Comprehensive Empirical Equation for Assessing Atmospheric Corrosion Progression of Steel Considering Environmental Parameters

Arjun Sil[†] and Vanapalli Naveen Kumar

Dept of Civil Engineering, NIT Silchar, Assam, India, 788010

Atmospheric corrosion is a natural surface degradation process of metal due to changes in environmental parameters in the surrounding atmosphere. It is very sensitive to environmental parameters such as temperature, relative humidity, sulphur dioxide, and chloride, making it a major global economic challenge. Existing forecasting empirical corrosion models including the ISO standard are based on statistical analysis of experimental studies without considering the behavior of atmospheric parameters. The present study proposes a reliable global empirical model for estimating short and long-term atmospheric corrosion rates based on environmental parameters and corrosion mechanisms obtained from a parametric study. Repercussion of atmospheric corrosion rate due to individual and combined influences of environmental parameters specifies their importance in the estimation. New global empirical coefficients obtained for environmental parameters are statistically established (R^2 =0.998) with 95% confidence limit. They are validated using experimental datasets of existing studies observed at 88 different continental locations. The current proposed model can predict atmospheric corrosion by means of corrosion formation mechanisms influenced by combined effects of environmental parameters, further abating applicability limitations of location and time.

Keywords: Atmospheric corrosion, Empirical model, Corrosion rate, Prediction, Environmental parameters

1. Introduction

Atmospheric corrosion is a spontaneous process of metal degradation due to atmospheric exposure. It is one of the significant problems that widely affects the existing resources and economy. Steel is the pillar of modern civilisation and one of the most consumed metals globally. The annual cost of corrosion is estimated to be 2.5 trillion USD globally, such as 3% of the world's GDP [1] and 3 to 5% GDP of any industrialized country. The economic loss due to corrosion in India is estimated to be around 67 billion USD (4.2 % of GDP) [2]. Atmospheric corrosion studies are essential as per these economic statistics and have a significant role in the development of any region. Experimental studies are conducted across Europe [3,4], Australia [5], America [6], Spain [7], Brazil [8], Vietnam [9] and other countries [10] to develop empirical equations that could estimate atmospheric corrosion. As reported in the literature, very limited studies have been reported in Asia.

However, Corrosion is a chemical process of oxidation and reduction initiated by the standard potential or excess energy available due to the loss of electrons. It is similar to a thermodynamic process that works on the second law of thermodynamics and could be assessed under Faraday's law as in equations (1) and (2)

$$C_r = \frac{\triangle M}{\gamma.A.t} \tag{1}$$

$$\triangle M = \frac{Q}{F}\,\frac{M_w}{Z} \tag{2}$$

Where C_r (mm/y) is a corrosion rate, ΔM (g) is a metal loss, γ (mg/m^3) is metal density, A is exposed area (mm^2), t is exposed time, Q (c) is an electric charge, M_w (g)is molecular weight, Z is valence and F is a Faraday constant.

Furthermore, a proposed power-law function (3) holds suitable for corrosion kinetics [11] and is used to track atmospheric corrosion over time [12,13].

$M = At^B$ could be written in logarithmic as
$$log\,M = log\,A + B\,log\,t \tag{3}$$

[†]Corresponding author: silarjun@gmail.com

Where M (μm) is metal loss, t is the exposure time in years, A and B are constants.

The atmosphere surrounding the metal directly influences the process of corrosion. The studies of E. A. Tice [14] stated that the influence of sulfur dioxide (SO_2) on atmospheric corrosion is higher as it initiates corrosion in low humid environments and further increases the rate of corrosion. Similarly, several other studies [3,4,7,15,16] identified temperature (T), relative humidity (RH), sulphur dioxide (SO_2) and chloride (Cl⁻) as the most influential parameters of atmospheric corrosion. Many researchers have developed empiric models to describe and estimate atmospheric corrosion using specified environmental parameters. However, these empirical models have used environmental and corrosion loss data obtained from experimental studies [12,17-20] to statistically develop equations that estimate atmospheric corrosion.

Further, the international standard ISO 9223 [21] suggested an equation (4) for predicting atmospheric corrosion. ISO classifies atmospheric corrosion and environmental parameters based on their corrosion and deposition rates, respectively. These parameters vary widely based on the different locations categorized as rural, urban, marine and industrial regions. On the other hand, ISO expression is treated as a standard equation for estimating atmospheric corrosion regardless of location, but a significant difference between the observed experimental values and the estimated ISO values is observed in this study. In addition to RH and T another ISO parameter, time of wetness (TOW) defined as duration with RH and temperature greater than 80 percent and 0°c is used in a number of studies.

$$r_{corr} = 1.77 p_d^{0.52} exp\left(0.02RH + f_{st}\right) \cdot \\ + 0.102 s_d^{0.62} exp(0.033RH + 0.04T) \tag{4}$$

$$f_{st} = 0.15(T-10) \, when \, T \leq 10^o c, -0.054(T-10) \, otherwise$$

Where r_{corr} (μm/y) is the rate of corrosion, p_d is the sulphur dioxide in milligram/square decimeter/day (mdd), s_d is a chloride (mdd), T (°C) is the temperature, RH, and f_{st} is a factor for temperature. However, the ISO equation also works on the basic principle of the power-law function and is based on the regression of one-year experimental data.

Apart from ISO, extensive experimental programs ISOCORRAG [22] and MICAT [23] have statistically developed empirical equations using experimental data. Although these studies cover most of the environmental conditions prevailing in different continental locations, the empirical equations still have limitations as the under-

lying corrosion phenomena are not considered. The ISOCORRAG program exposed two types of specimens (flat and helix) at 53 locations in 13 countries for one, two, four and eight years. One-year experimental data is used to develop a dose-response function (5) and the study also attempted to improve the ISO classification system. Despite experiments in 13 countries, environmental data at test sites do not cover all standard ISO categories.

$$c_{st} = 0.085 so_2^{0.56} TOW^{0.53} exp\left(f_{st}\right) \\ + 0.24 Cl^{0.47} TOW^{0.25} exp\left(0.049T\right) \tag{5}$$

$$f_{st} = 0.098(T-10) \, when \, T \leq 10℃, \, -0.087(T-10) \, otherwise$$

Where c_{st} (μm/y) is corrosion rate, SO_2 (μg/m³) is sulphur dioxide, Cl (mdd) is the chloride, TOW, T (°C) is temperature, and f_{st} is a function for temperature. Although the above dose-response function has been developed using experimental data, higher values are estimated than those observed when used at different locations.

Further, another equation (6) [24] estimates atmospheric corrosion considering 100% RH. This study believes that dew induces corrosion at 100% RH and that other parameters help to accelerate the corrosion process.

$$c_r = K\left(100 + Cl + SO_2\right) 2^{\frac{T-25}{25}} \tag{6}$$

Where c_r (μm/y) is a corrosion rate, K is constant for material, Cl (μg/m³) is chloride, SO_2 (μg/m³) is sulphur dioxide, and T (°C) is temperature. The study claims that equation (6) estimates at par with ISO 9223 nevertheless found that, due to its RH presumption, it estimates approximately nine times more than ISO but follows its trend.

