhapura**
2011	July	98.2			
	August	148.6			
	September	76.2	150.8		
	October	242.0	275.1		
	November	188.3	102.3	188.3	
	December	45.3	77.5	45.3	
2012	Jan	158.7	40.4	158.7	
	Feb	140.1	147.3	140.1	
	Mar	122.0	48.7	122.0	75.2
	Apr	532.3	173.1	532.3	145.4
	May	152.0	0.9	152.0	0.2
	Jun	88.6	66.0	88.6	0.0
	Jul	41.1	135.0	41.1	23.9
	Aug	200.3	63.6	200.3	0.0
	Sep	180.0	28.5	180.0	16.2
	Oct	507.3	596.3	507.3	683.9
	Nov	207.4	265.0	207.4	242.1
	Dec	134.8	426.1	134.8	593.7
2013	Jan	90.90	298.7	90.91	203.3
	Feb	164.3	91.9	164.3	75.9
	Mar	108.3	71.3	108.3	232.6
	Apr	148.1	178.7	148.1	79.3
	May	404.50	146.7	404.5	57.4
	Jun	349.6	268.1	349.6	0
	July		130.6	100.3	95.3
	aug		91.2	132.5	147.1
	sep			300.5	9.3
	oct			475.3	

4.1.4 Variation of chloride deposition rate in exposure locations with the month

Table 4.5: Chloride deposition rate (g/m^2.day) in exposure locations

Year	**Month**	**Colombo**	**Peradeniya**	**Kollupitiya**	**Anuradhapura**
2011	July	100	*	-	-
	August	105	*	-	-
	September	95	*	-	-
	October	80	*	-	-
	November	70	*	250	-
	December	75	*	300	-
2012	January	70	*	350	-
	February	80	*	300	-
	March	65	*	380	*
	April	80	*	270	*
	May	90	*	400	*
	June	110	*	280	*
	July	115	*	250	*
	August	115	*	300	*
	September	100	*	315	*
	October	100	*	275	*
	November	100	*	200	*
	December	80	*	250	*
2013	January	85	*	250	*
	February	80	*	250	*
	March	85	*	300	*
	April	85	*	375	*
	May	110	*	400	*
	June	100	*	250	*
	July	-	*	250	*
	August	-	*	300	*
	Sept	-	-	375	*
	Oct	-	-	400	*

* Below 5

4.1.5 Variation of Sulphur deposition rate in exposure locations with the month

Table 4.6 Sulphur deposition rate in exposure locations

Year	Month	Colombo	Peradeniya	Kollupitiya	Mihinthale
2011	July	25		-	-
	August	20	*	-	-
	September	30	*	-	-
	October	22	*	-	-
	November	11	*	10	-
	December	16	*	15	-
2012	January	20	*	10	-
	February	18	*	20	-
	March	23	*	9	*
	April	24	*	28	*
	May	25	*	30	*
	June	20	*	14	*
	July	23	*	15	*
	August	21	*	28	*
	September	26	*	33	*
	October	22	*	28	*
	November	14	*	15	*
	December	14	*	17	*
2013	January	18	*	14	*
	February	16	*	20	*
	March	19	*	14	*
	April	22	*	25	*
	May	22	*	26	*
	June	21	*	13	*
	July	-	*	14	*
	August	-	-	26	*
	September	-	-	30	*
	October	-	-	19	*

As per the above results (Table: 4.5) it can be observed that relatively high chloride deposition rate is present in Kollupitiya which is more closure to the sea (approximately 100m). The location named as Colombo which is 1km away from coastal line shows relatively low concentration in chloride deposition rate. In the other two locations Anuradhapura and Peradeniya it can be observed that there is no presence of chloride and these locations are more than 90 km away from coastal line. When it is considered, the geographical situation of Sri Lanka it can be observed that there are no chloride emitting sources in mid of the country, therefore it can be decide that inside the country are free from chloride or considerably negligible amount.

According to the results shown in table 4.6 it can be observed that there are no sulphur deposition can be observed in Anuradhapura and Peradeniya, In the other two locations it can be observed that similar amount of sulphur deposition rate and those are comparatively low value. In Sri Lanka there are no highly polluted large cities and industrial areas comparative to the other countries, Only few factories are located in several places. Most of the factories in these industrial zones are garment industries and there is no highly emission of pollutions

4.1.6 Corrosion loss in exposure locations (mass loss)

Table 4.7: corrosion loss (mass loss) data

	Duration (month)	Corrosion loss/ mass loss (g/m^2)			
		Colombo	Peradeniya	Kollupitiya	Anuradhapura
2011	July- Aug	84.66	-	-	-
	Sep-Oct	175.32	58.66	-	-
	Nov-Dec	210.46	80.23	271.33	-
2012	Jan-Feb	288.72	102.45	498.53	-
	Mar-Apr	362.72	121.43	678.32	31.12
	May-jun	426.24	135.43	820.25	64.89
	Jul-Aug	462.26	155.34	898.53	84.16
	Sep-Oct	485.43	182.34	1045.68	110.32
	Nov-Dec	506.24	210.65	1254.26	132.41
2013	Jan-Feb	518.34	246.54	1366.11	154.23
	Mar-Apr	526.32	266.54	1597.34	176.45
	May-Jun	542.36	284.32	1684.56	190.00
	Jul-Aug	-	299.62	1786.50	201.54
	Sep-Oct	-	-	1832.32	210.68

4.2 Data Processing for Corrosion Model

As per the method described in 2.1.2.6 the average value of exposure data were calculated, the table 4.8 shows the summary of calculated data.

Table 4.8 Summary of field exposure program data

Data No.	**Location**	**Duration [month]**	**Average Humidity $(RH)_t$,%**	**Average Temperature $(T)_t$,^{0}C**	**Average Chloride Content $(Cl)_t$,mg/m^2.day**	**Average Sulphur Content $(SO_2)_t$,mg/m^2.day**	**Average Rain Fall $(RF)_t$,mm**	**Total Mass loss ,g/m^2**
1	Urban	2	81.25	28.55	102.50	22.50	123.40	84.66
2	Urban	4	80.75	28.40	95.00	24.25	141.25	175.32
3	Urban	6	80.58	28.21	87.50	20.67	133.10	210.46
4	Urban	8	79.69	27.89	84.38	20.25	137.18	288.72
5	Urban	10	79.95	27.84	82.00	20.90	175.17	362.72
6	Urban	12	79.83	27.96	85.00	21.17	166.03	426.24
7	Urban	14	80.07	28.05	89.29	21.29	159.55	462.26
8	Urban	16	80.50	28.05	90.63	21.63	182.56	485.43
9	Urban	18	80.69	28.00	90.56	20.78	181.29	506.24
10	Urban	20	80.25	27.93	89.75	20.40	175.92	518.34
11	Urban	22	80.20	27.87	89.32	20.41	171.58	526.32
12	Urban	24	80.42	28.09	90.63	20.50	188.80	542.36
13	Rural-wet	2	84.00	25.15	0.00	0.00	212.50	58.66
14	Rural-wet	4	84.88	24.70	0.00	0.00	151.50	80.23
15	Rural-wet	6	83.33	24.55	0.00	0.00	132.17	102.45
16	Rural-wet	8	82.81	24.83	0.00	0.00	126.88	121.43
17	Rural-wet	10	82.05	25.03	0.00	0.00	108.20	135.43
18	Rural-wet	12	81.88	25.05	0.00	0.00	106.67	155.34
19	Rural-wet	14	82.14	25.09	0.00	0.00	136.07	182.34
20	Rural-wet	16	82.84	25.00	0.00	0.00	162.31	210.65
21	Rural-wet	18	82.94	24.86	0.00	0.00	165.94	246.54
22	Rural-wet	20	83.03	25.02	0.00	0.00	161.85	266.54
23	Rural-wet	22	82.95	25.68	0.00	0.00	166.00	284.32
24	Rural-wet	24	82.94	24.97	0.00	0.00	161.42	299.62
25	Marine	2	79.69	27.96	275.00	12.50	135.67	271.33
26	Marine	4	79.95	28.05	300.00	13.75	500.75	498.53
27	Marine	6	79.83	28.05	308.33	15.33	355.50	678.32
28	Marine	8	80.07	28.00	316.25	17.00	314.13	820.25
29	Marine	10	80.50	27.93	308.00	17.90	322.80	898.53
30	Marine	12	80.69	27.94	305.83	20.00	287.83	1045.68
31	Marine	14	80.25	28.04	294.29	20.14	266.14	1254.26
32	Marine	16	80.20	27.54	288.75	19.94	267.44	1366.11
33	Marine	18	80.42	28.60	294.17	19.89	247.56	1597.34
34	Marine	20	80.45	28.12	297.25	19.85	241.80	1684.56
35	Marine	22	80.76	27.75	295.23	19.86	232.95	1786.50
36	Marine	24	81.02	27.68	302.92	20.25	234.29	1832.32
37	Rural -Dry	2	77.75	28.98	0.00	0.00	110.50	31.12
38	Rural -Dry	4	76.25	29.48	0.00	0.00	55.25	64.89
39	Rural -Dry	6	74.92	29.68	0.00	0.00	40.67	84.16
40	Rural -Dry	8	75.44	29.61	0.00	0.00	118.00	110.32
41	Rural -Dry	10	77.60	29.00	0.00	0.00	178.00	132.41
42	Rural -Dry	12	78.58	28.57	0.00	0.00	171.58	154.23
43	Rural -Dry	14	78.54	28.69	0.00	0.00	169.36	176.45
44	Rural -Dry	16	78.47	28.69	0.00	0.00	151.81	190.00
45	Rural -Dry	18	78.08	29.24	0.00	0.00	148.44	201.54
46	Rural -Dry	20	77.63	28.96	0.00	0.00	134.05	210.68

Urban : Colombo 07, Rural wet : Peradeniya, Marine : Kollupitiya, Rural Dry: Anuradhapura

4.3 Corrosion model:

The constants of equation 20 (Model 1) was determined as per the method describe in clause 2.5, the obtained values of constants of model 1 are as follows.

α_1 =0.007, α_2=0.0015, α_3 =-0.0013, α_4=0.0008, α_5=0.0002

β_1=0.32, β_2=0.015, β_3=0.053, β_4=0.244 β_5=0.054

By substituting above values the equation 26 can be obtained. Therefore when climatic data and atmospheric data are available this equation can be used for the determination of the corrosion loss in any area of Sri Lanka.

$$C = (0.32RH + 0.015T + 0.53SO2 + 0.244Cl + 0.054RF)t^{0.001(7RH+1.5T+1.3S+08Cl+02RF)} \quad (26)$$

In the same way the constant of corrosion model shown in equation 25 (Model 2) was determined and obtained values of constants of model 2 are as follows.

A=6.82 B= 0.78 D=0.07 E= 93 F=0.31

G= 158 H= 1.70 J=0.023 K= 150 L= 0.18 T_o=7.3

By substituting above values the equation 27 can be obtained. Therefore when climatic data and atmospheric data are available this equation also can be used for the determination of the corrosion loss in any area of Sri Lanka.

$$y = 6.82\mathrm{t}^{0.78}\mathrm{RH}^{0.07}\left(1+\frac{\mathrm{SO2}}{93}\right)^{0.31}\left(1+\frac{Cl}{158}\right)^{1.70}\left(1+\frac{RF}{150}\right)^{0.18} e^{0.023(T+7.3)} \quad (7)$$

4.3.1 Model performance analysis

The figure 4.6 and 4.7 shows the percentage deviation of calculated corrosion loss from actual corrosion loss. This result can be used for the performance evaluation of model's goodness of fit with the data. Therefore these results show that more than 80% of data are within the ±10% deviation. That means the model's goodness of fit is in reasonably acceptable level or in another word the values obtained for the model constant are acceptable by means of goodness of fit.

