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A Carbonation and Chloride Induced Corrosion Model for Hot-dip Galvanised Reinforcement Bar Material in Concrete

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ABSTRACT

This paper focuses on methodological issues relevant to corrosion risk prediction models. A model was developed for the prediction of corrosion rates associated with hot-dip galvanised reinforcement bar material in concrete exposed to carbonation and chlorides in outdoor environment. One-year follow-up experiments, over five years, were conducted at various carbonation depths and chloride contents. The observed dependence of corrosion rate on the depth of carbonation and chloride content is complex indicating that the interaction between the carbonation and chloride influencing the corrosion. A non-linear corrosion model was proposed with statistical analysis to model the relationship between the corrosion rate and the test parameters. The main methodological contributions are (i) the proposed modeling approach able to take into account the uncertain measurement errors including unobserved systematic and random heterogeneity over different measured specimens and correlation for the same specimen across different measuring times, which best suits the measurement data; (ii) the developed model in which an interaction parameter is introduced especially to account for the contribution and the degree of the unobserved carbonation-chloride interaction. The proposed model offers greater flexibility for the modelling of measurement data than traditional models.

1. Introduction

The practice of hot-dip galvanised steel reinforcement bar (HDG) in concrete has been shown to be one of the most durable and technically suitable coating methods for corrosion protection [1-3]. In this method, zinc, in the form of hot dip galvanizing, is applied to the surface of steel forming zinc-iron alloy barrier around the steel which delays the onset of corrosion of the steel and enhances the durability of the concrete. HDG offers multifold advantages including substantially higher chloride threshold and lower corrosion rate for zinc corrosion in concrete than conventional steel. Furthermore, zinc's sacrificial action protects the steel even if the coating barrier is damaged.

However, HDG did not get wide acceptance in the past since because inconsistent and contradictory results were observed under some conditions and environments [4-6]. Uncertainties

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DOI: https://doi.org/10.30564/jbms.v3i2.3150

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exist in the literature related to the effectiveness of HDG as a long-term inhibition for chlorides and carbonation induced corrosion. The controversy arises due to several reasons. One obvious reason is the exposure to oxygen, carbon dioxide, chlorides, water and other chemical exposures in an actual environment that the relation between environmental exposures and corrosion status can be quite complex. For example, at high PH-value conditions, corrosion may start at very low chloride content due to the zinc's instability at high PH-values. The corrosion attack is determined by the relevant environmental exposures, their interactions and time. Therefore, it has stated that laboratory results must be viewed with caution due to the fact that the simulated environment might not fully match the actual environments [5]. However, although complex, it has been well recognized that chlorides and carbonation are the two main causes for corrosion of steel in concrete. Aggressive substances of chlorides and carbon dioxide under certain environments, such as temperature and moisture, are the key risk factors. The presence of chlorides and carbon dioxide can lead to the breakdown of the steel's passivity which affects the inhibitive properties of the coating zinc and causes spalling of the concrete over corroded steel and, consequently, structural breakage.

Chloride and/or carbonation induced corrosion models, have been used extensively to predict the corrosion rate (see recent reviews [7-8]). Models can be classified in physical-based (or process-based) and data-driven methods generally. Physical-based methods use explicit mathematical equations to model evolution of the corrosion rate. Data-driven methods use measurement data to build up statistical models for predicting the corrosion process based on empirical relationships between corrosion rate and input parameters. Both models have their merits and demerits and challenges still exist in the current state-of-the-art corrosion modeling. A major limitation is the large gap between the general corrosion models, dominated by physically-based approaches, and the understanding of complexes encountered in real world situations. For example, time-dependent characteristic of the chloride concentration, or carbonation levels, at a concrete surface has been rarely considered in predicting the chloride or the carbonation ingress [9]. Data-driven modelling approaches are becoming more popular due to the increasing availability of measurement tools and data; however, methodological problems exist with such approaches because interpreting experimental findings strongly depend on the features of the data and the statistical methods for analyzing the data. For example, many measurement data involve multiple measures on each specimen. The correlated measures within specimens are not always considered, however, in many studies. Moreover, correlation derived risk models for the in-service conditions are rare [10]. Not surprisingly, few reports have taken into account the complexity added by the interaction between chloride and carbonation in corrosion models. For risk assessment, the interaction between chloride and carbonation has a great influence on corrosion process and understanding the behavior of chloride, carbonation and their interaction is important for understanding how they induce the corrosion process [11]. The corrosion risk significantly increases when the concrete is exposed to both substances [11].