Further, many international agencies and individual researchers conducted experimental studies at different locations to develop a standard empirical equation. Also, a group of Japanese scientists [25], in association with the other organizations conducted experiments at 43 locations across Japan for one-year and developed equations by regression analysis of experimental data. Two different equations are suggested, one for inland as well as industrial atmospheres (7a) and the other for marine atmospheres (7b)

$$C_{ri} = 4.15 + 0.88T - 0.073RH - 0.032RF \\ + (2.913*10^{-6})Cl^- + 4.921SO_2 \tag{7a}$$

$$C_{rm} = 5.61 + (2.754*10^{-6})Cl^- + 6.155SO_2 \tag{7b}$$

Where C_{ri}, C_{rm} (mdd) are corrosion rates, T (^{o}c) is temperature, RH, RF (mm/month) is rainfall, Cl$^-$ (mdd) is chlorine and SO$_2$ (mdd) is the sulphur content. Since the two equations have been developed on the basis of the concentration of environmental parameters over a relatively short period of time, the corrosion rate estimated with this equation is significantly different from that of the ISO. The equation for marine locations predicts better than the equation for inland and industrial locations and is closer to ISO.

Further, the International Cooperative Program (ICP) developed a dose-response function (DRF) (8) for metal loss [26,27]. This experimental program has been carried out for eight years at 36 locations in 12 European countries. These DRFs have been developed for atmospheric corrosion with a focus on the effect of air pollutants, specifically SO$_2$. This study does not consider the effect of chloride content and depends solely on SO$_2$, but predicts small variations in line with ISO.

$$Ml = 34SO_2^{0.33} \times exp\{0.02RH + f_{ws}(T)\}t^{0.33} \qquad (8)$$

$$f_{ws} = 0.083(T-10) \, when \, T \leq 10°C, \, -0.032(T-10) \, otherwise$$

Where Ml (g/m^2) is the metal loss, RH, f_{ws} (T) is a function for temperature and t (years) is exposure time.

Apart from fitting the experimental data as in the various studies, another empirical model [28] suggested adjustment factors for environmental parameters considering various environmental conditions and their effects on the parameters using ISOCORRAG data. Since the source data itself has its limitations, the proposed equation (9) does not estimate at par with the observed experimental values.

$$y = At^B \left(\frac{TOW}{C}\right)^D \left(1 + \frac{SO_2}{E}\right)^F \left(1 + \frac{Cl}{G}\right)^H e^{J(T+T_o)} \qquad (9)$$

Where y (μm) is a metal loss, t (y) is the time of exposure, TOW (h/y), SO$_2$ (μg/m^3) is sulphur dioxide, Cl (mdd) is chloride, T ($^{\circ}$C) is temperature and A, B, C, D, E, F, J, T$_o$ are the empirical constants. An empiric expression (10) for estimating atmospheric corrosion was developed in another experimental study conducted over five years in Vietnam [29] at five different locations. This equation is sensitive to sulfur dioxide because its effect in the equation is insignificant due to its lower intensity at the test locations.

$$K_{corr} = -8.78T + 5.25RH + 0.0081TOW + 0.77Cl - 10.228 \qquad (10)$$

Where K$_{corr}$ (g/m^{2}y) is corrosion, T ($^{\circ}$C) is temperature, RH (%), TOW (h/y), and Cl (mdd) is the chloride content. Due to the mildness of the environmental parameters at the test sites, this expression (10) has a limited scope and

Table 1 Compiled existing equations extracted from the literature

Author	Reference	Equation	Equation No
ISO 9223	(ISO 2012)	$r_{corr} = (1.77 * p_d^{0.52} * exp(0.02 * RH + f_{st})) + (0.102 * s_d^{0.62} * exp(0.033 * RH + 0.04 * T))$	4
ISO CORRAG	(ISOCORRAG Int. Atmos. Expo. Progr. Summ. Results 2011)	$c_{st} = (0.085 * so_2^{0.56} * TOW^{0.53} * exp(f_{st})) + (0.24 * cl^{0.47} * TOW^{0.25} * exp(0.049T))$	5
L Lazzari	(Lazzari 2017)	$c_r = K * (100 + cl + so_2) * (2^{\frac{T-25}{25}})$	6
Kenkyu Kai	(Uhlig's Corros. Handb. 2011)	$c_{ri} = 4.15 + (0.88 * T) - (0.073 * RH) - (0.032 * RF) + ((2.913 * 10^{-6}) * cl^-) + (4.921 * so_2)$	7
Kucera V	(Kucera et al. 2001, 2007)	$c_{rm} = 5.61 + ((2.754 * 10^{-6}) * cl^-) + (6.155 * so_2)$	8
Klinesmith D	(Klinesmith et al. 2007)	$Ml = 34 * so_2^{0.33} * (exp\{0.02 * RH + f_{ws}(T)\}) * t^{0.33}$	9
Le Thi Hong Lien	(Townsend 2009)	$y = At^B \left(\frac{TOW}{C}\right)^D \left(1 + \frac{so_2}{E}\right)^F \left(1 + \frac{cl}{G}\right)^H e^{J(T+T_o)}$	10

[Note: r_{corr}, c_{st}, c_r, c_{ri}, c_{rm}, K_{corr} = rate of corrosion, p_d = sulphur dioxide, s_d = chloride, T = temperature, RH = relative humidity, f_{st} = function for temperature, TOW = time of wetness, SO$_2$ =sulphur dioxide, Cl= chloride, K =constant for material =1, RF = rainfall, Ml= metal loss, f_{ws} (T)= function for temperature, A=13.4, B=0.98, C=3800, D=0.46, E=25, F=0.62, G=50, H=0.34, J=0.016, T$_o$=20 are empirical constant values for the present study, conversion factors for mdd and g/m^{2}y to μm/y are 4.572 and 0.125 repsectively]

often overestimates the corrosion rate compared to the ISO. Table 1 summarizes all of the equations suggested in the previous studies considered for this study.

It is apparent from the literature that these existing equations were framed solely on the basis of the regression analysis of the experimental data, without any concern for the characteristics of the environmental parameters and the corrosion phenomenon. These experimental datasets are also limited to local environmental conditions in their respective regions and do not cover all regular scenarios. Thus, these equations do not even estimate at the same level as ISO 9223 equation, since they do not imbibe the corrosion mechanism.

Corrosion rate and process are governed by the individual and combined effects of environmental parameters rather than their intensity. In order to estimate accurate corrosion rates, these individual and combined influences must be understood as per corrosion phenomena. There is a primary need to develop a comprehensive equation that estimates reliable corrosion rate for any continental locations based on actual parametric influences. In the present study, an attempt was made to develop and propose a global empiric equation to estimate the atmospheric corrosion of carbon steel, which accepts the sensitivity of environmental parameters and satisfies the basic corrosion phenomenon.

2. Parameters Characteristics Influencing Corrosion Rate

Dew formed by condensed water on the metal surface acts as a thin electrolyte film and provides ample oxides to corrode the metal. Dew is formed by four mechanisms on metal surface, such as when the temperature is lower than the ambient temperature, due to the adsorption between the metal surface and the water molecules, due to the hygroscopic effects of the salts (chlorides) and the effect of the sulphite formed patinas. The mechanisms and chemical process for corrosion initiation imply the impact of environmental parameters such as temperature, RH, chlorides and sulphur dioxides on atmospheric corrosion. Therefore these parameters are considered as the prime parameters for the present study.

