Effects of $Na_2Cr_2O_7$ Inhibitor on the Corrosion Potential Response of Steel Reinforced Concrete in Saline Medium

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Abstract

Electrochemical monitoring method of the open circuit potential was used to investigate the effect of the concentrations of $Na_2Cr_2O_7$ *on the corrosion potential response of steel reinforced concrete in sodium chloride medium. In the study, five different concentrations of* $Na_2Cr_2O_7$ *admixtures were employed in a system of replicated samples of steel-reinforced concrete specimens partially immersed in 3.5% NaCl to simulate marine and saline environments. Forty days measured responses from these were subjected to the statistical analyses of the Normal and the Weibull distribution functions and tested using the Kolmogorov-Smirnov goodness of fit criteria. Results obtained from the analyses identified 4 g* $Na_2Cr_2O_7$ *with optimal averaged potential response inhibition performance by the Normal model which showed better agreements in its models of* $Na_2Cr_2O_7$ *potential test data than that obtained from the Weibull model of the same data. These bear pertinent implications on the need for suitability studies of appropriate statistical distribution for studying performance of corrosion inhibitors even as suggestions were proffered for addressing results conflicts among replicates of steel reinforced concrete samples employed.*

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1. Introduction

Corrosion degradation of reinforcing steel in concrete is a major cause of service failure in reinforced concrete infrastructure worldwide. Usually, steel embedded in concrete is protected from corrosion degradation by the high alkalinity of the concrete pore structure which is at a pH greater than 12.5 (Tang et al, 2012; Nürnberger, 2007). However, the reduction of this alkalinity could be induced by environmental agents of corrosion the major of which include chloride ingress through natural sources of marine environments or man-made saline sources of de-icing salts applications on concrete infrastructures. This renders reinforcing steel in concrete susceptible to corrosion deterioration and consequent premature dilapidation of the reinforced concrete structures. Maintenance, repair and restoration to forestall grievous and unprecedented collapse of these concrete structures usually constitute considerable portion of the budget of many countries globally (Tang et al, 2012; Sideris and Savva, 2005).

The ubiquitous nature of corrosion of reinforcing steel in concrete structures and its insidious grave consequences had necessitated the propositions of many methods for delaying corrosion initiation and arresting the progressive deterioration of steel reinforcement in concrete. From these, the use of corrosion inhibitors had been identified in studies as a viable means of mitigating corrosion menace in reinforced concrete structures. According to ISO 8044 1989, a corrosion inhibitor could be defined as a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration (Söylev and Richardson, 2008). From this definition, two important requirements could be identified for a chemical substance that would qualify as a corrosion inhibitor. These requirements include reduction of corrosion rate by the chemical substance and its presence, at suitable concentration, in the corrosion system.

Both ascertaining corrosion rate reduction and determination of suitable concentration for the optimal reduction of corrosion rate require effective monitoring of the corrosion system. Such monitoring techniques usually require electrochemical and non-destructive methods of measurement and subsequent comparison, especially in different corrosion systems, of the corrosion status of reinforcing steel in concrete structures. A lot of these electrochemical measuring methods for monitoring corrosion of steel in concrete had been described in literature (Song and Saraswathy, 2007). Many of them, however, require very costly and highly sophisticated equipments. Also, a good number of them suffer the setback of been applicable for monitoring laboratory setup of corrosion system only but find no suitability for monitoring corrosion in field applications of reinforced concrete structures.

The open circuit potential (OCP) monitoring system has been known as a good monitoring method that is both suitable for monitoring probability that corrosion is occurring in steel reinforcement embedded in concrete. This method, which had been employed in many studies (Loto, 2012; Okeniyi et al 2012a; Omotosho et al, 2011; Loto 2011a; Loto, 2011b, Omotosho et al, 2010; Burubai and Dagogo, 2007; Song and Saraswathy, 2007), utilizes simple equipments which are very easy to setup both in the laboratory as well as in the field applications for diagnosing corrosion risks in reinforced concrete structures. Also, standard for interpreting measurements from the OCP monitoring method exists, especially, that which had been provided by the American Society for Testing and Materials (ASTM) generally known as ASTM C876 (Song and Saraswathy, 2007).