The purpose of this paper is to develop a correlation derived risk model for the prediction of the corrosion rate to address these, mainly methodological issues. The model predicts corrosion rates for hot-dip galvanised reinforcement bar material in concrete exposed to carbonation and chlorides in real world situations with regard to atmospheric attack in an outdoor environment. Long-term follow-up measurement data, one-year follow-up experiments for over five years, were conducted at various carbonation depths and chloride contents. A non-linear corrosion model was proposed with statistical analysis to model the relationship between the corrosion rate and the test parameters. From the methodological point of view, the main contribution of the present work consists in the approach developed to deal with the measurement errors including unobserved systematic and random heterogeneity over different measured specimens and correlation for the same specimen across different measuring times which were properly taken into account in the model. Such issues are often neglected in the literature. Secondly, an interaction parameter was introduced especially to account for the contribution and the degree of the unobserved carbonation-chloride interaction. The proposed model offers greater flexibility for the modelling of measurement data than traditional models.

2. Methods and Materials

2.1 Measurement Data

The measurement data used in this study were collected from seven-year long-term follow up measurement. The data include 336 specimens of hot-dip galvanized reinforcement bar material in concrete exposed to carbonation and chlorides in real world situations with regard to atmospheric attack in outdoor environment. Corrosion rates on the depth of carbonation and chloride content were measured using PH indicator sprayed onto

the freshly broken surface, which was possible to measure the carbonation depth after a few minutes. The detailed experimental procedure can be referred from the paper [12].

2.2 Model

The proposed model predicts the corrosion rate given environmental exposures under real outdoor condition (i.e. different chloride concentration, carbonation level, etc). Since corrosion processes are complex which involves multiple environmental parameters, their interactions with each other and many uncertainties, the development of the model involved two stages. In the first stage, a suitable model structure and key risk parameters were selected using the Akaike information criterion [13]. In the second stage, the model equation was formulated. The proposed model has several new features that extend the current corrosion models in the literature:

(1) The model predicts time dependent corrosion rate base on full historical corrosion data;

(2) The model identifies the important environmental parameters as key risk conditions;

(3) The model takes into account the random and uncertain nature of different specimens and parameters over time.

(4) The model accounts for correlation among measured outcomes over time in the same specimen.

The model equation is based on a multivariate nonlinear regression as

$$y^{corr}it = a_0 + a_1 \sqrt{t} + \beta_1 x^{CH}it + \beta_2 x^{CO2}it + \beta_3 x^{CH}it . x^{CO2} + g_1 x^R it + u_i + e_{it} \qquad (1)$$

where

- $y^{corr}it$ presents the corrosion rate for the i-th specimen at time t
- $x^{CH}it$ is the chloride content for the i-th specimen at time t
- $x^{CO}it$ is the carbonation level for the i-th specimen at time t
- $x^R it$ is the corrosion resistance for the i-th specimen at time t
- u_i is the random effect by specimens
- e_{it} presents the measurement errors, random noise and other source of uncertainties
- a, b and g are the model coefficients
- t represents the time

The model emphasizes the following aspects:

● accounts the random and uncertain nature of different specimens presented using random variable u_i

● accounts for correlation among measured outcomes over time in the same specimen: correlation ($y^{corr}it$,

$y^{corr}it'$) ¹ 0

● accounts for all the measurement and modeling uncertainties using a stochastic variable e_{it}.

The model relaxes the restriction that the measurements taken at different times for the same specimen are not correlated. Such uncorrelated restriction is one of the most common assumptions made in many corrosion models which can lead to misleading inferences because there is a good reason to believe that the correlations exist among the measurements for the same specimen at different time. For example, an average correlation coefficient for the corrosion rate measures of the same specimen is 0.5, which shows strong correlations. We shall demonstrate below in the discussion section that it is inaccurate and misleading to draw conclusions if such correlations are ignored. The correlation structure for the same specimen i was modeled as sphericity characteristic meaning that correlations of the measures for the same specimen are the same.