The intensity of the environmental parameters is largely affected by the geographical location and seasons of a year. However, each factor has its own impact on the rate of atmospheric corrosion. Furthermore, the various equations available in the literature are most suitable only for prediction at that particular experimental location. Indeed, in all equations, environmental parameters are neither given the same importance nor exhibit similar behavior. As

all the equations mentioned in Table 1 are derived from experimental studies, the individual and combined influences of the environmental parameters on atmospheric corrosion are naturally assimilated. These partially rooted environmental parameters influences on atmospheric corrosion in all equations are shown in Figs 1, 2, 3 and 4 by varying parametric values within ISO ranges at similar intervals. The range of environmental parameters considered for this study is shown in Table 2. Since it is almost not viable to convert TOW to RH, instead of 80% of RH, 2500 h/y of TOW is considered in equations (5), (9) and (10), and the increments to it are applied as of for RH. Further, the RF in equation (7) is an additional factor and is made constant for the analysis.

2.1 Effect of RH on Atmospheric Corrosion

The natural electrochemical corrosion process takes place in the presence of an electrolyte film. ISO 9223 expresses the sustained duration of electrolyte film with a RH of more than 80% and a temperature not less than 0 °C as TOW. However, TOW itself implies that RH is the fundamental parameter responsible for the formation and sustenance of the electrolyte film. Also low RH may not initiate corrosion but may cause hygroscpic corrosion or capillary condensation in the existing process. Therefore, RH is considered instead of TOW [30] for the present study. The appropriate ISO range of 80% - 100% of RH [31] is varied to plot Fig. 1 in order to observe the trend of equations with a change in RH.

With an increase in RH at a constant temperature, the rate of corrosion increases, indeed, an increase in the rate of corrosion could be observed in all equations except equation (7a). However, the initial estimation of equations (6) and (7a) is unreliably higher than all other equations, and there is a prolonged increase in equations (5), (9) and (10) with an increase in RH and nowhere near ISO. As shown in Fig. 1, it can be noted that only equation (8) predicts along with the ISO equation (4) and accepts the influence of RH.

2.2 Temperature effect on Atmospheric Corrosion

Generally, with an increase in temperature, the rate of electrochemical reaction and diffusion process increases on a condition forming electrolyte film, which increases the corrosion rate [32]. However, temperature has an intricate effect [33] on atmospheric corrosion and may not have individual effect, because its effect is interrelated with RH. Indeed, temperature and relative humidity combinations have three important conditions with different effects on atmospheric corrosion based on electrolyte film, such as constant temperature with increasing
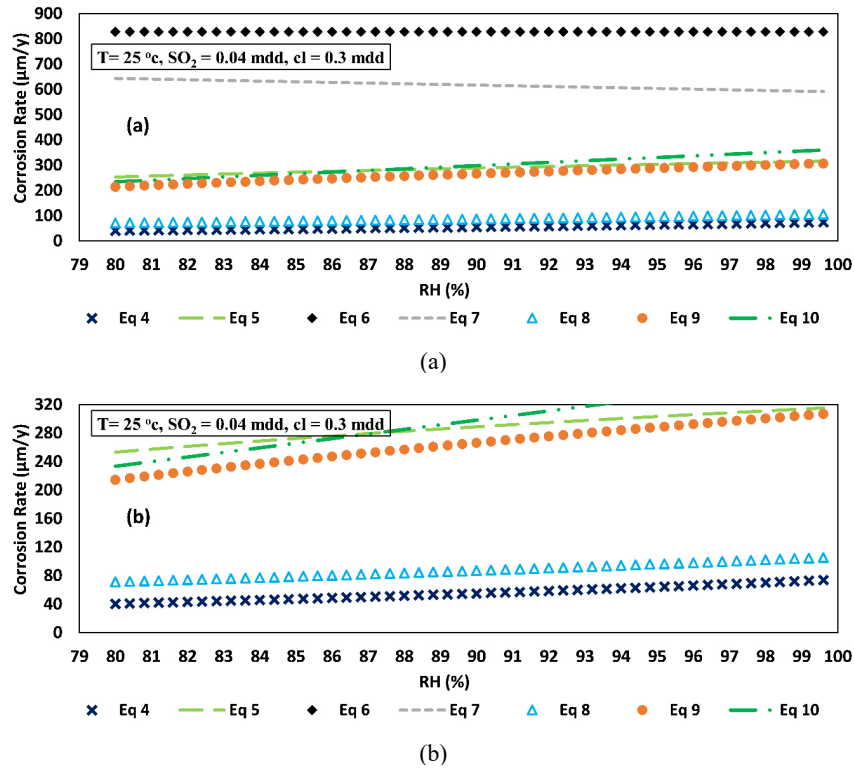
(a)

(b)

Fig. 1 (a) Effect of RH variance on corrosion rate in all existing equations mentioned in Table 1, (b) enlarged view of Figure 1 (a) for equations 4, 5, 8, 9.
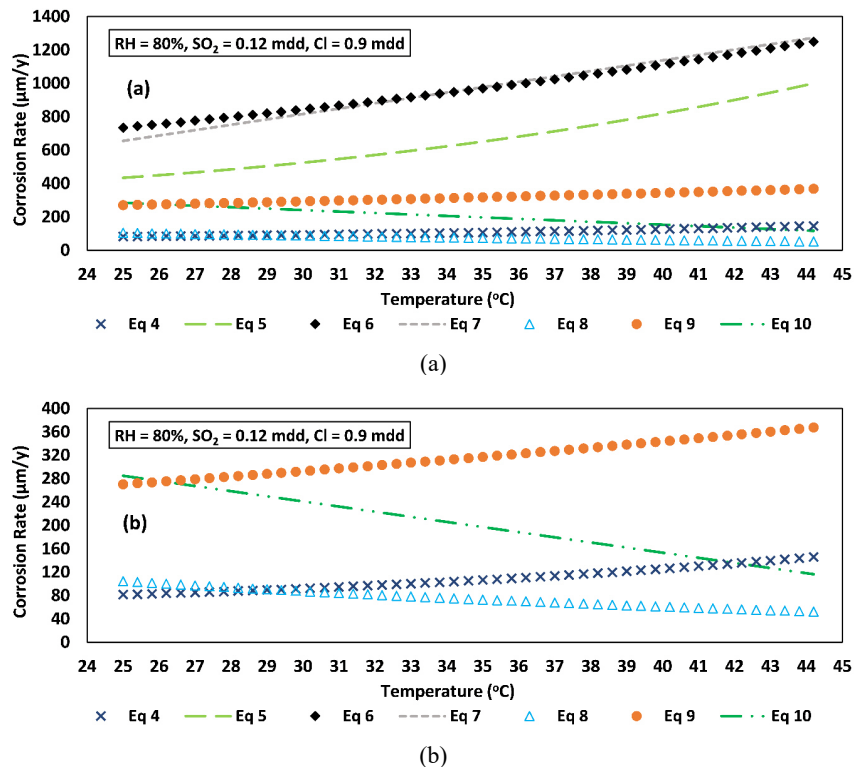

(a)

(b)