Although the open circuit potential measuring method has been studied for relationship between its potential measurements and corrosion rate in well established laboratory conditions, the generalization of the results had not been possible (Song and Saraswathy, 2007). This is both due to the wide variation of corrosion rate that could be possible within narrow range of open potential readings and the stochastic response in the potential readings that could results in the dynamic active-passive mechanism of the corrosion system. The consequences from these had included prevalent conflicting interpretations and contradicting reports in corrosion inhibitor studies.

According to Haynie (2005), variations and stochastically differing results require the use of statistical methods of probability distributions for the treatment of corrosion data for assessing the prevalent conditions in the corrosive environments. However, this approach had been identified as a neglected one among the tools for interpreting and requisite treatment of corrosion data. By this, there is paucity of studies in literature deliberating on suitability or otherwise of statistical probability distribution for studying performance of inhibitor admixtures on the corrosion of steel reinforcement in concrete. This paper therefore studies the suitability of the Normal and Weibull modeling tool applications for investigating corrosion potential performance of $Na_2Cr_2O_7$ on the corrosion of reinforcing steel in concrete immersed in NaCl, simulating marine or saline environments.

2. Materials and Methods

Reinforced concrete blocks

Twelve reinforced concrete block samples used for the experiment were produced as replicates blocks of size 100 mm × 100 mm × 200 mm. Embedded in each block was 150 mm length of steel rebar which was symmetrically placed across the width of the block with the remaining length of the rebar protruding for electrochemical connections. Each of the concrete blocks was made of water and a mixture of Portland cement, sand and granite stones in a mix proportion of 1:2:4 (C:S:G). The formulation used for the reinforced concrete specimens was 300.0 kg/m^3 of cement, 149.7 kg/m^3 of water, 890.6 kg/m^3 of sand, and 1106.3 kg/m^3 of granite stones. The water/cement (w/c) ratio was 0.499. For these reinforced specimen samples, the $Na_2Cr_2O_7$ admixture concentrations were varied from 0 g (for the control specimen replicates) in increments of 2 g up to 10 g of $Na_2Cr_2O_7$. The inhibitor admixed concrete blocks were moulded with wood covered with non-absorbent material that is non-reactive with concrete and cured in a curing room for 28 days. The rebar protrusion was painted with glossy paint.

2.1 Experimental Procedure

Corrosion test setup

Steel reinforced concrete samples were partially immersed, longitudinally, in plastic bowls containing 3.5% NaCl solution (Zhou et al, 2012; Zafeiropoulou et al, 2011). In each bowl, the test solution was made up to just below the reinforcing steel rebar but was not touching it. From these, open circuit potential (OCP) measurements were taken versus Cu/CuSO$_4$ electrode (CSE), using a high impedance digital multimeter according to ASTM C876, in five days interval through an experimental period of forty days.

Data Analysis

Probability distribution modelling

Test data of the potential response from the corrosion test setup were subjected to statistical analysis of the Normal and the Weibull distribution functions (Okeniyi et al, 2012a; Okeniyi et al, 2012b; Omotosho et al, 2011). While the application of the Normal distribution for modelling data had been described elsewhere (Okeniyi et al, 2012b), the Weibull distribution is an extreme-value modelling distribution with probability density function, pdf (Omotosho et al, 2011; Montgomery and Runger, 2003):

$$f(x) = \frac{k}{c}\left(\frac{x}{c}\right)^{k-1} \cdot \exp\left\{-\left(\frac{x}{c}\right)^{k}\right\} \qquad 1$$

Where k is the shape parameter and c is the scale parameter. Estimations of these parameters were done as described in Omotosho et al (2010) and these find usefulness for computing the Weibull predictions of the mean μ_W and the standard deviation σ_W, respectively, using the relationships (Murthy et al, 2004; Montgomery and Runger, 2003):

$$\mu_W = c\Gamma\left(1+\frac{1}{k}\right) \qquad 2$$

$$\sigma_W = \sqrt{c^2\left\{\Gamma\left(1+\frac{2}{k}\right) - \left[\Gamma\left(1+\frac{1}{k}\right)\right]^2\right\}} \qquad 3$$

where Γ(·) is the gamma function of (·).