It can be seen that the model is a dynamic model in specimen and time. The novelty and generalization of the proposed model lies in the application of these new features. The model coefficients, a, b and g, determine the effects on corrosion rates of their correspondent model parameters or environmental factors which were calculated by Maximum likelihood method (MLE) [14]. MLE provides better and more accurate results than least square method in general. Furthermore, time serial analysis technique was used to test for the statistical significance of the effect of the estimate. Statistical significance is a statistical assessment of the probability that the relationship exists which presents the accuracy of the model. The significance is measured using p-value. 95% confidence interval ($p < 0.05$) was chosen as probability threshold for the statistical significance for the confidence level. After determining the significant parameters, the final models were developed incorporating only these parameters for different corrosion measurement outputs. The results are presented in the third section.

3. Results

Table 1 shows the results. Effect estimates are presented as 95% confidence intervals. p-values are provided which show the statistical significance of the effect estimates. For example, p<0.01 means 99% probability the true effect lies in that estimated interval. The sign of the estimate depends on the sign of the estimated slope of the model parameter. A positive sign means a positive correlation between the parameter and the model output.

Table 1 shows that chloride concentration, carbonation level, chloride-carbonation interaction, crack width and

Table 1. Significance Analysis of the Independent Variable

Parameter	Estimate	Standard Error	df	t	Sig.	95% Confidence Interval	
						Lower Bound	Upper Bound
a_0	-512,332810	96,613337	1224,352	-5,303	0,000	-701,878848	-322,786772
t	-172,593211	113,573595	1247,640	-1,520	0,129	-395,409522	50,223100
x^{CH}	-14,575465	5,515497	372,582	-2,643	0,009	-25,420871	-3,730058
x^{CO2}	27,867155	11,444345	344,743	2,435	0,015	5,357627	50,376684
$x^{CH}x^{CO2}$	-4,378792	3,431653	532,164	-1,276	0,203	-11,120040	2,362456
x^R	75,400366	37,197950	1088,903	2,027	0,043	2,412597	148,388135

Table 2. Parameter Estimates (Dependent Variable: y^{corr})

Parameter	Value	Standard Error	t	Sig.	95% Confidence Interval	
					Lower Bound	Upper Bound
a_0	-126,373	87,521	-1,444	0,149	-298,056	45,310
t	-638,260	103,055	-6,193	0,000	-840,415	-436,104
x^{CH}	-28,219	3,553	-7,942	0,000	-35,188	-21,249
x^{CO2}	-19,066	6,026	-3,164	0,002	-30,887	-7,246
$x^{CH}x^{CO2}$	-4,968	2,107	-2,358	0,019	-9,102	-0,835
x^R	-23,967	35,353	-0,678	0,498	-93,316	45,382

pH concentration were strongly predictive of corrosion rate. Chloride concentration, carbonation depth and crack width had the same, or nearly the same, significant positive effect per unit on corrosion rate. Increased chloride concentration, carbonation depth and crack width had progressively increasing effect on y^{corr}. The results indicate the PH concentration could induce the increase of the corrosion rate too. An interesting result was obtained here regarding the chloride-carbonation interaction. The interaction was found to have a significant impact on corrosion rate. Association between y^{corr} and the interaction depended on the levels of both factors. Roughly speaking, y^{corr} can be expected to change by 1.8+0.35x when chloride concentration increases by 1 given x depth of carbonation. The increase of y^{corr} is bout 1.4+0.35CH when carbonation depth increases by 1 given CH concentration of chloride.

For higher concentration of CH, significant higher y^{corr} was present at higher levels of carbonation (13 mm depth) than at lower level of carbonation (11 mm). The study also showed that y^{corr} is in inverse proportion with the square-root of exposure time. The increase of y^{corr} slows down in time.

Corrosion rate has shown to be strongly dependent on chloride concentration, carbonation level, PH concentration but has a weak dependence on crack growth (significance at the 8% level). Increases of carbonation, pH values and crack width has been found to potentially increase the corrosion rate. At pH 7-8 (the average pH used in this study) the corrosion potential decreases

significantly with the increase of chloride concentrations. From the experiments it is not apparent that the exposure times are correlated with y^{corr}.

4. Discussion

4.1 Methodological Issues

One of the most striking features of the proposed methodology is that it allows for taking into account the uncertain measurement errors including unobserved systematic and random heterogeneity over different measured specimens and correlation for the same specimen across different measuring times, which best suits the measurement data. Misleading inferences could be obtained if we neglect such measuring correlations within specimens. Figure 1 illustrates the specimen-based corrosion rate changes in our experimental data which are subject to random fluctuations. A linear regression trend line fitted to all the specimens' lines is displayed in the figure which roughly shows a positive relationship between carbonation depth variation and corrosion rate. Therefore, simple regression models fail to capture randomness between-specimen fluctuations and the correlations within specimen. Therefore, model's standard errors are biased and the model results are inaccurate. Because of space limitations, we only show the comparison results for y^{corr}. Such inaccurate predictions existed in the calculation of other corrosion outputs as well.

