

Analyses of Corrosion Potential from Inhibitor-Admixed Steel-Reinforced Concrete: Implication on Steel-Rebar Corrosion Risk/Probability

Analyses of Corrosion Potential from Inhibitor-Admixed Steel-Reinforced Concrete

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Abstract—Statistical analyses of three probability density functions, from Normal, Rayleigh and Weibull distributions, were applied for studying steel-rebar corrosion risk/probability in inhibitor admixed steel-reinforced concrete immersed in aggressive media of 3.0% NaCl and 0.5 M H₂SO₄. For these, different concentrations, ranging from 0 M to 0.29 M, of K₂CrO₄ were admixed in two-set steel-reinforced concrete with each set partially immersed in each of the aggressive test-solutions and which were monitored using open circuit potential techniques as per ASTM C876–91 R99. Analyses of the 30-days test-response from these showed that most of the corrosion test-data distributed like the Weibull and like the Normal distributions while just a few test-datasets distributed like the Rayleigh distribution, according to the Kolmogorov-Smirnov goodness-of-fit statistics. All the probability distribution fittings identified, in agreements, the 0.15 M K₂CrO₄ admixed steel-reinforced concrete with the least probability of corrosion risk in both of the acidic and the neutral saline test-solutions. These bear implications on the use of probability distribution analyses for economical monitoring of steel-rebar corrosion risk/probability and corrosion inhibitor admixture effects in steel-reinforced concrete in aggressive service-environments.

Keywords—Corrosion potential, steel rebar, potassium chromate, probability density fitting functions, Kolmogorov-Smirnov statistics, acidic and neutral saline

I. Introduction

Corrosion-induced degradation of steel-reinforced concrete is leading to increase in safety risks to life and loss of properties by the increasing incidence of collapsed concrete buildings/infrastructure in coastal and industrial environments, globally [1-2].

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In Nigeria, statistics made available by Lagos State Physical Planning and Development Authority show that the coastal region of the city of Lagos [3-4] have the highest frequency of collapsed building structures possibly because of their nearness to water bodies containing chloride and sulphate ions. Chloride ions from the Atlantic salt water and sulphate ion from constant sewer waste deposit from increased anthropogenic activity in the Lagoon and Atlantic. All these substances are responsible for the attack on concrete infrastructure which essentially results in the destruction in the passive film on steel rebar and eventual pitting and reduction in the effective diameter of the steel rebar [1-3, 5-7]. Catastrophic cracking and failure occurs afterwards because the structure is unable to support the load for which it was designed.

Combating these collapses by preventing corrosion of steel rebar in concrete is a critical step towards prolonging infrastructure lifespan. One of such ways is the use of corrosion inhibitors to forestall steel rebar corrosion. However, inhibition performance on concrete steel-rebar corrosion requires adequate monitoring and requisite interpretation of monitored data as per relevant standards by corrosion experts [8]. The engagement of these high technicalities could therefore be highly cost-intensive especially for a developing country like Nigeria. Lengthy engagements of highly technical professionals at monitoring actual steel-rebar corrosion and consequent inhibitor admixture effects using requisite complimentary techniques [9] would culminate in high costs of corrosion monitoring. This is potent at affecting the effectual fund that would be available for the repair and maintenance of the corrosion deteriorated regions of the steel-reinforced concretes.

Solution to this would be in the form of ascertaining region of high corrosion risk/probability in steel-reinforced concrete at which point the other corrosion monitoring techniques for complementing corrosion inference and confirmations can then be applied. A simple and economic approach of monitoring corrosion risk/probability is the use open circuit potential (OCP) techniques [8-9] but as a corrosion test-data monitoring method, it is prone to stochastic deviations from the corrosive condition in the corrosion test-system [10-13].

One of the approach for tackling these stochastic deviations, as proposed by the ASTM G16-95 R04 [10], is the use of the statistical analysis of probability distributions for detailing prevailing actual corrosion conditions from the scatter of corrosion test-data. However, while studies have

compared the Normal and the Weibull distributions for studying distribution of corrosion potential, no experiment have deliberated on the comparisons involving the use of the Rayleigh distribution with others distributions for analyzing corrosion test-data. A new technique of this nature requires the use of a well-known inhibitor for serving as basis for the test of effects of inhibitors yet unknown. Such inhibitor that has been well-known for inhibiting steel-reinforcement corrosion in aggressive environments includes K_2CrO_4 . Therefore, the objective of this study is to investigate the statistical analyses of the Normal, Rayleigh and the Weibull probability density functions for detailing corrosion risk/probability from OCP monitored steel-reinforced concrete immersed in aggressive and admixed with K_2CrO_4 inhibitor.