Goodness-of-fit test statistics

To ascertain the compatibility of the OCP data to each of the statistical distributions employed, the Kolmogorov–Smirnov (K-S) goodness of fit test (Thas, 2010; Soong, 2004; Izquierdo et al, 2004; Roberge, 2003) was used. This measures the absolute difference between empirical distribution function $F^*(x)$ and theoretical distribution function $F(x)$ (Thas, 2010; Soong, 2004) through the statistics

$$D_n = D(x_1, \ldots, x_n) = \sup_{-\infty<x<\infty} \left|F^*(x) - F(x)\right| \qquad 4$$

The *D*-value evaluation from Equation **Error! Reference source not found.** was used for direct computation of the K-S *p*-value using procedures that had been described in Okeniyi and Okeniyi (2011). By this, criteria could be set such that, for $\alpha = 0.05$ significant level, K-S *p*-value $< \alpha$ for a probability distribution model of corrosion test data indicate that such data did not follow that distribution while K-S *p*-value $\geq \alpha$ showed that the test data followed the distribution model.

3. Results and discussions

Measured experimental data

Plots of the measured data of open circuit corrosion potential response through the forty days experimental period are presented in Fig. 1 for the reinforced concrete samples admixed with different replicated concentrations of $Na_2Cr_2O_7$ and immersed in 3.5% NaCl. While it could be deduced from the plots, that the corrosion potential response of the control samples had, by the fortieth day overshot the potential response of the remaining samples with inhibitor admixture, thus depicting inhibition, the plots still exhibit stochastic variability among the samples. This variability could make interpretation or evaluation of the performance of the concrete admixture on the rebar corrosion difficult, hence, re-affirming the need for the use of statistical modeling tool for evaluating this variability and aiding result interpretations.