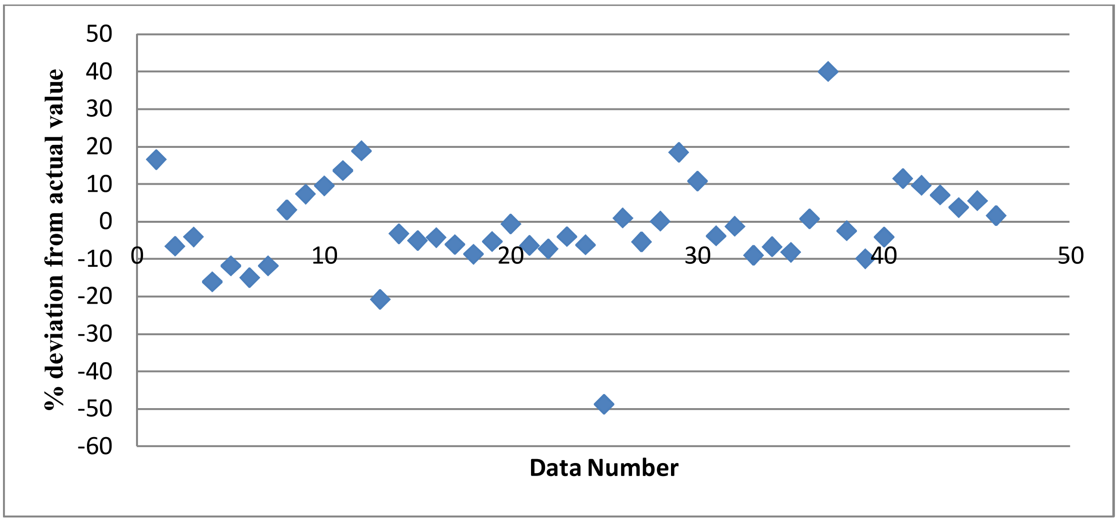


Figure 4.6: Percentage deviation from actual value (Model 1)

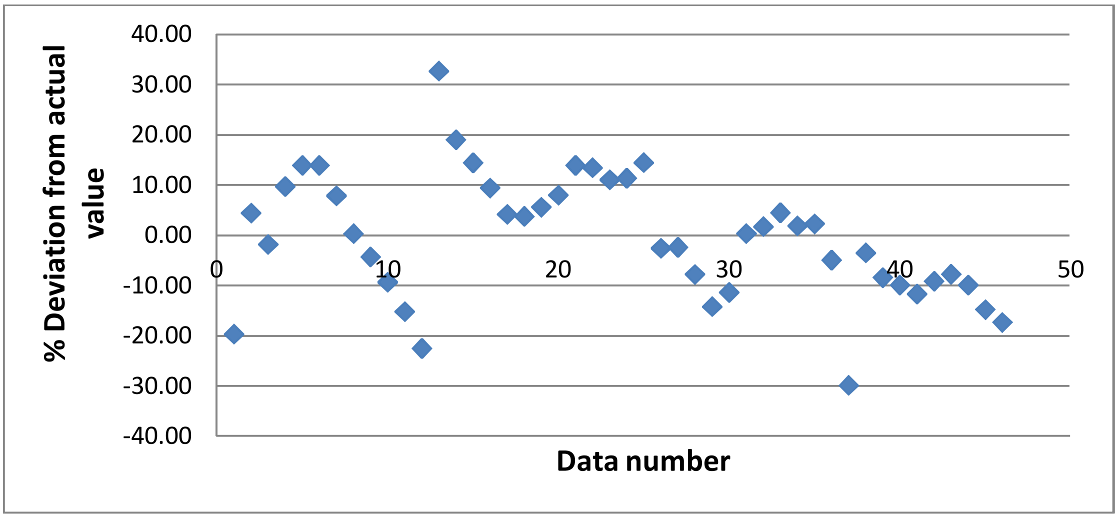


Figure 4.7:Percentage deviation from actual value (Model 2)

The figures 4.8 , figure 4.9, figure 4.10 and figure 4.11 shows the graphical representation of comparison of actual corrosion loss with forecasted corrosion loss calculated by model 1 and model 2 .

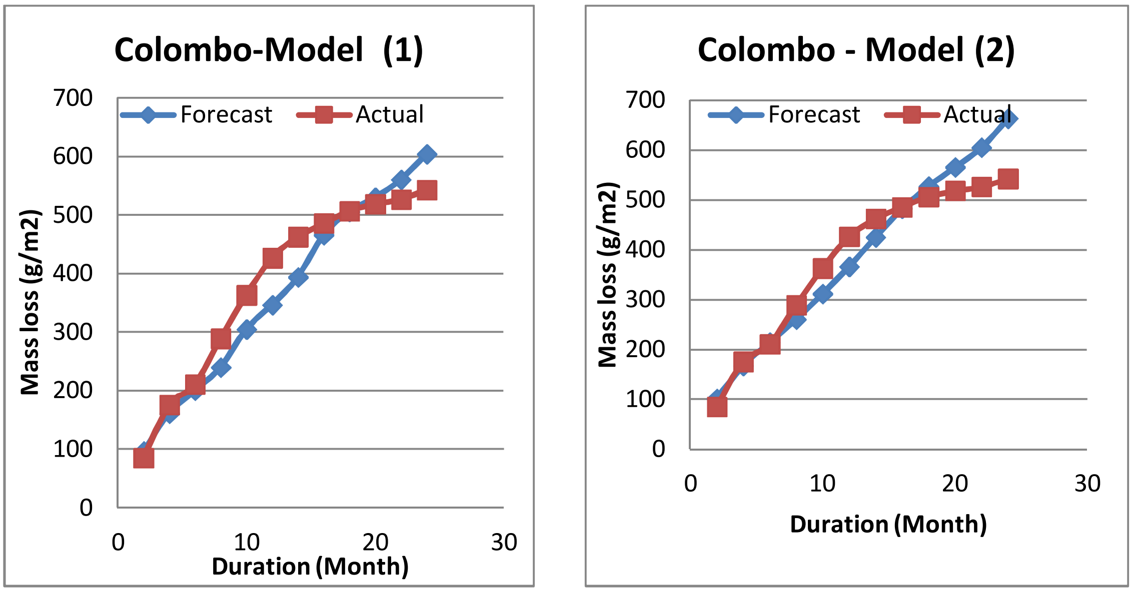


Figure 4.8 : Comparison of actual mass loss with forecasted mass loss in Colombo

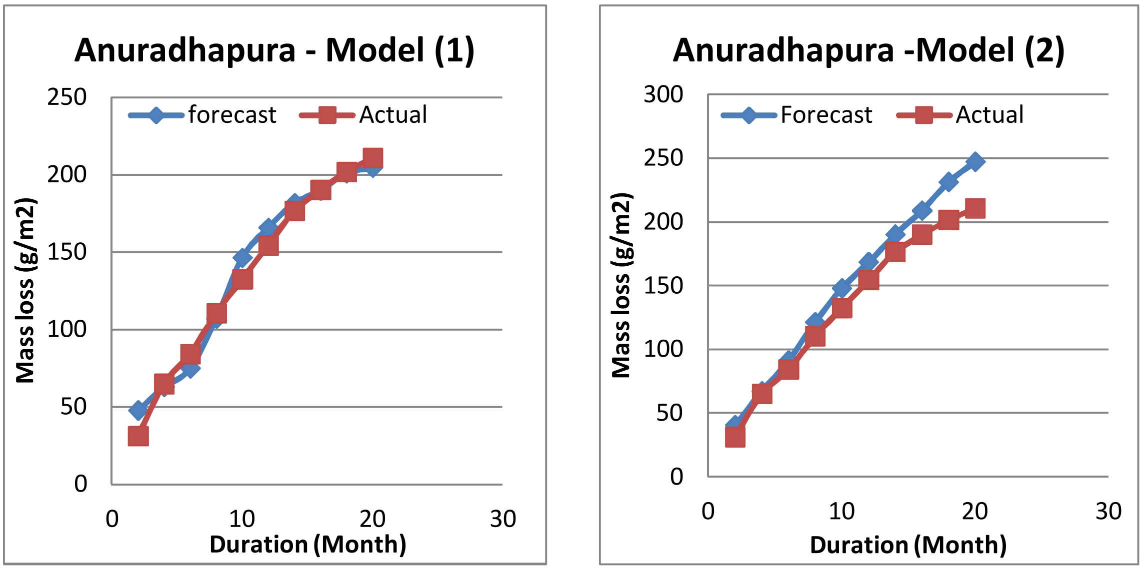


Figure 4.9 : Comparison of actual mass loss with forecasted mass loss in Anuradhapura

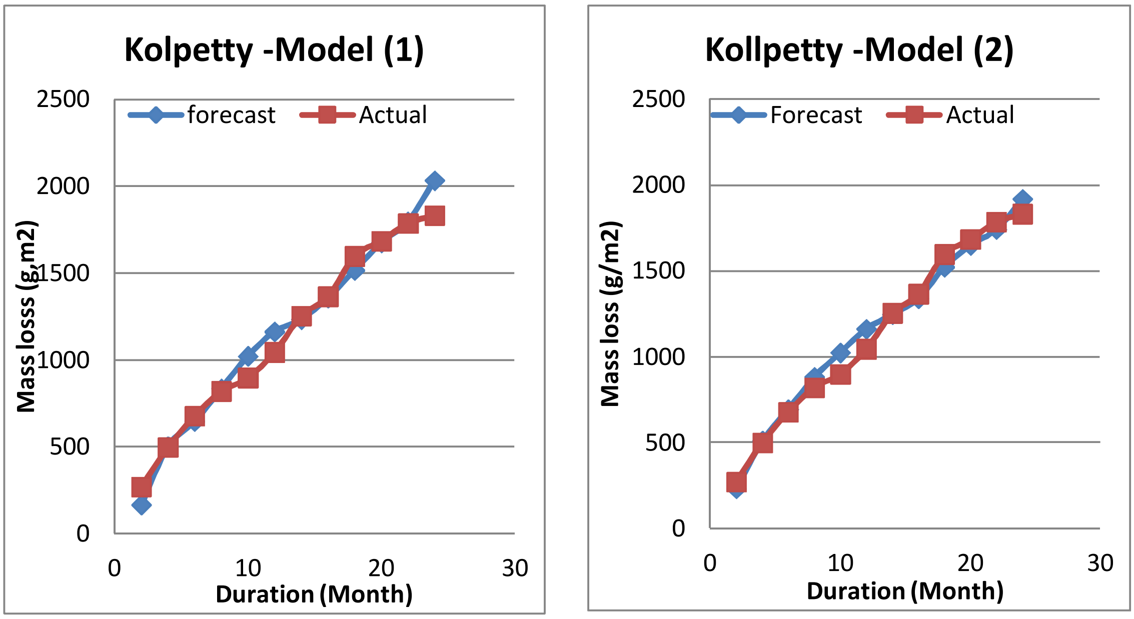


Figure 4.10: Comparison of actual mass loss with forecasted mass loss in Kollupitiya