II. Experimental Procedure

A. Concrete Sample Preparations

Steel-reinforced concrete blocks were prepared according to standard procedures in [2,13] from potable water and a mixture of clean natural sand from Ijako, South-West Nigeria, Portland cement and gravel stones in a 1:2:4 (C:S:G) mix ratio. The reinforced concrete specimens were made of constituents with parameters as stated: 320.0 kg/m³ of cement,

140 kg/m³ of water, 700 kg/m³ of sand and 1150kg/m³ of gravel. The water/cement (w/c) ratio = 0.44 [2-3, 13-14].

Binary groups of 100mm × 100mm × 160mm steel-reinforced concrete blocks were made. The first group consisted of first seven concrete blocks that were partially immersed in the 0.5 M H_2SO_4 test-solution, while the second group consisted of seven concrete blocks that were partially immersed in 3.0% NaCl medium. The seven blocks in each group were made with different concentrations of K_2CrO_4 inhibitor admixture, see Table 1. Also, each block was admixed with fixed amount of sodium chloride (0.1M) for accelerating corrosion to study admixture effects. All the chemicals used were of high purity analytical grade. The steel rebar chemical composition used for the experiment was: 0.3% C, 0.25 % Si, 1.5% Mn, 0.04% P, 0.64% S, 0.25% Cu, 0.1% Cr, 0.11% Ni and 98.61% Fe. Several pieces of 160mm length with 10mm diameter rods were cut from the original long length for placement in the concrete mix. This was followed by mill scale and rust stains removal from the steel specimens by an abrasive grinder before insertion in each concrete block. Steel placement in the concrete made ensured 20mm length protruded at one end of the concrete block while the remaining 140mm were embedded in the block. This was painted to prevent atmospheric corrosion [13,15] and thereafter used for electrical connection.

Table 1: List of steel-reinforced concrete specimens with admixed inhibitor and immersed test-solution

S/No	Admixture	Test-solution	S/No	Admixture	Test-solution
1.	0.0M K_2CrO_4 (Control)	0.5M H_2SO_4	2.	0.0M K_2CrO_4 (Control)	3.0% NaCl
3.	0.05M K_2CrO_4	0.5M H_2SO_4	4.	0.05M K_2CrO_4	3.0% NaCl
5.	0.10M K_2CrO_4	0.5M H_2SO_4	6.	0.10M K_2CrO_4	3.0% NaCl
7.	0.15M K_2CrO_4	0.5M H_2SO_4	8.	0.15M K_2CrO_4	3.0% NaCl
9.	0.19M K_2CrO_4	0.5M H_2SO_4	10.	0.19M K_2CrO_4	3.0% NaCl
11.	0.24M K_2CrO_4	0.5M H_2SO_4	12.	0.24M K_2CrO_4	3.0% NaCl
13.	0.29M K_2CrO_4	0.5M H_2SO_4	14.	0.29M K_2CrO_4	3.0% NaCl

B. Corrosion Potential Measurement

The concrete block samples were partly immersed in their separate test medium such that the liquid level was just below the bare part of the steel rebar. Corrosion potential measurements were obtained by placing a copper/copper sulphate electrode (CSE) securely on the block samples [16-17]. A complete electrical circuit was made by connecting one of the two lead terminals of a Mastech® digital multimeter to a copper sulphate electrode while the other was connected to the bare end of the embedded reinforcement. Measurements were taken at three different points on each concrete block directly over the embedded steel rebar [13,15,17]. The mean of the three measurements was calculated as the potential reading for the embedded rebar in 2-day intervals for a 30-day period. Experiments were conducted under free corrosion potential and at ambient temperature.