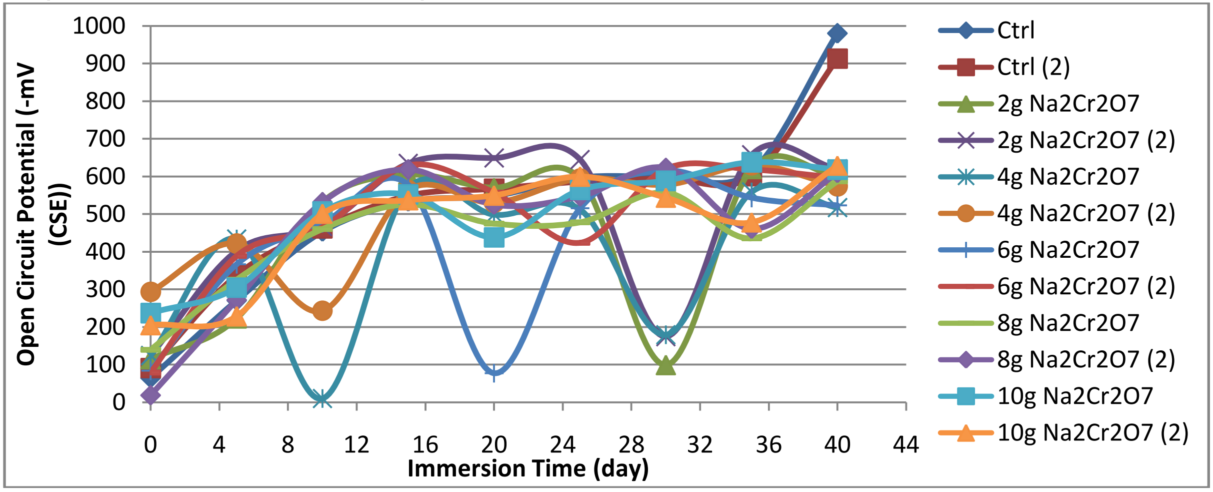
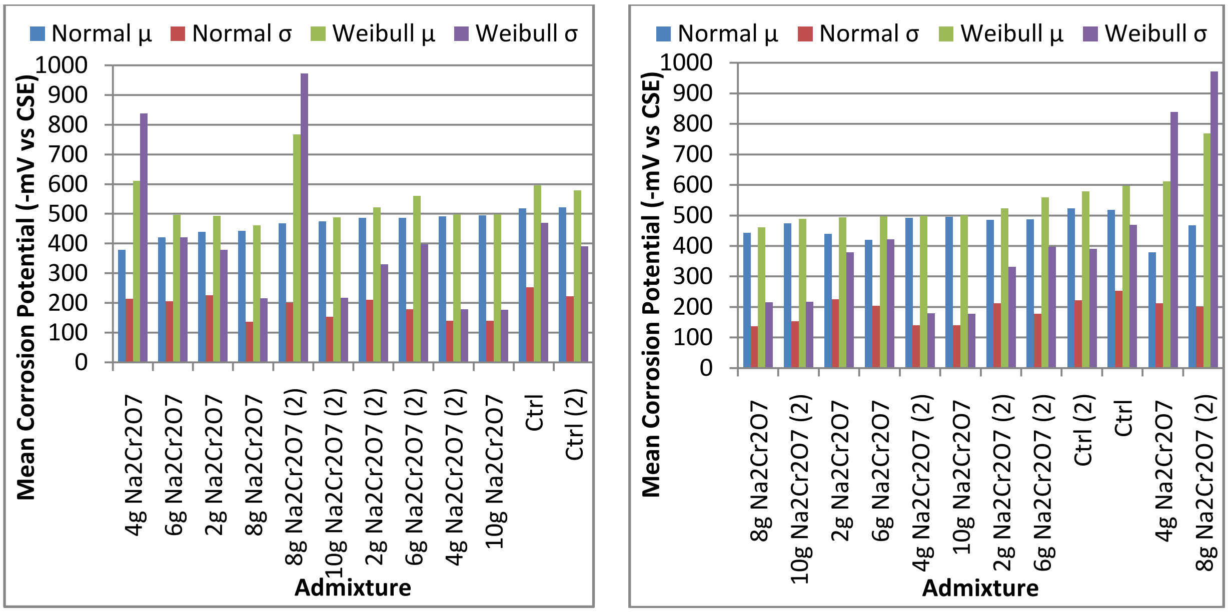


Fig. 1 Corrosion potential response of $Na_2Cr_2O_7$ admixtures in reinforced concrete samples

Statistical modeling and analyses

Results of the Normal pdf and that of the Weibull pdf models of the potential response data of $Na_2Cr_2O_7$ admixture concentrations in steel reinforced concrete samples are presented in ranking order in Fig. 2. In this figure, rankings by the Normal model are shown in Fig. 2(a) while that by the Weibull model are shown in Fig. 2(b). From these, it could be observed that while the Normal pdf model identified the 4 g $Na_2Cr_2O_7$ sample with optimal, more positive corrosion potential inhibition ranking, the Weibull pdf modeled this same sample as exhibiting corrosion potential even more negative (and higher corrosion probability) than the replicate samples of control specimens. Also, while the Normal model agrees in the ranking order of the effectiveness of the replicate samples of the 8 g $Na_2Cr_2O_7$ replicate samples, Fig. 2(a), the Weibull model identified one of these samples with optimal corrosion potential inhibition performance and its replicate as exhibiting the most negative corrosion potential (and the highest or most severe corrosion probability) in all the samples studied in this work, Fig. 2(b). Thus, while the Normal pdf model were in agreement that all concrete samples admixed with $Na_2Cr_2O_7$ exhibited better corrosion potential performance than the control samples though with slight discrepancies in the ranking order of replicate samples, the Weibull pdf model identified two samples admixed with $Na_2Cr_2O_7$ performing exhibiting worse performance than the two replicates of control samples. A close observation of the plots showed that these two samples, the 4 g $Na_2Cr_2O_7$ and the replicate of 8 g $Na_2Cr_2O_7$, both exhibited very high values of Weibull pdf model standard deviations (Weibull σ) which were even higher than the Weibull mean models for these samples. This portends wide range of scattered corrosion potential data in the Weibull model of these test data, even as it genders questions on how well these sets of data followed the Weibull distribution modeling function.