Fig. 2 (a) Effect of Temperature variance on corrosion rate in all existing equations mentioned in Table 1, (b) enlarged view of Figure 2 (a) for equations 4, 8, 9, 10.
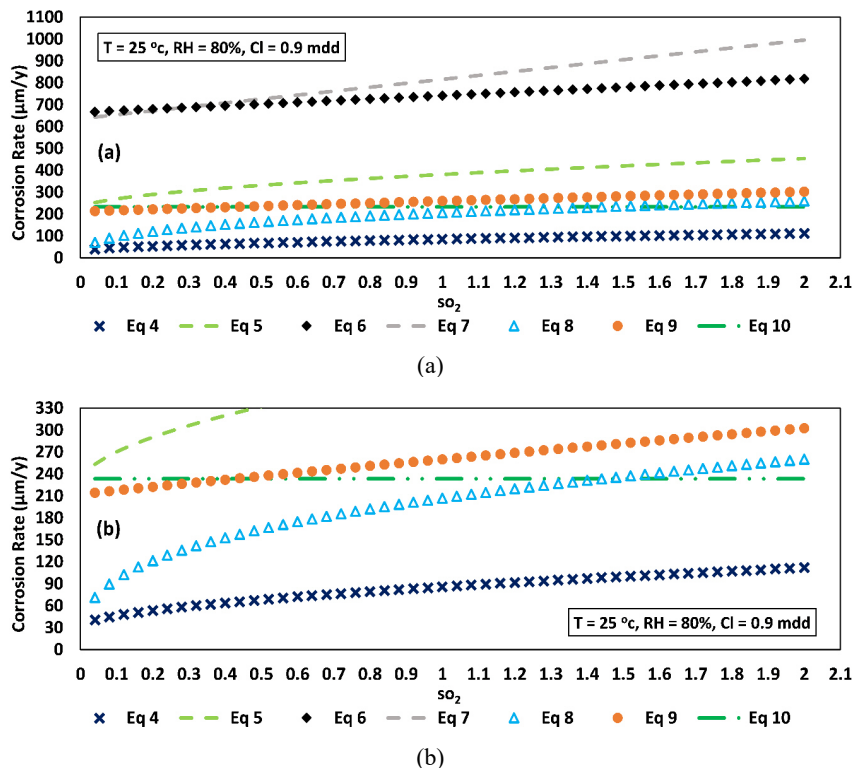
(a)

(b)

Fig. 3 (a) Effect of SO₂ variance on corrosion rate in all existing equations mentioned in Table 1, (b) enlarged view of Figure 3 (a) for equations 4, 8, 9, 10.
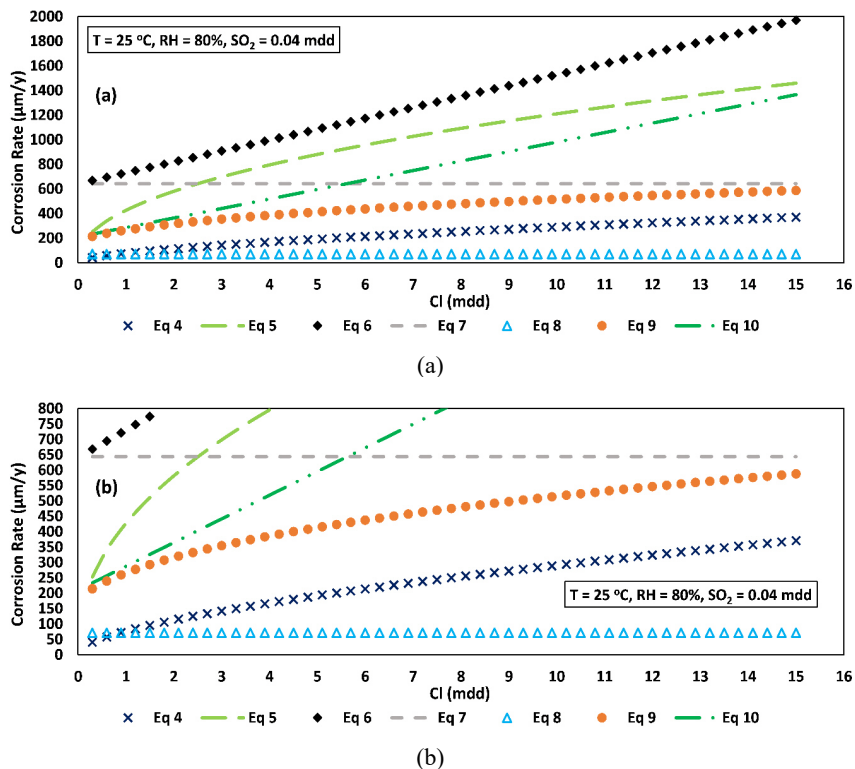

(a)

(b)

Fig. 4 (a) Effect of Cl variance on corrosion rate in all existing equations mentioned in Table 1, (b) enlarged view of Figure 4 (a) for equations 4, 7, 8, 9, 10.

Table 2 Environmental parameters range considered for analysis

S.No.	Environmental Parameter	ISO Range
1	Temperature (T in °C)	25 – 45
2	Relative Humidity (RH in %)	80 – 100
3	Sulphur Dioxide (SO_2 in mdd)	0.04 – 2
4	Chloride (Cl^- in mdd)	0.3 – 15

RH accelerates corrosion rate, increasing temperature with constant RH exhibits a steady shift in the increase in corrosion rate and increasing temperature with reducing RH has a decelerating effect on the increase in rate of corrosion (Table 3). Further, to investigate temperature mechanisms of all equations, Fig. 2 is plotted by varying temperature from 25 °C to 45 °C, keeping with all other parameters constant.

If the temperature rises with constant RH, there would be a steady increase in the corrosion rate. However, equations (5), (6) and (7a) show a high increase in corrosion rate with higher initial predictions, and equations (8) and (10) show a substantial decrease in corrosion rate against phenomena and equations (4) and (9) show a steady increase in corrosion rate as per fundamental phenomena. It should be noted that no equation accepts the basic temperature mechanism and does not estimate at the same level as the ISO equation (4).

2.3 Effect of Sulphur Dioxide on Atmospheric Corrosion

Sulphur dioxide is an accelerating factor for atmospheric corrosion, as it acts as a catalyst for the electrochemical corrosion process. Sulphate ions are formed by oxidation of sulphur dioxide with available oxygen and by electrons released from the anodic process. These sulphate ions act as an autocatalyst to react with iron to form iron sulphate and increase the rate of corrosion. Electrolyte film is acidified by iron sulphate, which further accelerates the corrosion process. As a whole, the sulphur dioxide could be considered as a catalyst for the corrosion process [34,35].

However, Fig. 3 shows the sensitivity of all equations to the behavior of SO_2. As shown in Fig. 3, with an increase in sulphur dioxide, the equations (4), (6) and (9) show a controlled increase from their initial corrosion rate. However, equations (5) and (7a) have a significant increase in the the corrosion rate compared to the others. In equation (10), a downward shift in the corrosion rate with an increase in SO_2 is observed. However, equation (8) has an accelerated increase in the corrosion rate and it could be specified that it partially exhibits a corrosion mechanism. It could be noted that only equation (8) estimates are closer to the ISO and partially accepts the mechanism.

2.4 Effect of Chloride on Atmospheric Corrosion

Atmospheric salinity enhances the formation of surface electrolyte at low RH and does not form a stable bond with ferrous metal. Chloride reacts with hydrogen ions to form HCl and HCl reacts with mild steel to form $FeCl_2$, which is repeated as a cycle resulting in continuous electrochemical corrosion. Sulfur dioxide with chloride has a synergistic effect on the rate of corrosion [36] and a dissimilar effect with a change in temperature and concentration of chloride could also be observed. However, in all the other cases, Fig. 4 is plotted exhibiting increasing chloride, Fig. 4 shows an increase in all equations except for equations (7a) and (8), and no equations are estimated at the same level as ISO equation (4).