The presence of the correlations among y^{corr} measures

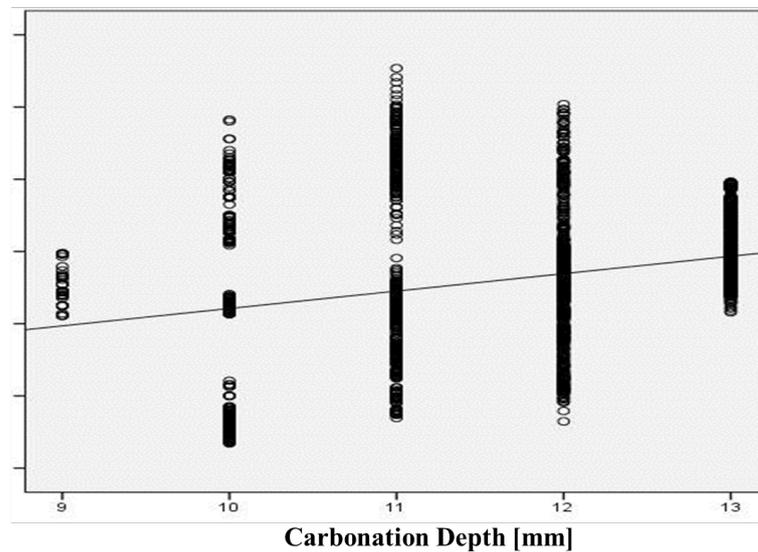**Corrosion Rate Variation**

Figure 1. The specimen-based corrosion rate variation vs carbonation depth. Circles represent the specimens. Large variation in specimen can be observed. A linear relationship indicates a correlation between them.

for the same specimen introduces methodological problems in significance testing. The correlations indicate nested sources of variation. If we ignore it, we underestimate the error variance of the estimated coefficients and inflate the significance levels. This can increase the likelihood of a Type I error. The existence of such correlations has been rarely been taken into account in the corrosion models.

4.2 Chloride and Carbonation Interaction

The interaction effect between chloride and carbonation on corrosion rate was identified in this study. Although research on this topic is lacking because most studies have focused on the chloride and carbonation penetrations independently, relatively few studies have demonstrated that their combination could lead to rapid deterioration [15]. Therefore, these results are consistent with the large body of scientific evidence although there are disputes on some levels in the literature.

The change of structure due to carbonation can reduce the binding capacity of the solid phase in concrete leading to a higher amount of free chlorides in the pore solution. The coexistence of chloride and carbonation is related to the effect of carbonation on the liberation of bound chlorides leading to a higher penetration rate and higher corrosion rate. However, for chloride, penetration only occurs in pores that contain water which is completely different from that of carbonation [16]. One report suggested that once the carbonation front reaches the rebar location. The chloride concentration threshold needed to

initiate corrosion could be significantly reduced [17].

5. Conclusions

Corrosion risk prediction models of concrete structures have been widely studied in the literature. This paper developed a model for the prediction of corrosion rates associated with hot-dip galvanised reinforcement bar material in concrete exposed to carbonation and chlorides in outdoor environment. Our proposed modelling approach adds some new methodological aspects to these important studies, namely, (i) able to take into account the uncertain measurement errors including unobserved systematic and random heterogeneity over different measured specimens and correlation for the same specimen across different measuring times, which best suits the measurement data; (ii) detailed study of the contribution and the degree of the unobserved carbonation-chloride interaction.

Among the study factors, chloride, carbonation, chloride-carbonation interaction, crack width, pH concentration and exposure time were found to be associated with the corrosion risk. This is the first study accounting for randomness between-specimen fluctuations and the correlations within specimen and experimental finding indicating that the chloride-carbonation interaction has noticeable effect on corrosion. Our study results suggest that there is potential for reducing corrosion risk by controlling the risk factors.

Finally, the developed model offers greater flexibility for the modelling of corrosion data and the proposed modeling approach is easily implemented in common

statistical software packages with small computational load.

Acknowlegments

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