(a) (b)

Fig. 2 Ranking models of $Na_2Cr_2O_7$ inhibition performance by potential response in reinforced concrete samples (a) Normal pdf model (b) Weibull pdf model

The results of testing how well the modeled data followed each of the statistical distribution models employed in this paper, using the Kolmogorv-Smirnov goodness of fit statistics, are presented in Fig. 3. This showed that all the modeled data of corrosion potential response of steel reinforced concrete samples followed both the Normal pdf model and the Weibull pdf model at the significance level of $\alpha = 0.05$, shown in the figure. By this, it could be surmised that discrepancies observed in the pdf models depend more on the applied pdf model than on the corrosion potential data. Thus, because the Normal pdf exhibited better agreements in its models of these data than the Weibull pdf, it is adjudged as the suitable pdf model for describing the performance of the $Na_2Cr_2O_7$ admixtures on the corrosion potential of the concrete reinforcing steel specimens in this study.

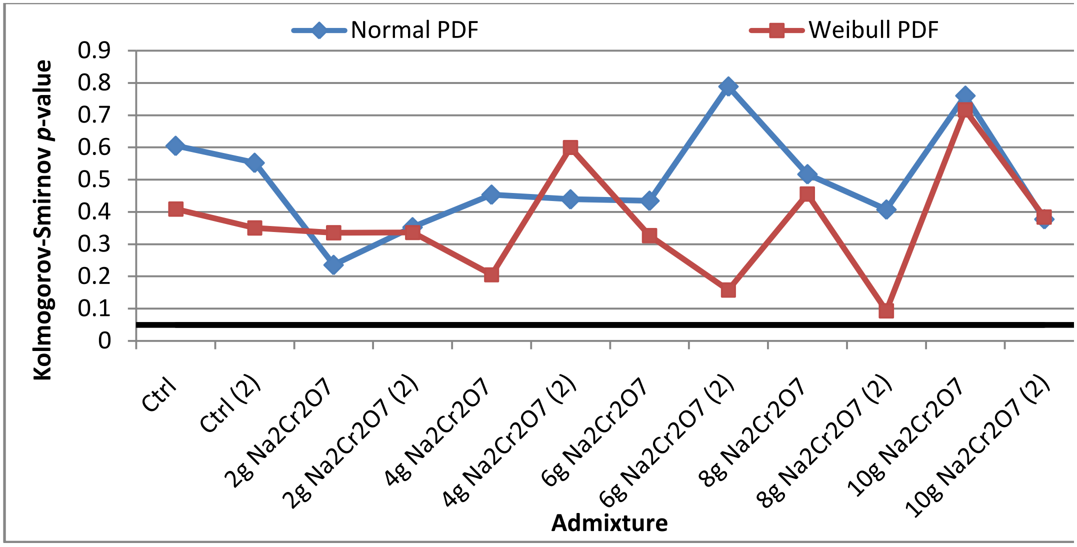


Fig. 3 Kolmogorov-Smirnov goodness of fit test results of how well the corrosion potential response data of $Na_2Cr_2O_7$ admixtures in reinforced concrete samples follows the Normal and the Weibull distribution functions

From the foregoing considerations, the Normal pdf model results are employed for estimating averaged model of $Na_2Cr_2O_7$ performance on the corrosion potential response of steel reinforced concrete immersed in saline media, in this study. The plots of this averaged performance model are presented in Fig. 4. From this figure, the 4 g $Na_2Cr_2O_7$ admixture is modeled as exhibiting optimal corrosion potential inhibition performance among all the samples studied in this experimental work. This was followed in order by the 6 g $Na_2Cr_2O_7$, the 8 g $Na_2Cr_2O_7$, the 2 g $Na_2Cr_2O_7$ and then the 10 g $Na_2Cr_2O_7$ before the control sample.