As a summary of existing equations sensitivity to environmental parameters, it is observed that no equation stratifies all corrosion mechanisms and is insensitive to at least one environmental parameter. Equations (6) and (7a) initially estimate the unreliable high corrosion rate regardless of the parameters, whereas equations (5) and (9) follow almost the same rate trend for all scenarios. However, equations (4) and (10) do not account for variations in RH and temperature, respectively. Equations (5) and (8) have unrealistic variations with changes in chloride and sulfur dioxide. It should be noted that no equation

Table 3 Summary for the influence of environmental parameters on atmospheric corrosion

Case No.	Temperature	Relative Humidity	Sulphur Dioxide	Chloride	Atmospheric Corrosion trend
1	Minimum	VMH	Minimum	Minimum	Significant Increase
2	VMH	Minimum	Medium	Medium	Increase
3	High	VMH	Medium	Medium	Slow Progress
4	Medium	Medium	VMH	Medium	Increase
5	Medium	Medium	Medium	VMH	Increase

Note: VMH-varying min to high

Table 4 Codes for respective test sites/locations found from ISOCORRAG (2011) and Fernández-Pérez et al. (2015) data

S. No	Location	Code	S.No	Location	Code
1	Meteorológico	C1	45	Bergisch Gladbach	D 1
2	Policía S/C Tenerife	C2	46	Helsinki	SF 1
3	Oceanográfico	C3	47	Otaniemi	SF 2
4	Ofra	C4	48	Ahtari	SF 3
5	Facultad de Química	C5	49	Saint Denis	F 1
6	Pajalillos	C6	50	Ponteau Martigues	F 2
7	Isamar	C7	51	Picherande	F 3
8	Garimba	C8	52	Saint Remy, Ies Landes	F 4
9	Ayto. Puerto Cruz	C9	53	Salins de Giraud	F 5
10	Botánico	C10	54	Ostende, Belgium	F 6
11	Montañeta	C11	55	Paris	F 7
12	Buenavista	C12	56	Auby	F 8
13	El Palmar	C13	57	Biarritz	F 9
14	Las Raíces	C14	58	Choshi	JAP 1
15	Izaña	C15	59	Tokyo	JAP 2
16	Unelco Caletillas	C16	60	Okinawa	JAP 3
17	La Planta	C17	61	Judgeford, Wellington	NZ 1
18	La Oficina	C18	62	Oslo	N 1
19	El Bueno	C19	63	Borregaard	N 2
20	Unelco Granadilla	C20	64	Birkenes	N 3
21	Los Cristianos	C21	65	Tannanger	N 4
22	Vilaflor	C22	66	Bergen	N 5
23	Cueva del Polvo	C23	67	Svanwik	N 6
24	Guía de Isora	C24	68	Madrid	E 1
25	San Sebastián	C25	69	El Pardo	E 2
26	Valle Gran Rey	C26	70	Lagoas – Vigo	E 3
27	El Cedro	C27	71	Baracaldo, Vizcaya	E 4
28	Valverde	C28	72	Stockholm Vanadis	S 1
29	Aeropuerto de El Hierro	C29	73	Bohus Malmon, Kattesand	S 2
30	Aeropuerto de La Palma	C30	74	Bohus Malmon, Kvarnvik	S 3
31	El Paso	C31	75	Stratford, East London	UK 1
32	Puerto Naos	C32	76	Crowthorne, Berkshire	UK 2
33	Los Llanos	C33	77	Rye, East Sussex	UK 3
34	Fuencaliente	C34	78	Fleet Hall	UK 4
35	San Andrés y Sauces	C35	79	Kure Beach, N. Carolina (N.C)	US 1
36	Iguazu	ARG 1	80	Newark–Kerney, New Jersey	US 2
37	Camet	ARG 2	81	Panama Fort Sherman Costal s	US 3
38	Buenos Aires	ARG 3	82	Research Triangle Park, N.C	US 4
39	San Juan	ARG 4	83	Point Reyes, California	US 5
40	Yubany Base	ARG 5	84	Los Angeles, California	US 6
41	Boucherville	CND 1	85	Murmansk	SU 1
42	Kašperske Hory	CS 1	86	Batumi	SU 2
43	Praha- Bečchovice	CS 2	87	Vladivostok	SU 3
44	Kopisty	CS 3	88	Oymyakon	SU 4

estimates at the same level as the ISO equation (4), although equation (8) estimates are close to ISO, it does not accept the influence of sulfur dioxide and chloride on atmospheric corrosion.

It could be affirmed that no equation satisfies all the underlying basic corrosion mechanisms and their trends also deviate from the ISO equation, even though they are developed using experimental data. These scenarios of existing equations justify the need to develop a new empirical atmospheric corrosion model that is realistically good for all corrosion mechanisms and could be used to estimate atmospheric corrosion regardless of location.

The sophisticated individual and combined effects on the rate of atmospheric corrosion due to variability in environmental parameters are qualitatively formulated in Table 3 on the basis of parametric analysis. Case numbers 4 and 5 in Table 3 are applicable in combination with cases 1 to 3. The observations made (Table 3) on environmental parametric variations in the present study are incorporated reliably by statistical regression analysis for the development of empirical equations, and the accuracy of the developed equation is compared with the experimental studies ISOCORRAG [22] and Fernández-Pérez [37]. The test locations of the two studies are assigned shortcodes in Table 4 to identify the locations while shown in the figures. In fact, the first 35 entries in Table 4 with the prefix 'C' are from Fernández-Pérez, and the remaining ones are from ISOCORRAG with the prefix named after test countries.

3. Statistical Evaluation

Statistical analysis is a mathematical process that helps to extract the hidden reasons, relationships, configurations and trends of the dataset used for further simulation [38] with reliability. Two methods of statistical analysis are available, such as descriptive statistics and inferential statistics. Descriptive statistics are used to draw the correlations from the empirical coefficients of the different equations used to understand the relationship between the individual parameters and the dependency of the corrosion rate on each parameter. Further, an averaging technique for obtaining the atmospheric corrosiosn data is used in the statistical evaluation. The ISO standard categories of environmental parameters with certain suitable intervals are used as input sample data for statistical analysis to obtain the proposed equation with acceptable R^2.

3.1 Non-linear Regression and Sensitivity Analysis

Multiple regression analysis is the most reliable descriptive statistics for developing an equation that provides the best relationship between a dependent variable and multiple independent variables [39]. Statistical multiple regression analysis is used to investigate the individual and combined influence of each independent variable on the dependent variable. However, the correlations obtained from the analysis applicable to various continental locations are used to obtain the proposed equation with 95% confidence limit, including upper and lower confidence limits (UCL and LCL at 5% significant level). The general equation using multiple regressions considered when two independent variables X_1 and X_2 are used to predict a dependent variable Y that could be expressed as:

$$Y = a + b_1 X_1 + b_2 X_2 \tag{11}$$

Multiple regression analysis ascertains the discrete values of a, b_1 and b_2 that provides the most accurate prediction and could be treated as a slope constant and standardized values of X_1 and X_2, respectively.