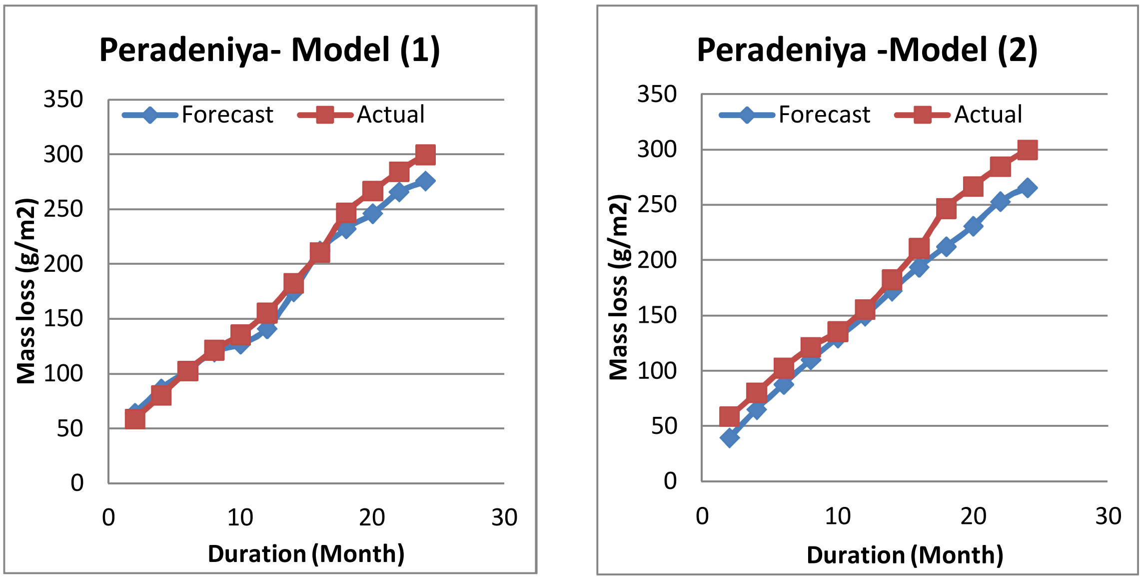


Figure 4.11: Comparison of actual mass loss with forecasted mass loss in Peradeniya

4.3.2 Model validation

The table 4.9 shows the mass loss due to corrosion in different locations in Sri Lanka and the same determined by the corrosion model 2.

Table 4.9: Comparison of Forecasted mass Loss with Actual mass Loss

Location	**Duration [months]**	**Actual Mass Loss due to Corrosion [g/m²]**	**Predicted Mass Loss due to Corrosion [g/m²]**	**Deviation [%]**
Colombo	36	840.2	909.8	8.2
Colombo	66	1350	1462	8.2
Peradeniya	36	382.4	364.3	4.7
Peradeniya	64	520	570	9.6
Nawala	4	140	152	8.5
Puttalam	2	531	374	29
Puttalam	4	950	667	30

According to the results of Colombo, Nawala and Peradeniya, the model shows good forecasting capability and the deviation is below the 10 %.

In the case of Puttalam there is a considerable difference in forecasted value and actual value. Possible reason is the range of data used for the calibration does not cover the actual environmental condition in Puttalam (Eg. For chloride deposition rate the calibrated data range is 0-316 mg/m^2.day but the actual value is 436 mg/m^2.day . In addition to that the location of specimen mounted was closed to the sea about 25m from the sea. Therefore, the specimens are directly exposed to the sea breeze and this provides excess moisture to the sample that was not represented by relative humidity. These kinds of conditions such as sea breeze are not considered in the formation of model and also for the determination of loss of mass due to corrosion model relative humidity and temperature values were obtained from Department of Meteorology Sri Lanka but the actual values are much higher than the measured value due to sea breeze (Eg : measured value for relative humidity is 82 but near to the sea the atmosphere is always saturate with sea water and therefore the RH is always near to 100). Therefore, in order to obtain more accurate results it is required to measure on the spot value of atmospheric variable such as relative humidity and temperature instead of use of area data from Meteorological Department

Further the method given in ISO standard [3] for the measurement of chloride deposition rate (Wet candle method) is not suitable for the areas where it directly exposure to the sea breeze because the candle will be saturated within few days and further absorption of chloride will be limited and shows relatively low values.

Table 4.10 Comparison of test results obtained by models with ISO method.

Location	**parameter**	**Value (Annual Average)**	**ISO Category**	**ISO Category (based on atmospheric variables)**	**Model 1**	**Model 2**
Colombo	Temperature	**28.09**				
	Relative humidity	**80.42**	**T5**		**357**	**366**
	Chloride deposition rate	**90.62**	**S2**			
	Sulphur deposition rate	**20.5**	**P1**			
	Corrosion loss	**426**	**C4**	**C4**	**C3**	**C3**
Peradeniya	Temperature	**24.97**				
	Relative humidity	**82.87**	**T5**			
	Chloride deposition rate	**0**	**S0**		**155**	**149**
	Sulphur deposition rate	**0**	**P0**			
	Corrosion loss	**155**	**C2**	**C3**	**C2**	**C2**
Kollupitiya	Temperature	**27.68**				
	Relative humidity	**80.73**	**T5**		**1139**	**1164**
	Chloride deposition rate	**302.92**	**S3**			
	Sulphur deposition rate	**19.7**	**P1**			
	Corrosion loss	**1045**	**C5**	**C5**	**C5**	**C5**
Anuradhapura	Temperature	**28.96**				
	Relative humidity	**77.5**	**T3-T4**			
	Chloride deposition rate	**0**	**S0**		**165**	**168**
	Sulphur deposition rate	**0**	**P0**			
	Corrosion loss	**154**	**C2**	**C2-C3**	**C2**	**C2**

Relative Importance Analysis' was conducted for independent variables (i.e. atmospheric variables) of the developed model by means of change of corrosion loss per unit variation of each atmospheric variable. The table 4 shows that the percentage relative importance of each variable under selected three different atmospheric conditions (1, 2, 3). For the convenience of comparison, the environmental conditions were selected so that chloride deposition rate was varied when other environmental conditions remain unchanged. According to the results given in table 4 it was observed that the contribution of each variable to total corrosion loss depends on the atmospheric condition and in this case temperature is the most important factor that determines the corrosion loss while rain fall is the least important factor.

Table 4.11: Percentage relative importance of atmospheric variables under different environmental conditions

	Average Humidity $(RH)_t$ [%]	**Average Temperature $(T)_t$ [^{0}C]**	**Average Chloride Content $(Cl)_t$ [mg/m^2.day]**	**Average Sulphur Content $(SO_2)_t$ [mg/m^2.day]**	**Average Rain Fall $(RF)_t$ [mm]**
Relative Importance (%) under Atmospheric condition (1) (RH =80, T=24, Cl=25, SO_2=13, RF=270)	2.37	63.41	25.36	7.69	1.17
Relative Importance (%) under Atmospheric condition (2) (RH =80, T=24, Cl=160, SO_2=13, RF=270)	2.65	71.05	16.37	8.61	1.31
Relative Importance (%) under Atmospheric condition (3) (RH =80, T=24, Cl=300, SO_2=13, RF=270)	2.80	74.81	11.94	9.07	1.38

5. Conclusions

1. Development of many corrosion models has been reported in all over the world. Due to high diversity of environmental condition from place to place even in the local area of same country, It is difficult to obtain a universal corrosion model with acceptable accuracy because when the environmental conditions are more diverse level of accuracy of models output becomes low. Therefore Most of these models show good performance only within the predefined conditions.

2. When it is consider the Sri Lankan atmospheric condition, it was observed environmental condition throughout the country varies in a similar pattern therefore; it is possible to develop a one corrosion model for Sri Lanka with considerable accuracy.

3. The corrosion rate of metal is mainly depends on its environment and the long term corrosion loss follow the parabolic equation. It means that the initial corrosion rate is higher than the long term corrosion rate and the corrosion rate is decreased with the time mainly due to corrosion product deposited on the metal surface and act as a barrier to further contact of base metal with environment.

4. For mild steel it was observed there is a considerable difference in mass loss due to corrosion under different atmospheric conditions in Sri Lanka, Therefore, it was possible to develop a relation between corrosion of mild steel and atmospheric variables. The developed corrosion model shows good performance in prediction of corrosion.

5. In practice, development of a `corrosion map' is a massive and costly exercise therefore it has to be an all-country effort with field stations throughout the country in all major cities and industrial areas. But in case of Sri Lanka there are no highly polluted large cities and industrial areas comparative to other countries, only few factories are located in several places and the geographical area is very small. Therefore, it would not be a difficult task to develop a corrosion map with the model developed in this research work.

6. The advantage of this model is that to develop a corrosion map for Sri Lanka it is not necessary to place (Expose) Samples in all over Sri Lanka to measure the mass loss. According to this model if the environmental data are available in a particular location then it is possible to calculate the mass loss in that particular location. However further work is necessary to be done to fine tune the constants of the model by placing more samples in selected location in Sri Lanka

7. Stainless steel grade 304 and 316 do not show considerable mass loss under the selected atmospheric conditions and there is no detectable differences under different atmospheric condition therefore it is not possible to determine mass loss due to corrosion of stainless steel (304, 316) as a function of atmospheric variables.

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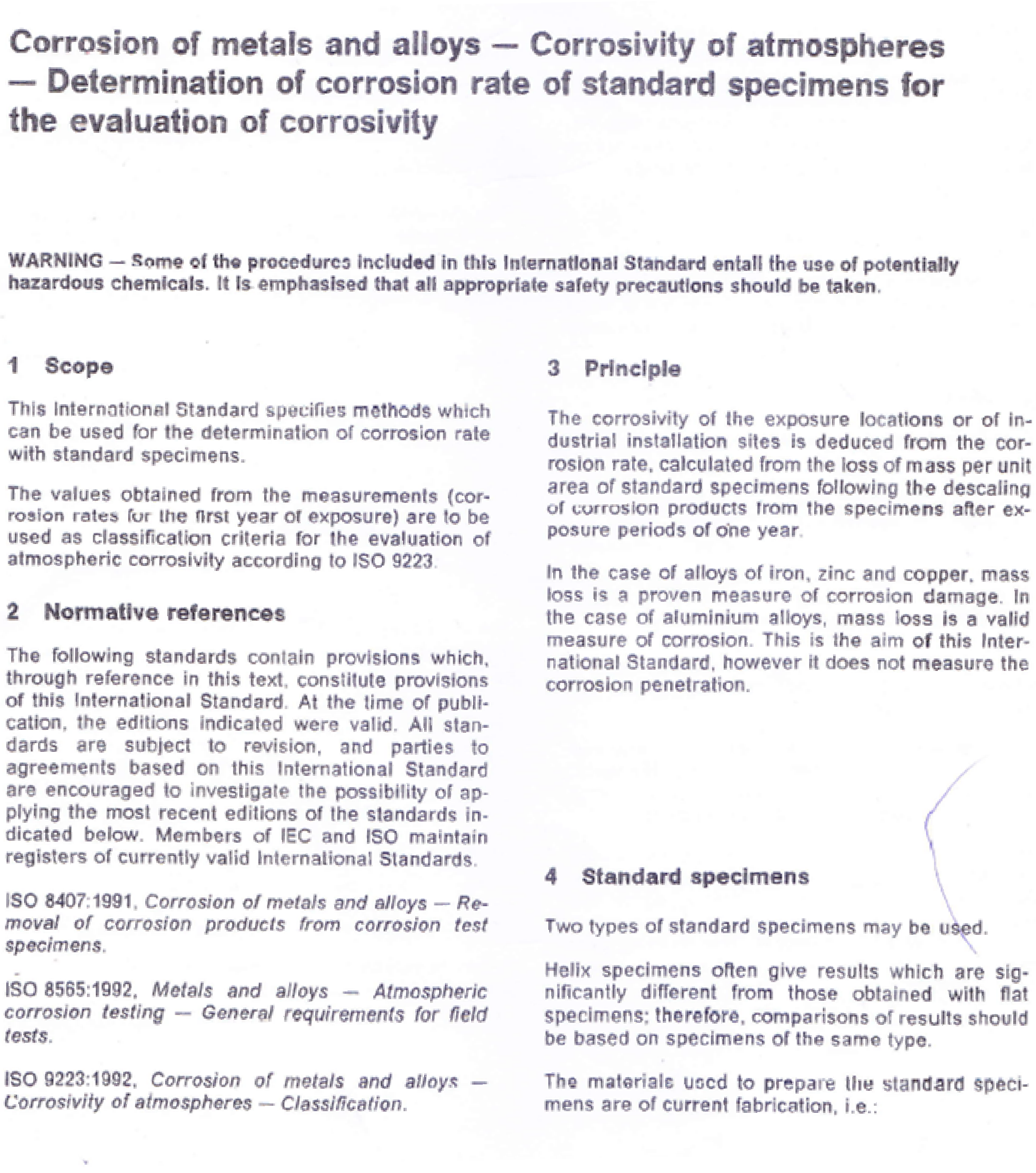
[24] Corrosion of Metals and Alloys - Removal of Corrosion Products from Corrosion Test Specimens, International Standard Organization, ISO 8407.