C. Statistical Analyses of Test-Data of Corrosion Potential Measurements

The statistical analyses applied to the test-data of corrosion potential measurements include the Normal, the Weibull and the Rayleigh probability distribution function (pdf) models. The probability density functions of the Normal, the Weibull and the Rayleigh distributions are respectively given by [18-20]:

$$f_N(x) = \frac{1}{\sigma_N \sqrt{2\pi}} \exp \left[-\frac{(x - \mu_N)^2}{2\sigma_N^2} \right] \quad (1)$$

$$f_W(x) = \left(\frac{k}{c}\right) \left(\frac{x}{c}\right)^{k-1} \exp \left[-\left(\frac{x}{c}\right)^k \right] \quad (2)$$

$$f_R = \frac{x}{c_R^2} \exp \left[-\frac{1}{2} \left(\frac{x}{c_R}\right)^2 \right] \quad (3)$$

Where x is the measured test-data of corrosion potential, μ_N and σ_N are the Normal mean and standard deviation, k and c are the Weibull shape and scale parameters and c_R is the Rayleigh scale parameter related to the Weibull scale parameter c by [18]:

$$c_R = \frac{\sqrt{2}}{2} c \quad (4)$$

Estimation of the Normal mean employed the well known formula for μ_N as:

$$\mu_N = \frac{1}{n} \sum_{i=1}^n x_i \quad (5)$$

Where n is the number of the examined data points of corrosion potential measurements. For the 30-day experimental period in this study, $n = 15$. The estimation of the Weibull mean μ_W and Rayleigh mean μ_R employed the respective relationships [14,18]:

$$\mu_W = c \Gamma \left(1 + \frac{1}{k} \right) \quad (6)$$

$$\mu_R = c_R \sqrt{\frac{\pi}{2}} \quad (7)$$

Where $\Gamma(\cdot)$ is the gamma function of (\cdot)

Compatibility of the dataset of corrosion potential from each specimen of concrete slab to these probability distribution functions were studied using the Kolmogorov-Smirnov K-S goodness-of-fit (GoF) statistics [21]. This K-S GoF measures the absolute difference between empirical distribution function $F^*(x)$ and theoretical distribution function $F(x)$ by the statistics:

$$D_n = D(x_1, \dots, x_n) = \sup_{-\infty < x < \infty} |F^*(x) - F(x)| \quad (8)$$

Consequently, at a significant level of $\alpha=0.05$, the p -value of the K-S GoF test is subjected to the test of hypothesis:

$$\begin{aligned} H_0 &: p \geq \alpha \\ H_A &: p < \alpha \end{aligned} \quad (9)$$

Where H_0 is the null, and H_A is the alternative, hypothesis that the test-data of corrosion potential distributed or does not distributed like a particular probability distribution function.

III. Results and Discussion

A. Distribution Analyses of Test-Results of Corrosion Potential

The results from the distribution analyses of the test-measurements of corrosion potential are presented in Fig. 1(a) for concrete samples immersed in the H_2SO_4 medium and in Fig. 1(b) for concrete samples immersed in NaCl medium. These also include linear plots of corrosion risk/probability according to the specifications of the American Society for Testing and Materials, ASTM standard designation C876-91 R99 [8-9,22]. From these, the Weibull distribution function exhibited over-prediction of the mean corrosion potential in the H_2SO_4 -immersed steel-reinforced concrete samples except the H_2SO_4 -immersed concrete with 0.05M K_2CrO_4 admixture having its corrosion potential over-predicted by the Rayleigh. In the NaCl medium, however, the over-prediction of mean corrosion potential from the steel-reinforced concrete samples was exhibited by the Rayleigh probability distribution function. In spite of these over-predictions, the predictions of the mean corrosion potential by the statistical distribution functions employed in the study followed similar patterns for all steel-reinforced concrete samples, irrespective of their medium of test-immersion. Also notable from Fig. 1 was the identification of the 0.15M K_2CrO_4 with the optimal corrosion risk performance in both the acidic and the saline media by each of the distribution fitting functions.