3.2 Residual (ε_i)

Residual is defined as the difference between the predicted and observed values of the dependent variable. If predicted and observed values are y_i^* and y_i respectively then residual ε_i becomes

$$\varepsilon_i = y_i - y_i^* \tag{12}$$

Multiple regression correlation coefficient (R^2): coefficient of multiple regression or determination is a response variable that varies with the fitted regression line and could be expressed as

$$R^2 = \frac{\sum_{i=1}^{n} \left(y_i^* - y \right)^2}{\sum_{i=1}^{n} \left(y_i - y \right)^2} \tag{13}$$

Where y is the average of the observed value y_i. The fitness is related to the correlation coefficient R^2 from 0 to 1 , the higher the value, the better the fit.

3.3 Summary of Statistical Analysis

The atmospheric corrosion data used for statistical analysis was derived from the previous equations (Table 1) by adjusting the environmental parameters within the ISO ranges. Correlation factors derived from the regression analysis presented in Table 5 are used to provide an empiric equation for predicting atmospheric corrosion of steel elements.

Table 5 Coefficients of the proposed empirical equation with a 95% confidence limit (R^2 = 0.99877)

Coefficients	Mean value	Error	LCL[*]	UCL[*]
X_1	-283.07834	1.72017	-286.37834	-279.77834
X_2	2.11513	0.02116	1.70173	2.52853
X_3	2.90685	0.02116	2.49345	3.32025
X_4	33.77407	0.21155	33.36067	34.18747
X_5	52.43965	0.02821	52.38453	52.49477

*LCL-lower confidence limit, *UCL-Upper confidence limits

$$C_r = X_1 + (X_2 T) + (X_3 RH) + (X_4 SO_2) + (X_5 Cl) \qquad (14)$$

Long-term corrosion $\quad C_{rt} = \dfrac{C_r}{2LN(t^{1.3})} \qquad (15)$

Where C_r (short-term corrosion rate) and C_{rt} (long-term corrosion rate) (µm/y), X_1, X_2, X_3, X_4 & X_5 are empirical coefficients, T is the temperature in °C, RH in %, SO_2 is sulphur dioxide in mdd, Cl is the chloride content in mdd and t is the time of exposure in years. The proposed empirical equation fits well with R^2=0.998. The fitness of the proposed empirical equation is discussed in the results and discussions. Equation (14) is a one-year estimate of short-term atmospheric corrosion and equation (15) is a more than one-year estimate of long-term corrosion.

4. Results and Discussions

A comprehensive empirical equation is proposed to estimate the atmospheric corrosion rate of structural steel based on environmental parameters. All of the existing equations that estimate the atmospheric corrosion rate were essentially limited by different factors. Nevertheless, the majority of available equations are obtained for specific regional or local atmospheric conditions that are not appropriate for other continental locations, and the trends of these equations differ from those of the ISO equations. In order to obtain a reliable global equation for estimating the initial corrosion rate and long-term corrosion rate, a detailed statistical analysis discussed above is carried out by assimilating both the corrosion mechanisms and the effects of the environmental parameters set out in Table 3.

As a result of the regression analysis, the proposed empirical model predicts atmospheric corrosion with a 95 % confidence limit and 0.998 R^2 value. However, Fig. 5 shows the difference (residual) between the predicted and the observed value of each environmental parameter, in the simple sense, the fitness with variation in the in-

dependent variable. The Fig. 5a shows a good fit pattern between the residual and temperature, indeed, the accurate prediction is found at an interval of 30 °C to 40 °C and most accurately at 35 °C. Fig. 5b shows variations between residual and HR, providing a good prediction at about 90% RH. Fig.s 5c and d show the variations of SO_2 and Cl with their residuals, respectively. Indeed, SO_2 becomes the key parameter predicting a higher corrosion rate. However, chloride provides correct predictive weights. All parameters give their intermediate ranges a good fit.

The experimental data available from ISOCORRAG [22] and Fernández-Pérez [37] are used to validate the proposed global empirical equation at the different continental locations referred to in Table 4. However, only the locations of the experimental sites of the two data sets and the respective codes assigned to them are shown in Table 4. Various ranges of environmental parameters have been covered, as the data sets of these studies are from different locations around the globe. These dynamic data sets are used to estimate the corrosion rate with the proposed equation and ISO 9223 equation and then to compare the estimated corrosion rate with the measured rate. These estimated and observed values for ISOCORRAG and Fernández-Pérez are shown in Fig.s 6 and 7. It has been observed that ISO 9223 overestimates the corrosion rate as compared to the observed / experimental values, but the proposed empiric equation have closely predicted in all continental locations. Fig.s 6 and 7 show that the proposed empirical equation estimates atmospheric corrosion at 99% accuracy at all 88 continental sites.

Since all the existing equations are not suitable for global prediction, a comparison between the proposed equation and ISO equation is carried out to expose the demerits of ISO 9223 according to the corrosion mechanism. Fig.s 8a and 8b show the sensitivity of the models to RH variation, considering higher and lower temperature, sulphur dioxide and chloride values. As per the corrosion mechanism, the electrolyte film evaporates quickly at higher temperatures and decelerates the corrosion process, re-
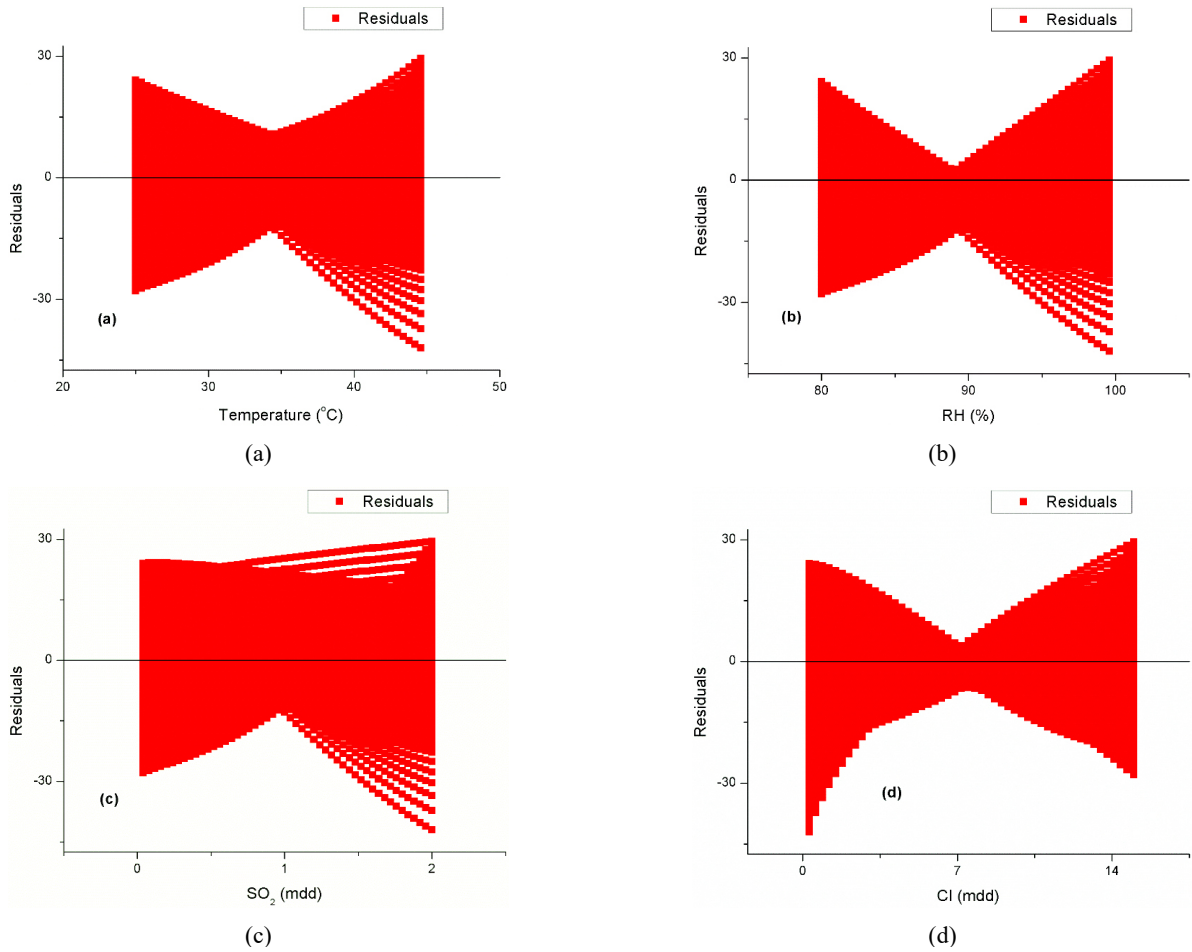
(a)