Appendix A



Corrosion of metals and alloys — Corrosivity of atmospheres — Determination of corrosion rate of standard specimens for the evaluation of corrosivity

WARNING — Some of the procedures included in this International Standard entail the use of potentially hazardous chemicals. It is emphasised that all appropriate safety precautions should be taken.

1 Scope

This International Standard specifies methods which can be used for the determination of corrosion rate with standard specimens.

The values obtained from the measurements (corrosion rates for the first year of exposure) are to be used as classification criteria for the evaluation of atmospheric corrosivity according to ISO 9223.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 8407:1991, *Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens.*

ISO 8565:1992, *Metals and alloys — Atmospheric corrosion testing — General requirements for field tests.*

ISO 9223:1992, *Corrosion of metals and alloys — Corrosivity of atmospheres — Classification.*

3 Principle

The corrosivity of the exposure locations or of industrial installation sites is deduced from the corrosion rate, calculated from the loss of mass per unit area of standard specimens following the descaling of corrosion products from the specimens after exposure periods of one year.

In the case of alloys of iron, zinc and copper, mass loss is a proven measure of corrosion damage. In the case of aluminium alloys, mass loss is a valid measure of corrosion. This is the aim of this International Standard, however it does not measure the corrosion penetration.

4 Standard specimens

Two types of standard specimens may be used.

Helix specimens often give results which are significantly different from those obtained with flat specimens; therefore, comparisons of results should be based on specimens of the same type.

The materials used to prepare the standard specimens are of current fabrication, i.e.:

Appendix A

Steel: unalloyed carbon steel (Cu 0,03 % to 0,10 %, $P < 0{,}07$ %)

Zinc: 98,5 % min.

Copper: 99,5 % min.

Aluminium: 99,5 % min.

Prior to exposure, all specimens shall be solvent degreased. Steel specimens with visable rust stains or corrosion products on their surfaces shall be polished with 120 grit abrasive paper prior to degreasing to remove these visible corrosion products. Copper, zinc and aluminium specimens shall not be used if visable corrosion products are present before exposure.

4.1 Flat plate specimens

The specimens are rectangular plates with dimensions of preferably 100 mm × 150 mm but at least 50 mm × 100 mm, and a thickness of approximately 1 mm.

4.2 Open helix specimens

The materials used to prepare the standard specimens are wires intended for thermal spraying.

Wires with a diameter, d, of 2 mm to 3 mm are cut to a length of approximately 1 000 mm. They are then rolled into a helix using a rod with a diameter of 24 mm.

5 Exposure of standard specimens

The preparation and the exposure of the weighed and marked standard specimens shall be done according to the specifications of ISO 8565.

Three specimens of each metal should be exposed for one year, starting at the beginning of the worst corrosive period of the year. Helix specimens must be exposed in upright position (see figure 1).

After exposure, the corrosion products formed on specimens shall be removed in accordance with the specifications of ISO 8407 and reweighed to the nearest 0,1 mg. Procedures suitable for chemical cleaning are given in annex A. The cleaning procedure should be repeated several times in equal cleaning cycles.

6 Expression of results

The corrosion rate, r_{corr}, for each metal, expressed in grams per square metre year [$\text{g}/(\text{m}^2 \cdot \text{a})$], is given by the equation

$$r_{\text{corr}} = \frac{\Delta m}{A \cdot t} \qquad \ldots (1)$$

where

Δm is the mass loss, in grams;

A is the surface area, in square metres;

t is the exposure time, in years.

The corrosion rate, r_{corr}, can also be expressed in micrometres per year (µm/a), and is given by the equation

$$r_{\text{corr}} = \frac{\Delta m}{A \cdot \varrho \cdot t} \qquad \ldots (2)$$

where

ϱ is the density, in grams per cubic centimetre, of the metal:

$$\varrho_{\text{Fe}} = 7{,}86 \text{ g/cm}^3$$
$$\varrho_{\text{Zn}} = 7{,}14 \text{ g/cm}^3$$
$$\varrho_{\text{Cu}} = 8{,}96 \text{ g/cm}^3$$
$$\varrho_{\text{Al}} = 2{,}70 \text{ g/cm}^3$$

Δm, A and t have the same meaning as the symbols in equation (1).

The corrosion rate for open helix specimens, r_{corr}, expressed in micrometres per year (µm/a), is given by the equation

$$r_{\text{corr}} = 0{,}25 \times \frac{\Delta m \cdot d}{m \cdot t} \qquad \ldots (3)$$

where

Δm is the mass loss, in milligrams;

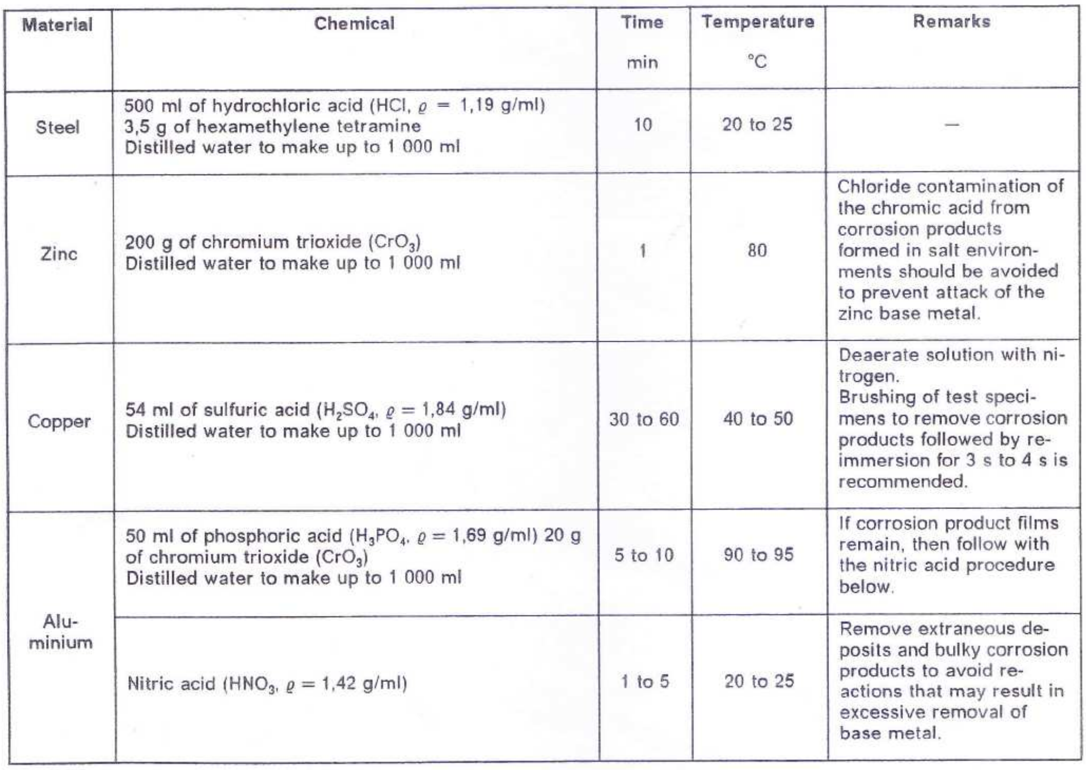
d is the wire diameter, in millimetres;

m is the original mass, in grams;

t is the exposure time, in years.

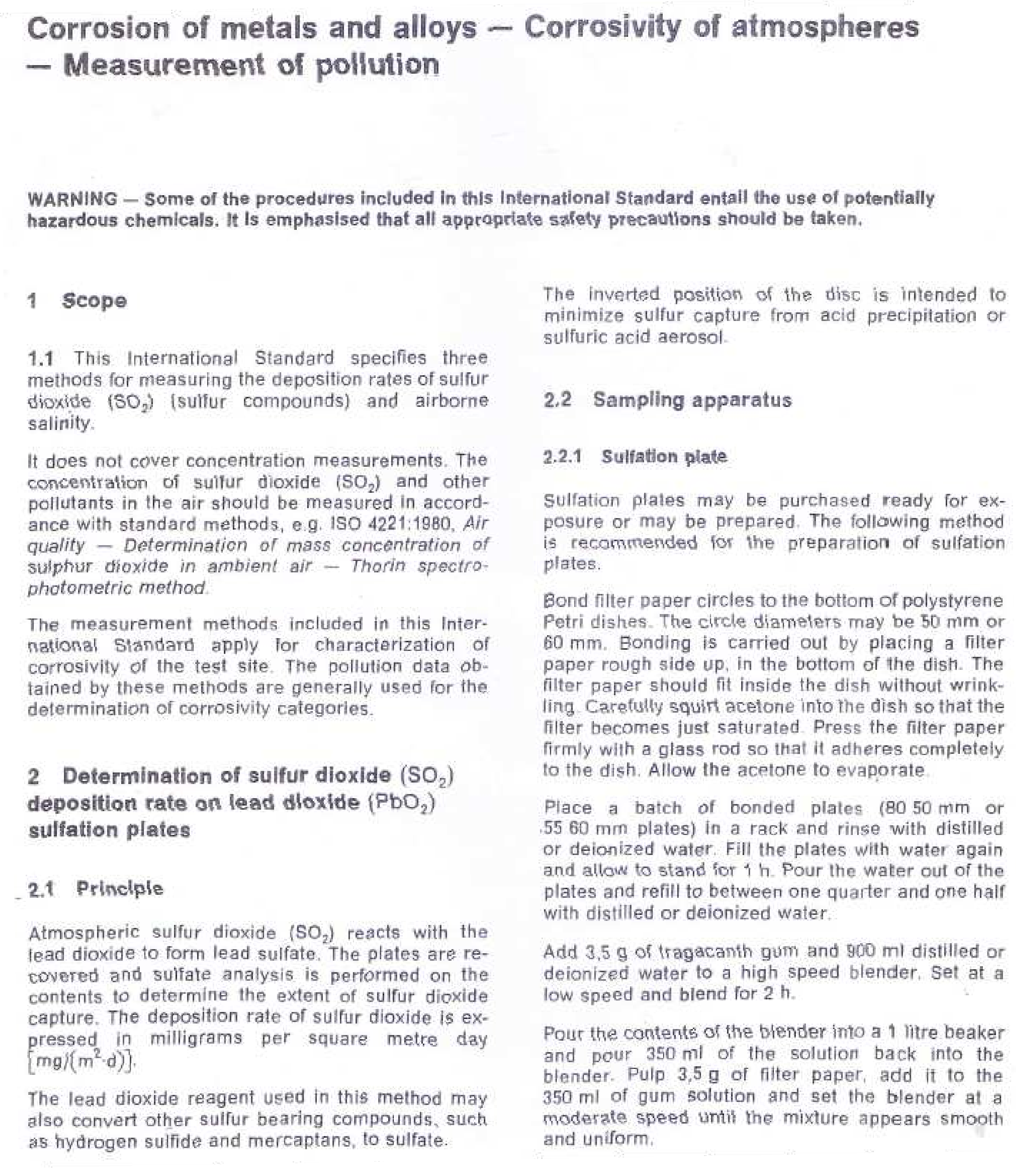
All single values and their mean values shall be represented in the test report.