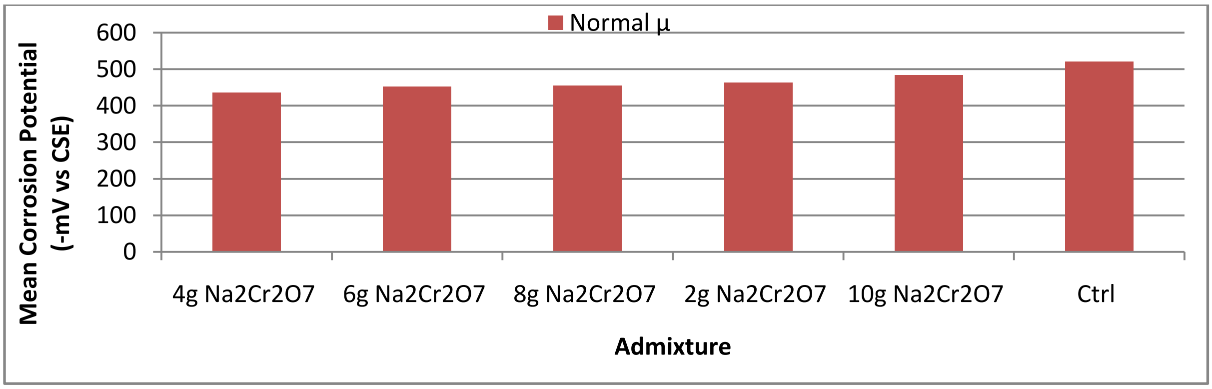


Fig. 4 Ranking of Normal averaged model of $Na_2Cr_2O_7$ performance on the corrosion potential response of steel reinforcement in concrete

These results bear implications on the need for studying suitability of statistical distribution functions for tackling inherent variability in corrosion test data and for aiding interpretation of the prevailing conditions in these datasets. Also, there is need for further studies deliberating on suitable statistical tools for handling discrepancies in results observed among replicate samples admixed with similar concentrations of inhibitor admixtures. Such studies would be useful for assessing significance or otherwise of observed or modeled discrepancies and which could serve as important tools for avoiding conflicting and contradictory reports of corrosion inhibitor performance.

4. Conclusions

Effects of $Na_2Cr_2O_7$ admixtures on the corrosion potential response of steel reinforced concrete in immersed saline medium had been studied using the Normal and the Weibull distribution functions. From these, the following conclusions can be drawn:

- The non-destructive test data of corrosion open circuit potential response, measured through the experimental period, exhibited stochastic data which require probability density fittings for modeling order and interpreting inhibitor performance;
- Results of Normal pdf model of the test data of corrosion potential response exhibited better agreements among the replicates of steel reinforced concrete samples studied than the results obtained from the Weibull pdf of the same datasets;
- The test data of corrosion potential response followed the Normal distribution and the Weibull distribution model at $\alpha = 0.05$ significant level, through the Kolmogorov-Smirnov goodness of fit statistics, by this, the discrepancies observed in the statistical models of the corrosion test data in the study were surmised to be due to the suitability of the statistical probability model for describing the test datasets, thus, because the Normal pdf exhibited less of these discrepancies, it was adjudged as the suitable pdf model for interpreting inhibitor performance in the corrosion setup system;
- By these, considerations, the application of the Normal pdf model identified the 4 g $Na_2Cr_2O_7$ admixture as exhibiting optimal more positive corrosion potential and thus the admixture with optimum inhibition performance, on the corrosion of steel reinforcement in concrete, among the other $Na_2Cr_2O_7$ admixture studied in this work;
- These bear implications of the need for studying suitability of statistical probability distribution models for requisite analyses and interpretation of corrosion test data results in the performance studies of corrosion inhibitor in steel reinforced concretes, even as these also genders suggestions for the use of further applications of necessary statistical tools for studying significance of discrepancies encountered among the replicates samples admixed similar concentrations of inhibitor admixtures.

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