(b)

(c)

(d)

Fig. 5 Residuals vs independent variable characteristics of environmental factors (a) Temperature, (b) RH, (c) SO₂ and (d) Cl.
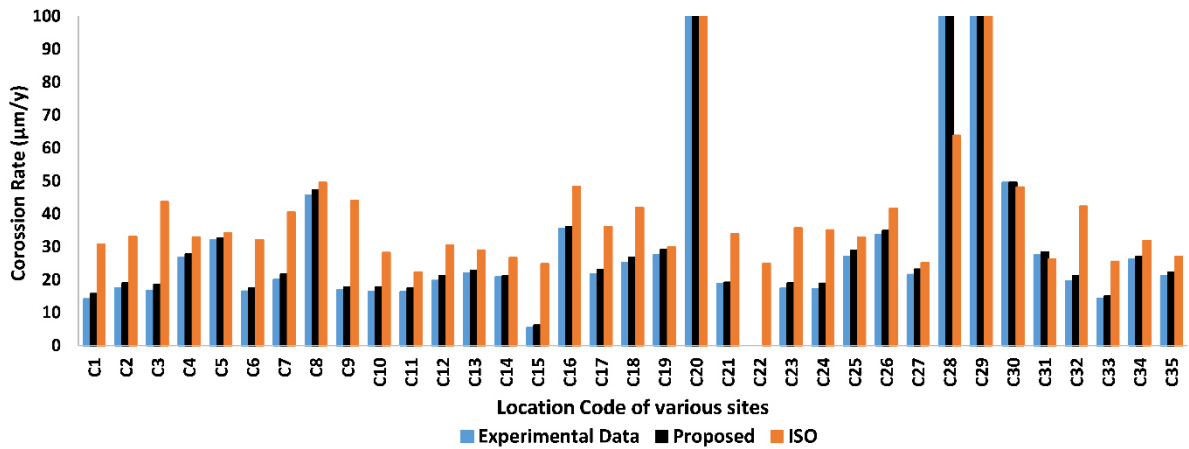

Fig. 6 Estimated corrosion rate using the proposed model and ISO for B M F Perez et al. (2015) data.

ducing the rate of increase in corrosion loss (slow upper shift) even though the other parameters are high, whereas in the other case corrosion rate increases while the temperature and other parameters are low. It could be observed

from Fig. 8a that at a low temperature, the rate of increase in corrosion loss is almost the same for both the proposed and the ISO models. However, at high temperatures, the proposed equation initially estimated a high corrosion rate,
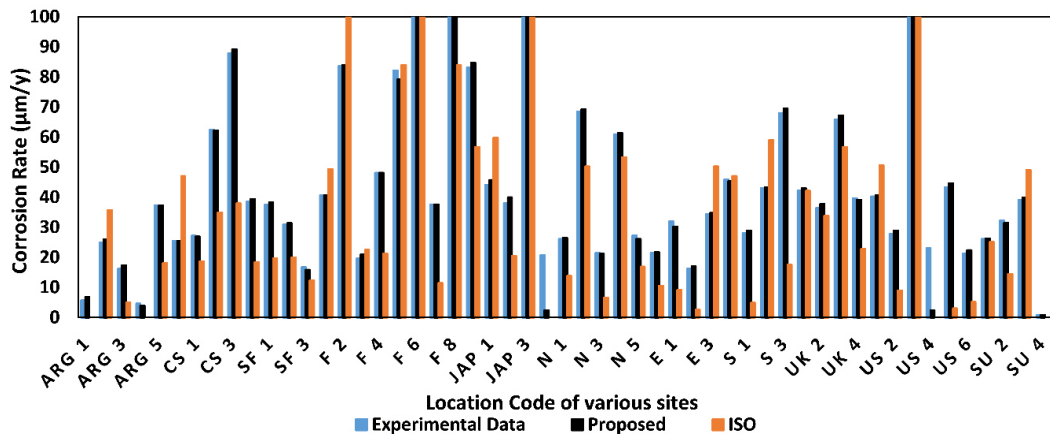
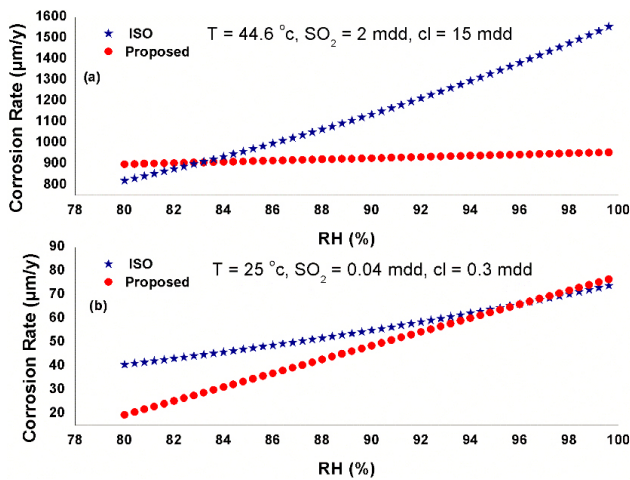**Fig. 7 Estimated corrosion rate using the proposed model and ISO for ISOCORRAG (2011) data.**