Appendix A



Material	Chemical	Time min	Temperature °C	Remarks
Steel	500 ml of hydrochloric acid (HCl, ϱ = 1,19 g/ml) 3,5 g of hexamethylene tetramine Distilled water to make up to 1 000 ml	10	20 to 25	—
Zinc	200 g of chromium trioxide (CrO_3) Distilled water to make up to 1 000 ml	1	80	Chloride contamination of the chromic acid from corrosion products formed in salt environments should be avoided to prevent attack of the zinc base metal.
Copper	54 ml of sulfuric acid (H_2SO_4, ϱ = 1,84 g/ml) Distilled water to make up to 1 000 ml	30 to 60	40 to 50	Deaerate solution with nitrogen. Brushing of test specimens to remove corrosion products followed by re-immersion for 3 s to 4 s is recommended.
Aluminium	50 ml of phosphoric acid (H_3PO_4, ϱ = 1,69 g/ml) 20 g of chromium trioxide (CrO_3) Distilled water to make up to 1 000 ml	5 to 10	90 to 95	If corrosion product films remain, then follow with the nitric acid procedure below.
	Nitric acid (HNO_3, ϱ = 1,42 g/ml)	1 to 5	20 to 25	Remove extraneous deposits and bulky corrosion products to avoid reactions that may result in excessive removal of base metal.

Appendix B



Corrosion of metals and alloys — Corrosivity of atmospheres — Measurement of pollution

WARNING — Some of the procedures included in this International Standard entail the use of potentially hazardous chemicals. It is emphasised that all appropriate safety precautions should be taken.

1 Scope

1.1 This International Standard specifies three methods for measuring the deposition rates of sulfur dioxide (SO_2) (sulfur compounds) and airborne salinity.

It does not cover concentration measurements. The concentration of sulfur dioxide (SO_2) and other pollutants in the air should be measured in accordance with standard methods, e.g. ISO 4221:1980, *Air quality — Determination of mass concentration of sulphur dioxide in ambient air — Thorin spectrophotometric method*.

The measurement methods included in this International Standard apply for characterization of corrosivity of the test site. The pollution data obtained by these methods are generally used for the determination of corrosivity categories.

2 Determination of sulfur dioxide (SO_2) deposition rate on lead dioxide (PbO_2) sulfation plates

2.1 Principle

Atmospheric sulfur dioxide (SO_2) reacts with the lead dioxide to form lead sulfate. The plates are recovered and sulfate analysis is performed on the contents to determine the extent of sulfur dioxide capture. The deposition rate of sulfur dioxide is expressed in milligrams per square metre day $[mg/(m^2 \cdot d)]$.

The lead dioxide reagent used in this method may also convert other sulfur bearing compounds, such as hydrogen sulfide and mercaptans, to sulfate.

The inverted position of the disc is intended to minimize sulfur capture from acid precipitation or sulfuric acid aerosol.

2.2 Sampling apparatus

2.2.1 Sulfation plate

Sulfation plates may be purchased ready for exposure or may be prepared. The following method is recommended for the preparation of sulfation plates.

Bond filter paper circles to the bottom of polystyrene Petri dishes. The circle diameters may be 50 mm or 60 mm. Bonding is carried out by placing a filter paper rough side up, in the bottom of the dish. The filter paper should fit inside the dish without wrinkling. Carefully squirt acetone into the dish so that the filter becomes just saturated. Press the filter paper firmly with a glass rod so that it adheres completely to the dish. Allow the acetone to evaporate.

Place a batch of bonded plates (80 50 mm or 55 60 mm plates) in a rack and rinse with distilled or deionized water. Fill the plates with water again and allow to stand for 1 h. Pour the water out of the plates and refill to between one quarter and one half with distilled or deionized water.

Add 3,5 g of tragacanth gum and 900 ml distilled or deionized water to a high speed blender. Set at a low speed and blend for 2 h.

Pour the contents of the blender into a 1 litre beaker and pour 350 ml of the solution back into the blender. Pulp 3,5 g of filter paper, add it to the 350 ml of gum solution and set the blender at a moderate speed until the mixture appears smooth and uniform.

Appendix B

Pour 400 ml of the previously prepared gum solution into the blender and blend at a moderate speed for 1 min.

Set the blender at a high speed and add 112 g of lead dioxide. Blend for 2 min and then turn the blender back to a low speed.

Carefully pipette 10 ml of the mixture into each 50 mm plate or 15 ml into each 60 mm plate. Make sure that the mixture spreads uniformly to the edge of each plate.

Place the rack of plates in an oven set at 40 °C to 50 °C for 20 h.

Remove the plates from the oven, allow to cool and seal them with tight-fitting covers to protect them until exposure begins.

Number the plates and expose them within 120 days of preparation. Retain at least three plates from each batch for reference.

2.2.2 Exposure rack

Brackets shall be used to hold the plates securely in an inverted position, so that the lead dioxide mixture faces downwards. The plates shall be horizontal and shall not be obstructed from normal winds and air circulation currents. The brackets shall be constructed from a material which has adequate resistance to atmospheric corrosion. They shall include a retaining clip or other provision to hold the plate in the event of strong winds. A typical bracket design is shown in figure 1.

Dimensions in millimetres

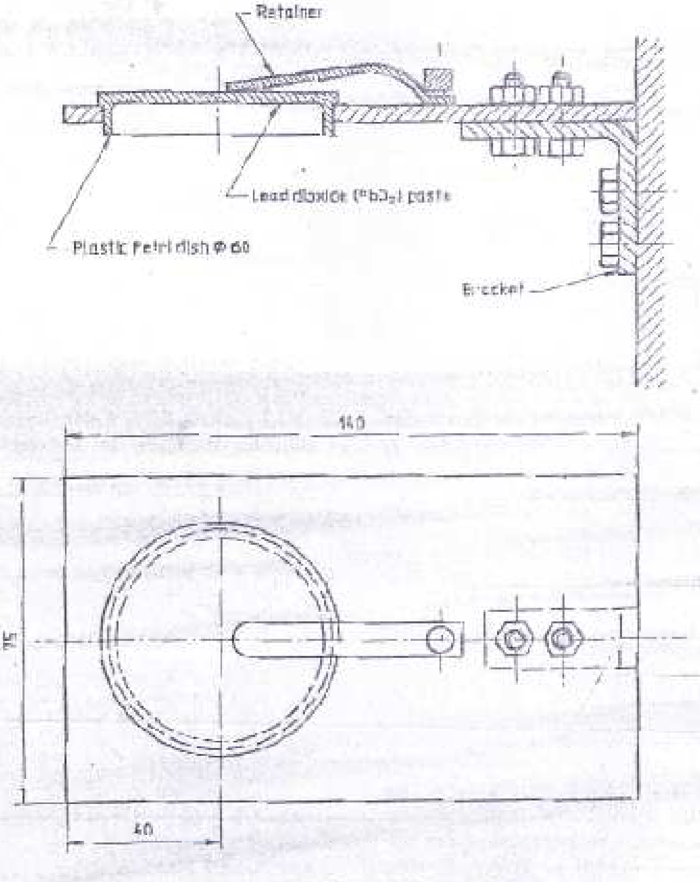
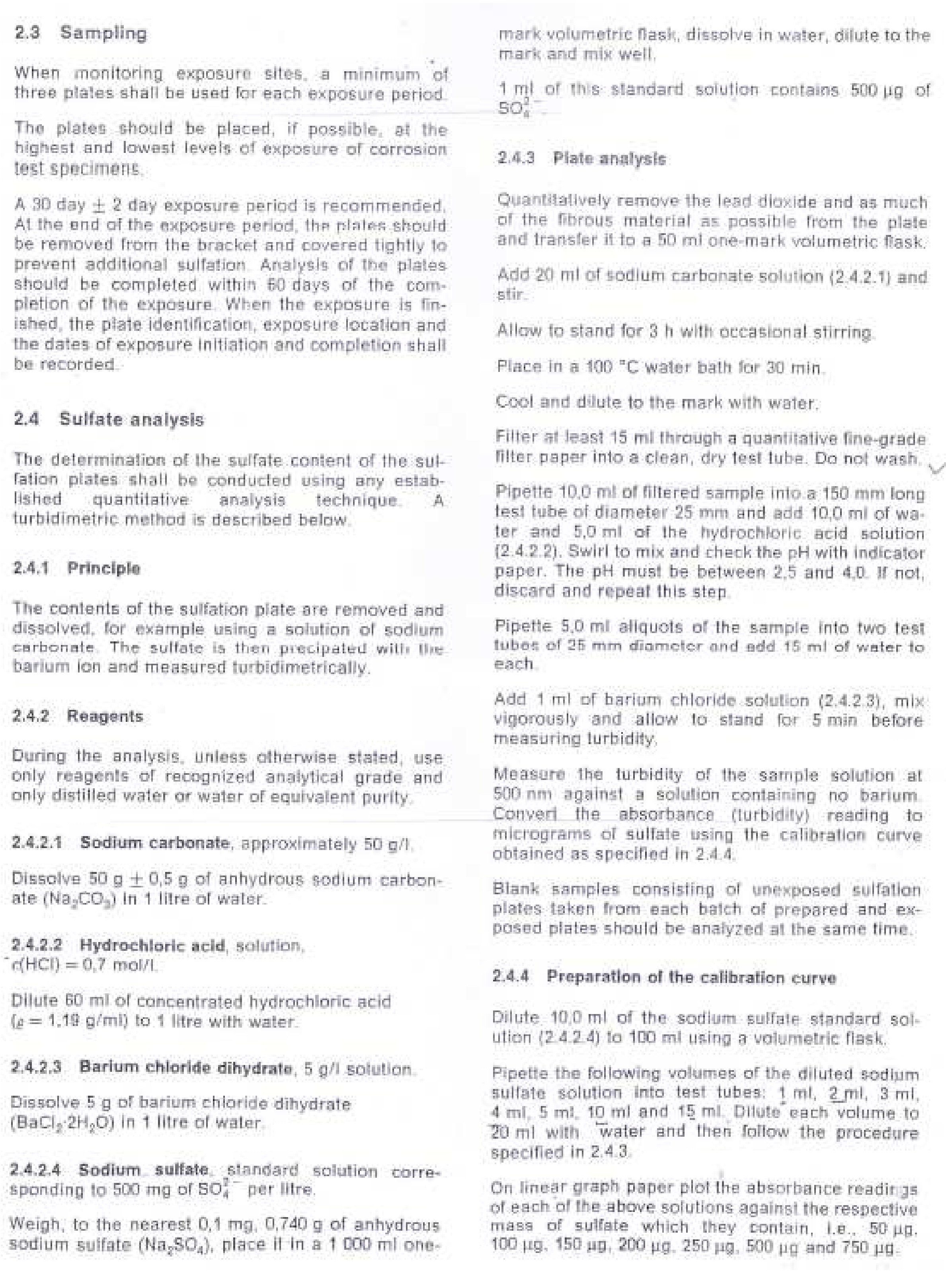


Figure 1 — Sulfation plate holder

Appendix B



2.3 Sampling

When monitoring exposure sites, a minimum of three plates shall be used for each exposure period.