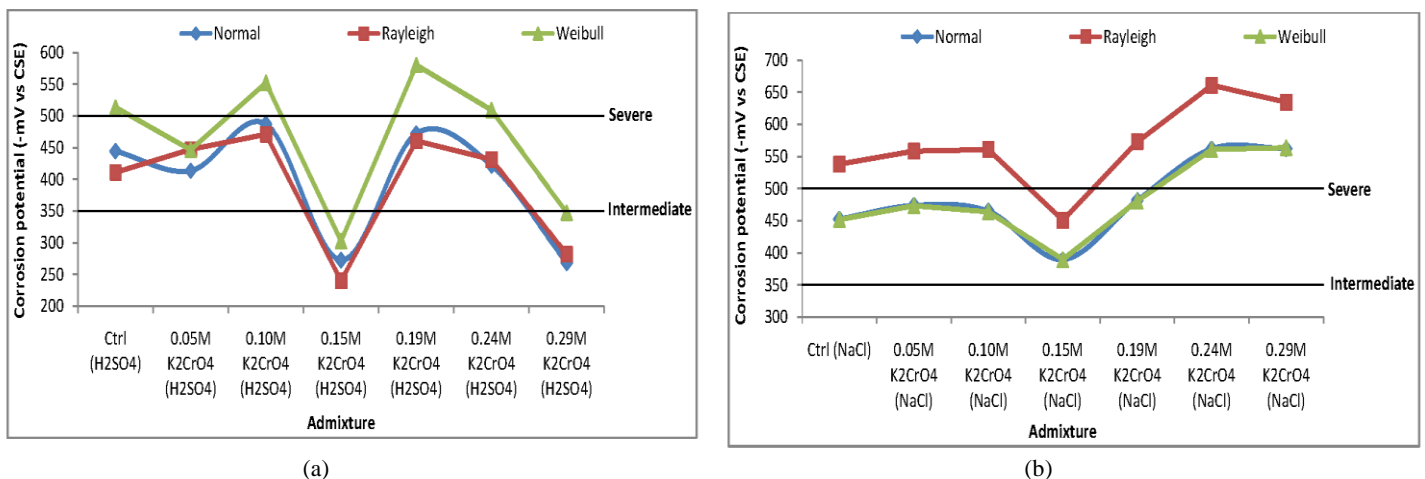


Fig. 1. Plots of statistical distribution predictions of mean corrosion potential in steel-reinforced concrete samples with linear plots of corrosion risk/probability as per ASTM C876-91 R99 [8-9,22]

In the H_2SO_4 medium for instance, the steel-reinforced concrete sample admixed with 0.15M K_2CrO_4 exhibited mean

corrosion potential of -272.47 mV vs CSE (Normal), -239.85 mV vs CSE (Rayleigh) and -302.44 mV vs CSE (Weibull). These represented corrosion risk mitigation when compared

with the control samples exhibiting mean corrosion potential of -444.60 mV vs CSE (Normal), -411.08 mV vs CSE (Rayleigh) and -513.31 mV vs CSE (Weibull). By the ASTM C876-91 R99 [22] interpretations, the 0.15M K_2CrO_4 mitigated corrosion risk from the high ($> 90\%$) corrosion risk/probability by the Normal and the Rayleigh, or severe corrosion risk/probability by the Weibull pdf, to the intermediate corrosion risks/probability in agreements by the three pdfs. The admixture exhibiting this kind of performance in the H_2SO_4 test-medium was the steel-reinforced concrete sample admixed with 0.29M K_2CrO_4 that exhibited mean corrosion potential of -268.20 mV vs CSE (Normal), -281.95 mV vs CSE (Rayleigh) and -347.47 mV vs CSE (Weibull).

In the NaCl medium, the optimal corrosion risk/probability mitigation by the 0.15M K_2CrO_4 admixed steel-reinforced concrete sample was at the mean corrosion potential of -389.53 mV vs CSE (Normal), -450.71 mV vs CSE (Rayleigh) and -389.47 mV vs CSE (Weibull). In comparison, the control sample in the NaCl medium exhibited mean corrosion potential of -452.33 mV vs CSE (Normal), -537.99 mV vs CSE (Rayleigh) and -451.64 mV vs CSE (Weibull). Although, only the corrosion potential predicted for the control sample in NaCl medium by the Rayleigh pdf was in the severe corrosion risk/probability range, the performance of the 0.15M K_2CrO_4 still represented mitigation of corrosion in the order that was not obtained from the other admixture concentration in their admixed steel-reinforced concrete. Also notable from Fig. 1(b) was the steel-reinforced concrete with 0.29M K_2CrO_4 admixture that exhibited severe corrosion risk/probability in the NaCl medium and which indicated corrosion risk/probability aggravation compared to the control sample in the NaCl medium. Comparison of this corrosion risk/probability aggravation by the 0.29M K_2CrO_4 in the NaCl medium to its performance of corrosion risk/probability mitigation in the H_2SO_4 medium exemplifies the selectiveness of aggressive environment of corrosion risk mitigation performance by this admixture. This bears implication of need for testing inhibitor admixture that had exhibited effective inhibition performance in a corrosive test-system before being employed as inhibitor in another type of corrosive test-environment.

B. Goodness-of-fit test-results

The discrepancies in the corrosion risk/probability predictions by the different probability distribution functions require ascertaining which of these distributions exhibited the descriptive statistics of the test-data of corrosion potential from the samples of steel-reinforced concretes in each of the test-media. For this, the results of the Kolmogorov-Smirnov (K-S) goodness-of-fit (GoF) test statistics were presented in Fig. 2. This figure also include the linear plot of the 0.05 significance level for directly interpreting test-datasets of steel-reinforced concrete sample distributing like each of the probability fitting functions.