Fig. 8 Non-linearity of the Proposed model and ISO for varying Relative Humidity (%) (a) T = 44.6 oC, SO₂ = 2 mdd & Cl = 15 mdd (b) T = 25 °C, SO₂ = 0.04 mdd & Cl = 0.3 mdd
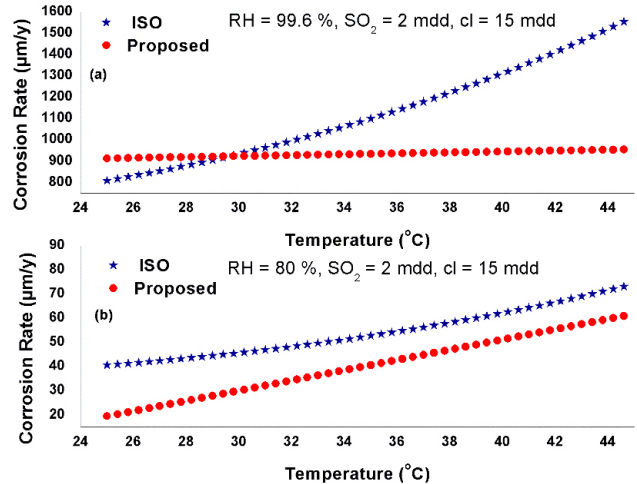
Fig. 9 Non-linearity of the Proposed model and ISO for varying Temperature (°C) (a) RH = 99.6%, SO₂ = 2 mdd & Cl = 15 mdd (b) RH = 80%, SO₂ = 0.04 mdd & Cl = 0.3 mdd

and there is a low increase in corrosion loss with an increase in RH. However, the ISO follows the same trend in both a low (25 °C) and a higher temperature (44.6 °C) that is against the basic corrosion mechanism and does not exhibit any intricate effect or act as an independent function. The influences of the environmental parameters ranges in Fig. 8a and 8b are comparable to those Cases 1 and 3 in Table 3, and the proposed equation also satisfies the same concerning the corrosion mechanism. It could therefore be stated from Fig.s 8a and 8b that the proposed empirical equation exhibits a better corrosion mechanism than ISO 9223 with a variation in RH.

Furthermore, Fig.s 9a and 9b are prepared to compare the behavior of models with an increase in temperature at higher and lower RH, sulphur dioxide and Cl respectively. At constant RH with an increase in temper-

ature, there would be a significant increase in corrosion loss based on the percentage of RH present in the atmosphere. Fig.s 9a and 9b show that at 80% RH with an increase in temperature, the rate of corrosion loss increased as per corrosion mechanism in both the proposed and the ISO equations, but at 99.6% RH, the increase in the rate of corrosion loss of the ISO equation is the same as that of 80%, which becomes not possible because the corrosion rate would not increase much at higher humidity as the electrolyte film could not be further enhanced with the temperature increase. In other words the increase in the rate of corrosion with an increase in temperature would be slow at a constant higher RH, sulphur dioxide and chloride. The proposed empirical equation accelerates at a very slow rate with an increase in temperature at a higher constant RH (as shown in Table 3), while

the ISO has a high increase in corrosion rate. As per the basic mechanism, with an increase in temperature, the proposed equation produces better results than the ISO.

Furthermore, it is observed that ISO exhibits the same pattern and behavior for all ranges of environmental parameters, regardless of the mechanism or phenomenon of

corrosion, whereas the proposed equation is consistent with the practical chemical corrosion mechanism. It could, therefore, be noted that the current equation is better than ISO for estimating the accurate corrosion rate following the corrosion mechanism.

Further, the combined behavior of temperature and RH with other environmental parameters is critical and should be reliably quantified. Fig. 10 is intended to investigate the potential of the proposed and ISO models for this combined behavior of environmental parameters and their effects on the rate of corrosion as per mechanism. The plots 10a, 10b and 10c are prepared by varying temperature and RH at the minimum, average and maximum levels of SO_2 and Cl respectively. The ISO eqaution at all ranges of environmental parameters shows the same corrosion rate trend with no concern for the corrosion mechanism as shown in Figs 10a, 10b and 10c. It could also be noted that the ISO estimates almost equal higher corrosion rates for the minimum and maximum values of SO_2 and Cl with varying temperatures and RH, which are not probable to appear as per the corrosion mechanism. The proposed empirical equation initially estimates lower corrosion rates at lower SO_2 and Cl values but increases with increase in T and RH as seen in Fig. 10a, while at medium and high levels of SO_2 and Cl, the proposed empirical equation initially estimates faster corrosion rates and continues to increase slowly with an increase in T and RH. However, ISO has the same trend for all values showing no significance for concentrations of SO_2 and Cl.

It could be noted that the new empirical equation estimates a reliable corrosion rate and behaves as per the chemical corrosion mechanism. As stated in the discussions, it could be summarized that the ISO 9223 model does not comply with the corrosion mechanism and the behavior of environmental parameters. The proposed empirical model estimates corrosion rates close to those measured rates by assimilating the corrosion mechanism in it.

5. Conclusion

The parametric study suggests that the rate of corrosion loss is highly regulated by the RH compared to other parameters. The intricate effect of RH and temperature is critical and has a major impact on the corrosion process. The other two parameters could be considered to be catalysts. The combined effects of environmental parameters on the corrosion rate are qualitatively summarized (Table 3). It could be noted that the empirical models put forward by previous studies do not satisfy the corrosion mechanism.
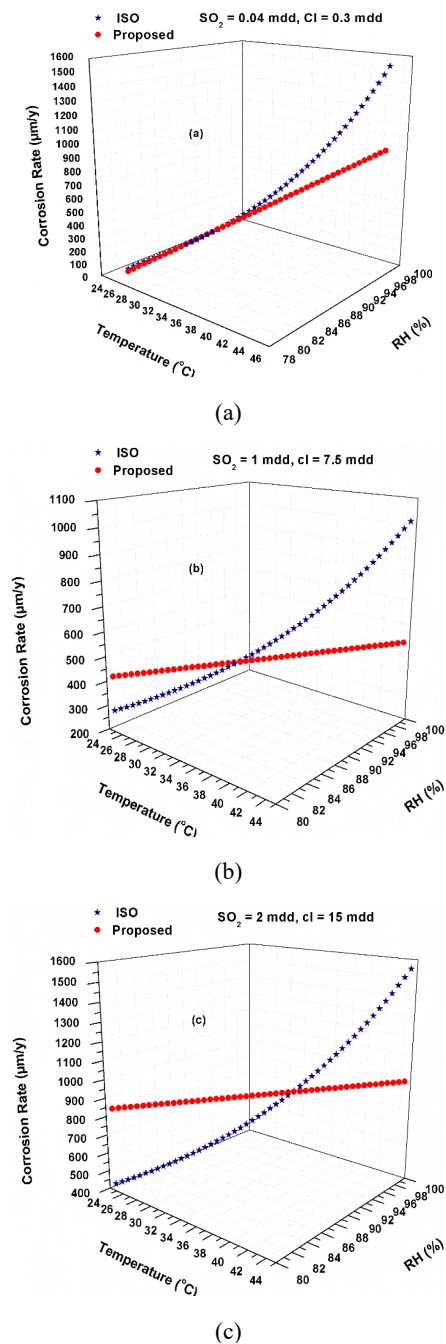

Fig. 10 Non-linearity of the Proposed model and ISO for varying RH (%), T (°C) with (a) minimum SO_2 and Cl⁻ (b) medium SO_2 and Cl⁻ & (c) high SO_2 and Cl⁻

Consequently, the statistical assessment is carried out by incorporating the observed behavior of environmental parameters (Table 3) in order to propose a global empirical model for estimating short (one-year) and long-term (more than one-year) corrosion, taking into account environmental parameters at any specific location for a particular exposure period. The fitness of the proposed empirical equation is highly reliable as the R^2 is 0.998 and the proposed equation estimates the corrosion rate having 95% confidence level with the experimental corrosion data (Fig. 6 and 7). Furthermore, it is noted that the proposed empiric equation is fitting feasibly for all the basic corrosion mechanisms and is extremely non-linear for environmental parameters T, RH, SO_2 & Cl (Fig.s 8 , 9 and 10) and could therefore be used reliably to estimate the corrosion rate at any continental location.

Acknowledgments

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