The plates should be placed, if possible, at the highest and lowest levels of exposure of corrosion test specimens.

A 30 day ± 2 day exposure period is recommended. At the end of the exposure period, the plates should be removed from the bracket and covered tightly to prevent additional sulfation. Analysis of the plates should be completed within 60 days of the completion of the exposure. When the exposure is finished, the plate identification, exposure location and the dates of exposure initiation and completion shall be recorded.

2.4 Sulfate analysis

The determination of the sulfate content of the sulfation plates shall be conducted using any established quantitative analysis technique. A turbidimetric method is described below.

2.4.1 Principle

The contents of the sulfation plate are removed and dissolved, for example using a solution of sodium carbonate. The sulfate is then precipated with the barium ion and measured turbidimetrically.

2.4.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

2.4.2.1 Sodium carbonate, approximately 50 g/l.

Dissolve 50 g ± 0,5 g of anhydrous sodium carbonate (Na_2CO_3) in 1 litre of water.

2.4.2.2 Hydrochloric acid, solution, $c(HCl) = 0,7$ mol/l.

Dilute 60 ml of concentrated hydrochloric acid ($\varrho = 1,19$ g/ml) to 1 litre with water.

2.4.2.3 Barium chloride dihydrate, 5 g/l solution.

Dissolve 5 g of barium chloride dihydrate ($BaCl_2 \cdot 2H_2O$) in 1 litre of water.

2.4.2.4 Sodium sulfate, standard solution corresponding to 500 mg of SO_4^{2-} per litre.

Weigh, to the nearest 0,1 mg, 0,740 g of anhydrous sodium sulfate (Na_2SO_4), place it in a 1 000 ml one-mark volumetric flask, dissolve in water, dilute to the mark and mix well.

1 ml of this standard solution contains 500 µg of SO_4^{2-}.

2.4.3 Plate analysis

Quantitatively remove the lead dioxide and as much of the fibrous material as possible from the plate and transfer it to a 50 ml one-mark volumetric flask.

Add 20 ml of sodium carbonate solution (2.4.2.1) and stir.

Allow to stand for 3 h with occasional stirring.

Place in a 100 °C water bath for 30 min.

Cool and dilute to the mark with water.

Filter at least 15 ml through a quantitative fine-grade filter paper into a clean, dry test tube. Do not wash.

Pipette 10,0 ml of filtered sample into a 150 mm long test tube of diameter 25 mm and add 10,0 ml of water and 5,0 ml of the hydrochloric acid solution (2.4.2.2). Swirl to mix and check the pH with indicator paper. The pH must be between 2,5 and 4,0. If not, discard and repeat this step.

Pipette 5,0 ml aliquots of the sample into two test tubes of 25 mm diameter and add 15 ml of water to each.

Add 1 ml of barium chloride solution (2.4.2.3), mix vigorously and allow to stand for 5 min before measuring turbidity.

Measure the turbidity of the sample solution at 500 nm against a solution containing no barium. Convert the absorbance (turbidity) reading to micrograms of sulfate using the calibration curve obtained as specified in 2.4.4.

Blank samples consisting of unexposed sulfation plates taken from each batch of prepared and exposed plates should be analyzed at the same time.

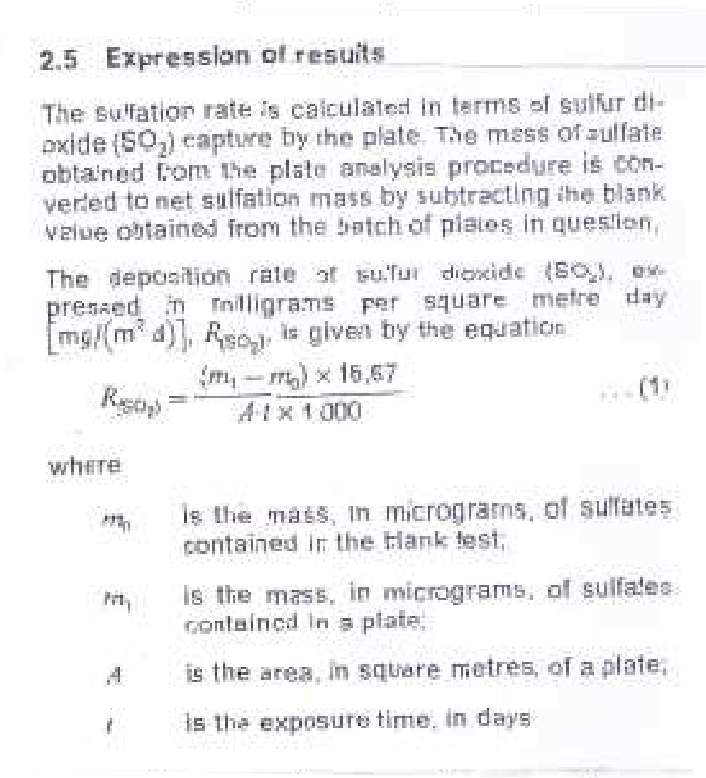
2.4.4 Preparation of the calibration curve

Dilute 10,0 ml of the sodium sulfate standard solution (2.4.2.4) to 100 ml using a volumetric flask.

Pipette the following volumes of the diluted sodium sulfate solution into test tubes: 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 10 ml and 15 ml. Dilute each volume to 20 ml with water and then follow the procedure specified in 2.4.3.

On linear graph paper plot the absorbance readings of each of the above solutions against the respective mass of sulfate which they contain, i.e., 50 µg, 100 µg, 150 µg, 200 µg, 250 µg, 500 µg and 750 µg.

Appendix B



2.5 Expression of results

The sulfation rate is calculated in terms of sulfur dioxide (SO_2) capture by the plate. The mass of sulfate obtained from the plate analysis procedure is converted to net sulfation mass by subtracting the blank value obtained from the batch of plates in question.

The deposition rate of sulfur dioxide (SO_2), expressed in milligrams per square metre day $\left[\mathrm{mg}/(\mathrm{m}^2\,\mathrm{d})\right]$, $R_{(SO_2)}$, is given by the equation

$$R_{(SO_2)} = \frac{(m_1 - m_0) \times 16{,}67}{A \cdot t \times 1\,000} \qquad \ldots (1)$$

where

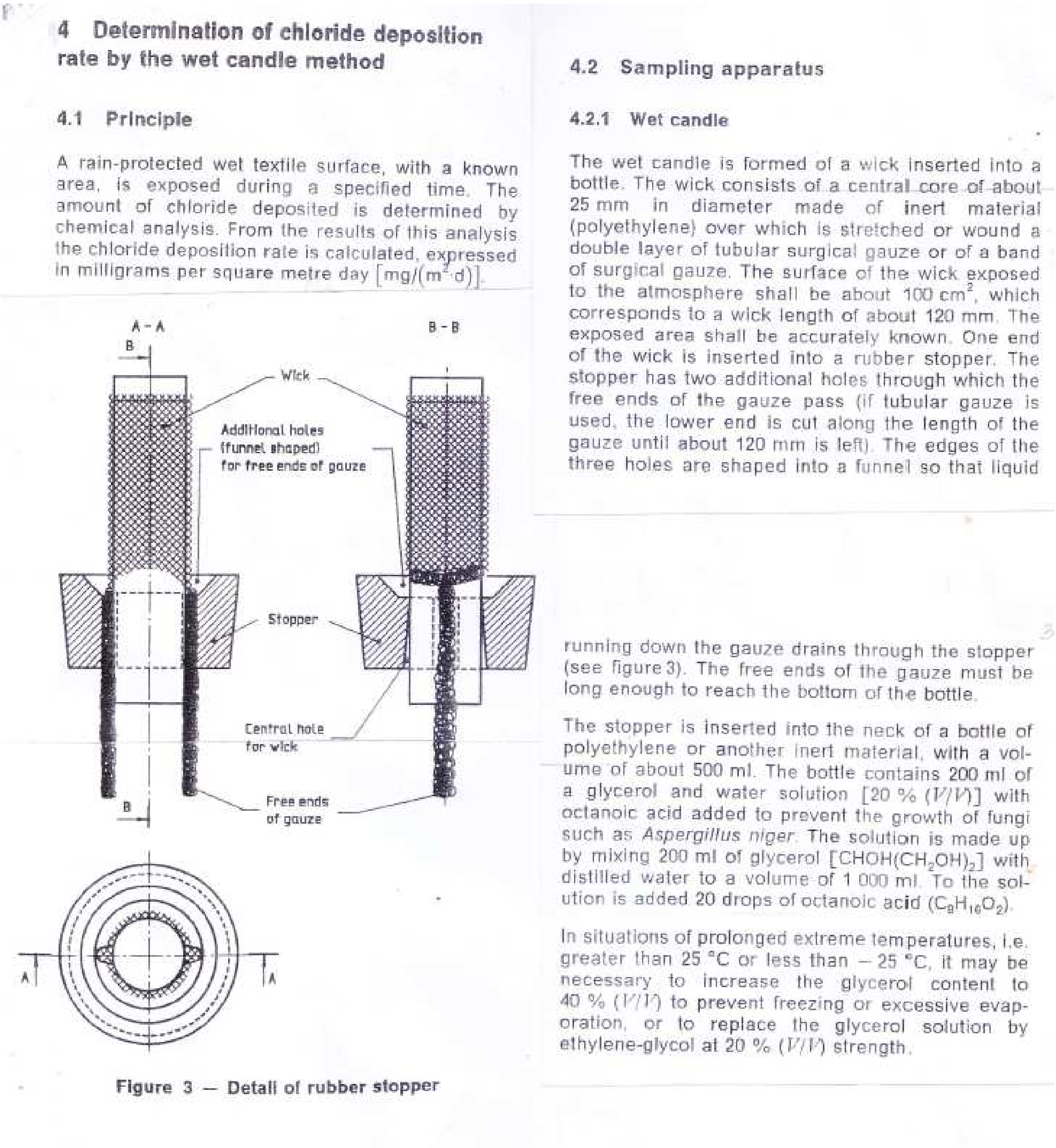
m_0 is the mass, in micrograms, of sulfates contained in the blank test;

m_1 is the mass, in micrograms, of sulfates contained in a plate;

A is the area, in square metres, of a plate;

t is the exposure time, in days

Appendix C



4 Determination of chloride deposition rate by the wet candle method

4.1 Principle

A rain-protected wet textile surface, with a known area, is exposed during a specified time. The amount of chloride deposited is determined by chemical analysis. From the results of this analysis the chloride deposition rate is calculated, expressed in milligrams per square metre day $[\mathrm{mg/(m^2 \cdot d)}]$.