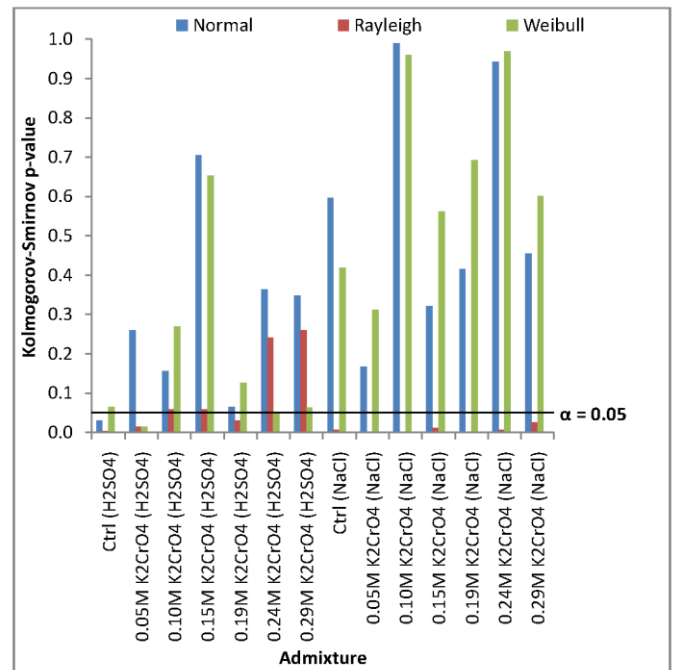


Fig. 2. Kolmogorov-Smirnov goodness-of-fit test-results of the fittings of corrosion test-data by the fitting models of the Normal, the Rayleigh and the Weibull probability distributions

From the figure, it could be observed that the datasets of corrosion potential from the control samples in the H_2SO_4 medium were not distributed like the Normal distribution while the dataset from the concrete sample with 0.05 M K_2CrO_4 in the H_2SO_4 medium were not distributed like the Weibull pdf. All the other samples, totalling thirteen for each of these pdfs, distributed like the Normal (i.e. excluding the control in H_2SO_4) and like the Weibull (i.e. excluding 0.05 M K_2CrO_4 admixed concrete in NaCl). The datasets of all the NaCl-immersed steel-reinforced samples in this study distributed like both the Normal and the Weibull probability distribution functions. These support the use of the Normal and the Weibull distributions as the descriptive statistics for detailing prevailing corrosion risk/probability and consequently, inhibitor performance in steel-reinforced concretes immersed in corrosive service-environments.

These were unlike the goodness-of-fit test results for the Rayleigh distribution model which identified only four admixed concretes with datasets that distributed like the Rayleigh pdf out of the fourteen steel-reinforced concrete samples being studied in this work. Also notable was that the four concrete samples with datasets that distributed like the Rayleigh pdf were samples immersed in the H_2SO_4 medium; no NaCl immersed sample in the study exhibited corrosion potential dataset that distributed like the Rayleigh. It could therefore be deduced from this study that cautions are required in the use of the Rayleigh distribution function model for describing test-data of corrosion potential from steel-reinforced concretes in aggressive service-environments.

iv. Conclusion

- The 0.15M K_2CrO_4 exhibited optimal performance at mitigating corrosion risk/probability both in the H_2SO_4 and in the NaCl corrosive test-systems. The performance by this 0.15M K_2CrO_4 admixture was unlike that by the 0.29 M K_2CrO_4 admixture that was selectively effective at mitigating corrosion risk/probability in the H_2SO_4 medium while it aggravated corrosion risk/probability in the NaCl-immersed concrete.
- The datasets of corrosion potential distributed like the Normal and like the Weibull distribution functions for most of the steel-reinforced concrete samples according to the Kolmogorov-Smirnov goodness-of-fit test statistics. This is unlike the distribution of datasets of corrosion potential that distributed like the Rayleigh pdf for only four out of the fourteen steel-reinforced concrete samples studied.
- These bear implications of need for requisite test in specific corrosive test-system of admixture performance at mitigating corrosion risk/probability in steel-reinforced concrete designed for such corrosive service-environment as well as the use of relevant statistical tool for ascertaining the probability distribution fitting followed by corrosion test-data, especially for economical interpretation of prevailing corrosion condition in a given corrosive environment.

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