Figure 3 — Detail of rubber stopper

4.2 Sampling apparatus

4.2.1 Wet candle

The wet candle is formed of a wick inserted into a bottle. The wick consists of a central core of about 25 mm in diameter made of inert material (polyethylene) over which is stretched or wound a double layer of tubular surgical gauze or of a band of surgical gauze. The surface of the wick exposed to the atmosphere shall be about 100 cm^2, which corresponds to a wick length of about 120 mm. The exposed area shall be accurately known. One end of the wick is inserted into a rubber stopper. The stopper has two additional holes through which the free ends of the gauze pass (if tubular gauze is used, the lower end is cut along the length of the gauze until about 120 mm is left). The edges of the three holes are shaped into a funnel so that liquid running down the gauze drains through the stopper (see figure 3). The free ends of the gauze must be long enough to reach the bottom of the bottle.

The stopper is inserted into the neck of a bottle of polyethylene or another inert material, with a volume of about 500 ml. The bottle contains 200 ml of a glycerol and water solution [20 % (*V*/*V*)] with octanoic acid added to prevent the growth of fungi such as *Aspergillus niger*. The solution is made up by mixing 200 ml of glycerol $[\mathrm{CHOH(CH_2OH)_2}]$ with distilled water to a volume of 1 000 ml. To the solution is added 20 drops of octanoic acid ($C_8H_{16}O_2$).

In situations of prolonged extreme temperatures, i.e. greater than 25 °C or less than – 25 °C, it may be necessary to increase the glycerol content to 40 % (*V*/*V*) to prevent freezing or excessive evaporation, or to replace the glycerol solution by ethylene-glycol at 20 % (*V*/*V*) strength.

Appendix C

4.2.2 Exposure rack

The wet candle is exposed on a rack under the centre of a roof as shown in figure 4. The roof should be a square of 500 mm side, inert and opaque. The candle should be attached so that the distance from the roof to the top of the wick is 200 mm and so that it is centred on the roof. The distance between the bottle and the ground level should be at least 1 m. The candle should be exposed towards the sea or other chloride source.

Dimensions in millimetres

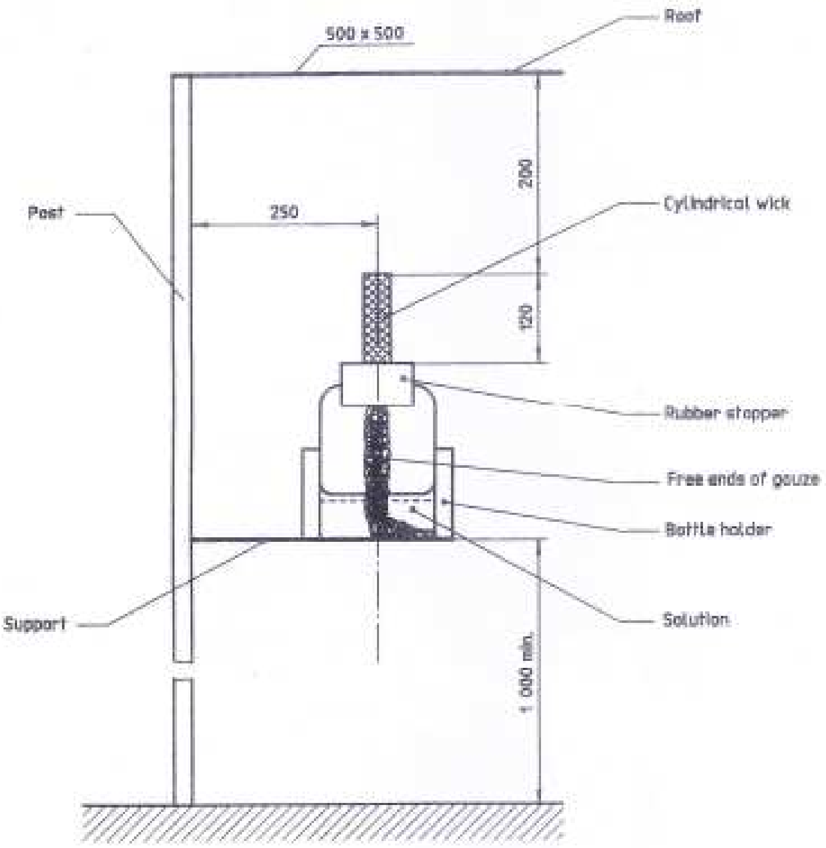


Figure 4 — Sampling apparatus assembly

4.3 Sampling

Install the prefabricated candle at the test location and carry out the following steps:

a) adjust the length of the exposed part of the wick to the desired value;

b) remove the stopper and wick from the bottle, wash the free ends of the gauze and the bottle with distilled water;

c) place 200 ml of the glycerol and water solution (see 4.2.1) in the bottle;

d) reassemble the wick and bottle;

e) place the candle in the exposed position according to figure 4.

The glycerol and water solution should be changed at monthly intervals as follows:

- loosen the stopper in the bottle;
- carefully wash down the wick with at least 200 ml of distilled water, ensuring that the washings run through the drain holes in the stopper and thence into the bottle;

Appendix C

- remove the stopper and wick from the bottle and wash the free ends of the gauze as they are withdrawn from the bottle;
- place the stopper and wick into a new bottle containing 200 ml of fresh glycerol and water solution, ensuring that the free ends of the gauze dip well into the solution; replace the candle in its holder;
- screw on the lid of the removed bottle tightly, making sure that it does not leak.

Mark the bottle clearly with the test site name, location and dates of exposure and removal.

The solution in the bottle is prepared for analysis according to 4.4.3.

4.4 Chloride analysis

A suitable chloride analysis is described below. Any other analytical procedure which provides satisfactory precision can be used.

4.4.1 Principle

The amount of chloride in a sample is determined by mercurimetric titration using diphenylcarbazone/bromophenol blue mixed indicator. The endpoint of the titration is indicated by the formation of a blue-violet complex of mercuric diphenylcarbazone in the pH interval 2,3 - 2,8.

4.4.2 Reagents

During the analysis, unless otherwise stated, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.4.2.1 Ethanol, 95 % (*V*/*V*).

4.4.2.2 Nitric acid, solution, $c(HNO_3) = 0{,}05$ mol/l.

Dilute 3 ml of nitric acid ($\varrho = 1{,}40$ g/ml) to 1 000 ml with water.

4.4.2.3 Sodium hydroxide, solution, $c(NaOH) = 0{,}25$ mol/l.

Dissolve 10 g of sodium hydroxide in water and dilute to 1 000 ml.

4.4.2.4 Sodium chloride, standard reference solution, $c(NaCl) = 0{,}025$ mol/l.

Dry the sodium chloride for 1 h at 300 °C. Dissolve 1,461 3 g in water and dilute to 1 000 ml in a volumetric flask.

4.4.2.5 Mercury(II) nitrate, standard volumetric solution, $c[Hg(NO_3)_2] = 0{,}012\,5$ mol/l.

Dissolve 4,283 0 g of mercury(II) nitrate monohydrate $[Hg(NO_3)_2 \cdot H_2O]$ in 50 ml of water acidified with 0,5 ml of nitric acid (HNO_3) ($\varrho = 1{,}40$ g/ml). Dilute to 1 000 ml with water in a volumetric flask. Filter if necessary and determine the exact concentration by titration using sodium chloride standard reference solution (4.4.2.4) as described in 4.4.3.

4.4.2.6 Mercury(II) nitrate, standard volumetric solution, $c[Hg(NO_3)_2] = 0{,}007\,05$ mol/l.

Dissolve 2,420 0 g of mercury(II) monohydrate $[Hg(NO_3)_2 \cdot H_2O]$ in 25 ml of water acidified with 0,25 ml of nitric acid ($\varrho = 1{,}40$ g/ml). Dilute to 1 000 ml with water in a volumetric flask. Filter if necessary and determine the exact concentration by titration using sodium chloride standard volumetric solution (4.4.2.4) as described in 4.4.3.

4.4.2.7 Mixed indicator solution.

Dissolve 0,5 g of diphenylcarbazone and 0,5 g of bromophenol blue in 75 ml of ethanol (4.4.2.1) and dilute to 100 ml with ethanol. Keep in a dark bottle in a refrigerator.

4.4.3 Analysis

Sample a known aliquot of the sample prepared according to 4.3 and containing not more than 20 mg of chloride ions. Determine the approximate content of chloride ions in the sample solution by preliminary titration using mercury(II) nitrate (4.4.2.5).

If the aliquot of the sample solution contains more than 2,5 mg of chloride ions, perform the titration using mercury(II) nitrate standard volumetric solution (4.4.2.5).

If the aliquot of the sample solution contains less than 2,5 mg of chloride ions, perform the titration using mercury(II) nitrate standard volumetric solution (4.4.2.6) and a microburette. In this case, perform a blank titration on 50 ml of water. If the aliquot contains less than 0,1 mg of chloride ions per litre, evaporate a suitable volume to 50 ml.

Add 5 to 10 drops of mixed indicator solution (4.4.2.7).

If a blue-violet or red colour develops add nitric acid solution (4.4.2.2) drop by drop until the colour changes to yellow and then add 1 ml more of the nitric acid solution. If a yellow or orange colour forms immediately when the indicator is added, develop the blue-violet colour by adding sodium hydroxide solution (4.4.2.3) drop by drop, then proceed with the acidification.

Appendix D

Corrosion of metals and alloys — Removal of corrosion products from corrosion test specimens

1 Scope

1.1 This International Standard specifies procedures for the removal of corrosion products formed on metal and alloy corrosion test specimens during their exposure in corrosive environments. For the purpose of this International Standard, the term "metals" refers to metals and alloys.

1.2 The procedures specified are designed to remove all corrosion products without significant removal of base metal. This allows an accurate determination of the mass loss of the metal which occurred during exposure to the corrosive environment.

1.3 These procedures may, in some cases, also be applied to metal coatings. However, possible effects from the substrate must be considered.

2 Procedures

2.1 General

2.1.1 A light mechanical cleaning treatment by brushing with a soft bristle brush under running water should first be applied to remove lightly adherent or bulky corrosion products. In some cases, this treatment will be sufficient to remove all corrosion products and no further treatment will be necessary.

2.1.2 If the treatment described in 2.1.1 does not remove all corrosion products it will be necessary to use other procedures. These are of three types:

a) chemical;

b) electrolytic;

c) more vigorous mechanical treatments.

Whichever method is used, it may be necessary to repeat the cleaning treatment to ensure complete removal of corrosion products. Removal shall be confirmed by visual examination. The use of a low-power microscope (i.e. ×7 to ×30) is particularly helpful with a pitted surface when corrosion products may accumulate in pits.

2.1.3 An ideal procedure should remove only corrosion products and not result in removal of any base metal. Two procedures can be used to confirm this point. One procedure uses a control specimen (2.1.3.1) and the other requires a certain number of cleaning cycles on the corroded specimen (2.1.3.2).

2.1.3.1 Uncorroded control specimens which should be similar chemically, metallurgically, and geometrically to the test specimens, should be cleaned by the same procedure as used for the test specimen. By weighing the control specimen before and after cleaning (weighing to the fifth significant figure is suggested, e.g. a 70 g specimen should be weighed to three decimal places), the metal loss resulting from the cleaning may be determined. The mass loss of the control specimen will reflect the mass loss of test specimens resulting from the cleaning procedure.

2.1.3.2 The cleaning procedure should be repeated several times with the corroded test specimen after removal of corrosion products is completed. The mass can be shown on a graph as a function of the number of equal cleaning cycles (see figure 1). In many cases the masses obtained in these cleaning cycles (applied after removal of corrosion products) will have a linear relation with cleaning cycles. Two lines, AB and BC, will be obtained. Line AB characterizes the removal of corrosion products and may not always be visible. Line BC characterizes the removal of substrate after the corrosion products are gone. By extrapolation of line BC to the ordinate axis, we obtain point D which characterizes the mass at zero number of cleaning cycles. In other cases the relation may not be linear and the most appropriate extrapolation shall then be made.

Appendix D

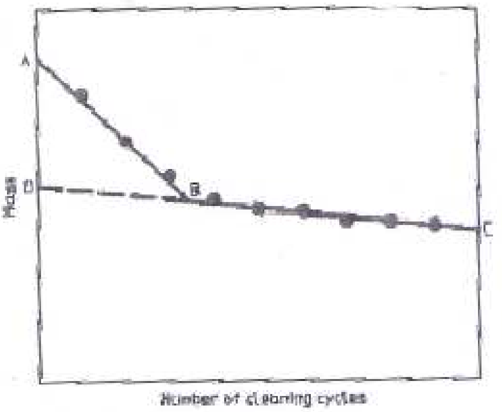


Figure 1 — Mass of corroded specimens after repetitive cleaning cycles

.1.3.3 The true mass of the specimen after removal of the corrosion products will be between oints B and D, depending on the degree of pro-ection furnished by the corrosion products during he cleaning procedure.

.1.4 The preferred cleaning method will be that which

a) provides efficient removal of corrosion products;

b) provides low or zero mass loss when applied to new uncorroded specimens (see 2.1.3.1);

c) provides a curve of mass as a function of the number of cleaning cycles, which is close to horizontal when the latter is plotted as the abscissa (see 2.1.3.2).

2.1.5 When chemical or electrolytic procedures are used, solutions freshly prepared with distilled or deionized water and reagent grade chemicals shall be used.

2.1.6 After cleaning, the metal specimen should be thoroughly rinsed, first with tap water and finally with distilled water. Then the specimen shall be dried in a oven and allowed to cool in a desiccator to the balance room temperature before weighing. An alternative drying procedure is to immerse the metal specimen in an ethanol solution and then dry with an air hand blower.

2.2 Chemical procedure

Chemical procedures involve immersion of the corrosion test specimen in a chemical solution which is specifically designed to remove the corrosion products with minimal dissolution of any base metal. Several procedures are listed in annex A (see table A.1).

2.2.1 Chemical cleaning is often preceded by light brushing of the test specimen to remove lightly adherent, bulky corrosion products.

2.2.2 Intermittent removal of specimens from the chemical solution for light brushing can often facilitate the removal of tightly adherent corrosion products.

2.2.3 Chemical cleaning is often followed by light brushing to remove loose products.

2.3 Electrolytic procedures

Electrolytic cleaning also can be used to remove corrosion products. Several methods of electrolytic cleaning of corrosion test specimens are given in annex A (see table A.2).

Electrolytic cleaning should be preceded by light brushing of the test specimen to remove lightly adherent, bulky corrosion products. Brushing should also follow electrolytic cleaning to remove any loose slime or deposits. This will help to minimize any redeposition of metal from reducible corrosion products, which would reduce the mass loss.

2.4 Mechanical procedures

Mechanical procedures can include scraping, scrubbing, brushing, ultrasonic methods, mechanical shock and impact blasting (grit blasting, water-jet blasting, etc.). These methods are often used to remove heavily encrusted corrosion products. Scrubbing with a bristle brush and a mild abrasive/distilled water slurry can also be used to remove corrosion products.

Vigorous mechanical cleaning will result in the removal of some base metal, so care should be exercised. These methods should be used only when others fail to provide adequate removal of corrosion products. As with the other methods, correction for metal loss due to the cleaning method is recommended. The mechanical forces used in cleaning shall be maintained as nearly constant as possible.

3 Test report

The test report shall include the following information:

a) reference to this International Standard;

b) the procedure used to remove corrosion products;

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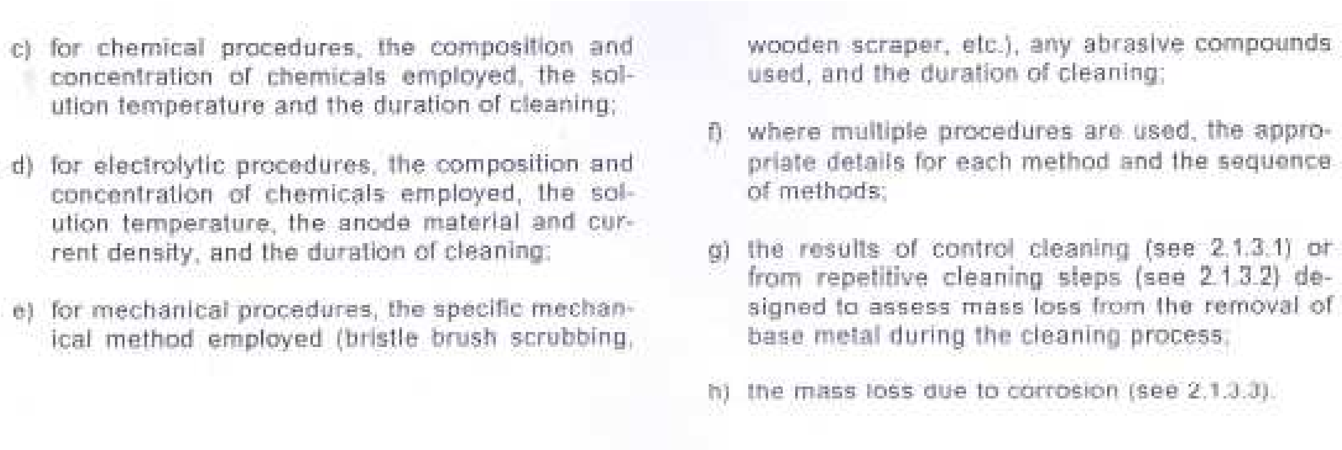

c) for chemical procedures, the composition and concentration of chemicals employed, the solution temperature and the duration of cleaning;

d) for electrolytic procedures, the composition and concentration of chemicals employed, the solution temperature, the anode material and current density, and the duration of cleaning;

e) for mechanical procedures, the specific mechanical method employed (bristle brush scrubbing, wooden scraper, etc.), any abrasive compounds used, and the duration of cleaning;

f) where multiple procedures are used, the appropriate details for each method and the sequence of methods;

g) the results of control cleaning (see 2.1.3.1) or from repetitive cleaning steps (see 2.1.3.2) designed to assess mass loss from the removal of base metal during the cleaning process;

h) the mass loss due to corrosion (see 2.1.3.3).

Appendix E

Macro Program Used to find out the best fit value of Constants

```
Sub looping()
Cells(1, 10) = 1
Cells(4, 10) =1
Cells(1, 11) = .1
Cells(4, 11) = 0.1
Cells(1, 12) = 1
Cells(4, 12) = 1
Cells(1, 13) = 0.1
Cells(4, 13) = 0.1
Cells(4, 14) = 1
Cells(4, 14) = 1
Cells(4, 15) =.1
Cells(4, 15) = .1
Cells(4, 16) = 1
Cells(4, 16) = 1
Cells(4, 17) = .1
Cells(4, 17) = .1
Cells(1, 18) = 0.001
Cells(4, 18) = 0.001
Cells(1, 19) = 1
Cells(4, 19) = 1
Cells(1, 26) = 1
Cells(4, 26) = 1
Cells(1, 27) = .1
Cells(4, 27) = .1
Cells(3, 24) = 1000
For p = 1 To 1000 Step 1
For a = -0.1 To 0.1 Step 0.1
Cells(4, 10) = Cells(4, 10) + a
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 10) = Cells(4, 10)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 10) = Cells(4, 10) - a
Next a
Cells(4, 10) = Cells(1, 10)

For b = -0.1 To 0.1 Step 0.1
Cells(4, 11) = Cells(4, 11) + b
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 11) = Cells(4, 11)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 11) = Cells(4, 11) - b
Next b
Cells(4, 11) = Cells(1, 11)
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Appendix E

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For c = -0.1 To 0.1 Step 0.1
Cells(4, 12) = Cells(4, 12) + c
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 12) = Cells(4, 12)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 12) = Cells(4, 12) - c
Next c
Cells(4, 12) = Cells(1, 12)

For d = -0.1 To 0.1 Step 0.1
Cells(4, 13) = Cells(4, 13) + d
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 13) = Cells(4, 13)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 13) = Cells(4, 13) - d
Next d
Cells(4, 13) = Cells(1, 13)

For e = -5 To 5 Step 5
Cells(4, 14) = Cells(4, 14) + e
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 14) = Cells(4, 14)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 14) = Cells(4, 14) - e
Next e
Cells(4, 14) = Cells(1, 14)

For f = -0.1 To 0.1 Step 0.1
Cells(4, 15) = Cells(4, 15) + f
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 15) = Cells(4, 15)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 15) = Cells(4, 15) - f
Next f
Cells(4, 15) = Cells(1, 15)

For g = -05 To 5 Step 5
Cells(4, 16) = Cells(4, 16) + g
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 16) = Cells(4, 16)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 16) = Cells(4, 16) - g
Next g
Cells(4, 16) = Cells(1, 16)
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Appendix E

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For h = -0.1 To 0.1 Step 0.1
Cells(4, 17) = Cells(4, 17) + h
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 17) = Cells(4, 17)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 17) = Cells(4, 17) - h
Next h
Cells(4, 17) = Cells(1, 17)



For j = -0.1 To 0.1 Step 0.1
Cells(4, 18) = Cells(4, 18) + j
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 18) = Cells(4, 18)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 18) = Cells(4, 18) - j
Next j
Cells(4, 18) = Cells(1, 18)

For t = -0.1 To 0.1 Step 0.1
Cells(4, 19) = Cells(4, 19) + t
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 19) = Cells(4, 19)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 19) = Cells(4, 19) - t
Next t
Cells(4, 19) = Cells(1, 19)

For k = -5 To 5 Step 05
Cells(4, 26) = Cells(4, 26) + k
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 26) = Cells(4, 26)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 26) = Cells(4, 26) - k
Next k
Cells(4, 26) = Cells(1, 26)


For l = -0.1 To 0.1 Step 0.1
Cells(4, 27) = Cells(4, 27) + l
If Cells(5, 24) < Cells(3, 24) Then Cells(1, 27) = Cells(4, 27)
If Cells(5, 24) < Cells(3, 24) Then Cells(3, 24) = Cells(5, 24)
Cells(4, 27) = Cells(4, 27) - l
Next l
Cells(4, 27) = Cells(1, 27)

Next p
End Sub
```