

Analysis of inhibition of concrete steel-rebar corrosion by $\text{Na}_2\text{Cr}_2\text{O}_7$ concentrations: Implications for conflicting reports on inhibitor effectiveness

J. O. Okeniyi¹, I. O. Oladele¹, I. J. Ambrose¹, S.O. Okpala¹, O. M. Omoniyi¹, C. A. Loto^{1,2}, A. P. I. Popoola²

1. Mechanical Engineering Department, Covenant University, Ota 112001, Nigeria;

2. Chemical, Metallurgical and Materials Engineering Department, Tshwane University of Technology, Pretoria 0001, South Africa

© Central South University Press and Springer-Verlag Berlin Heidelberg 2013

Abstract: Corrosion test data were measured using non-destructive electrochemical techniques and analysed for studying inhibition effectiveness by different concentrations of $\text{Na}_2\text{Cr}_2\text{O}_7$ on the corrosion of concrete steel-rebar in NaCl and in H_2SO_4 media. For these, specifications of ASTM G16-95 R04 were combined with the normal and the Gumbel probability density functions as model analytical methods for addressing issues of conflicting reports of inhibitor effectiveness that had generated concerns. Results show that reinforced concrete samples admixed with concentrations having 4 g (0.012 7 mol), 8 g (0.025 4 mol) and 6 g (0.019 1 mol) $\text{Na}_2\text{Cr}_2\text{O}_7$ exhibited, in that order, high inhibition effectiveness, with respective efficiency, η , of $(90.46 \pm 1.30)\%$, $(88.41 \pm 2.24)\%$ and $(84.87 \pm 4.74)\%$, in the NaCl medium. These exhibit good agreements within replicates and statistical methods for the samples. Also, optimal inhibition effectiveness model in the H_2SO_4 medium was exhibited by 8 g (0.025 4 mol) $\text{Na}_2\text{Cr}_2\text{O}_7$ concentration having $\eta = (78.44 \pm 1.10)\%$. These bear implications for addressing conflicting test data in the study of effective inhibitors for mitigating steel-rebar corrosion in aggressive environments.

Key words: corrosion inhibitor effectiveness; saline/marine and industrial/microbial environments; concrete steel-rebar; normal and Gumbel probability distribution functions; Kolmogorov-Smirnov statistics; tests of significance

1 Introduction

Steel reinforced concrete has remained an important and widely used man-made construction material globally due to the various applications of buildings and infrastructural developments to which it could be employed [1–5]. However, environmental induced corrosion degradation of the reinforcing steel (steel-rebar) in concrete had necessitated repairs, maintenances, rehabilitations for preventing premature failure of steel-reinforced concrete structures and its inherent unexpected risks to safety of life and properties [1, 6–7]. Usually, durability of steel-reinforced concrete is ensured by high alkalinity of the concrete pore environment under $\text{pH} > 12.5$, which protects the embedded steel by a thin stable passive oxide film strongly adherent to the steel surface from concrete hydrated products [8–11]. The breakdown of this passive oxide film, usually induced through reduction of concrete alkalinity, by environmental agents of corrosion renders steel-rebar in concrete susceptible to corrosion deterioration. Such environmental agents affect steel-rebar corrosion through the mechanisms of carbonation from atmospheric [12],

chloride ingress from saline/marine [13–15] or sulphate attack from acid rain in industrial [16] and from microbial activities [17–18] in sewage [19–20] environments. The service life of the reinforced concrete is affected by the by-products from these corrosion degradations which are characterised by low structural strength and expansive volume that induces stresses within the concrete. Such stresses progress into cracks, spalling, delamination and, if unchecked, eventual catastrophic collapse of the concrete structure [15, 19, 21–22].

Among several methods that had been proposed in literature for mitigating corrosion problems of steel-rebar in concrete, the use of corrosion inhibitor admixtures had been identified as a useful one for prolonging durability and service-life of reinforced concrete structures [2, 22–28]. In spite of the important contributions on the usefulness of corrosion inhibitors for repair and maintenance cost reductions [5, 26], conflicting reports had abounded on inhibitor effectiveness bordering on the determination of suitable inhibitor concentration for adequate rebar corrosion protection in aggressive environments [29–32]. While some studies reported effective corrosion inhibitions, others had requested the

need for further research, especially those that would be directed at investigating inhibitor concentrations.

The concentration of a corrosion inhibiting substance admixed in concrete plays a very deciding role on whether such substance would mitigate corrosion or not [5]. This is because a corrosion inhibitor, according to ISO 8044 1989, is required as a chemical substance to be added in suitable concentration for it to decrease the corrosion rate to acceptable level in the corrosive system [24, 30]. According to VAYSBURD and EMMONS [33], if an inhibiting substance was to be otherwise present in an unsuitable quantity in the corrosive system, it could, rather than inhibit, promote intensely localised corrosion attack on the reinforcing steel in concrete. These considerations necessitate detailed investigation of inhibitor concentration for attaining acceptable reduction in the corrosion rate of steel-rebar as an important requirement for responsible application of inhibitor admixtures in steel-reinforced concrete structures.

Most, studies of inhibitor effectiveness involve the use of non-destructive electrochemical monitoring methods, over time [34], which are usually characterised with high variability and stochastically scattered readings [24, 35–36]. These make interpretations difficult and could lead to non-uniformity in reports by investigators. The rational approach prescribed for addressing these inherent scatter in measurements of corrosion test results, by the standard of the American Society for Testing and Materials (ASTM), had been the use of the statistical tools described in ASTM G16-95 R04 [37–39]. However, there are dearth of studies in which the analytical methods described in this standard had been employed for investigating effectiveness of inhibitor admixture in steel reinforced concrete, especially for addressing variability and conflicts in corrosion test results.

This work therefore examines the use of the statistical methods prescribed in ASTM G16-95 R04 [37] for the analysis of the inhibition effectiveness of different concentrations of sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) on the corrosion of concrete steel-rebar in NaCl and in H_2SO_4 media. Dichromate are well known inhibitors [34, 40] and their compounds have been employed in studies by Refs. [24, 33, 35, 41–42]. But well known inhibitors, including commercial ones, are not spared from reports of conflicting inhibition effectiveness prevailing in Refs. [30, 32, 43–44]. These channeled the major intents in this work towards that of employing the established inhibiting properties of dichromate on steel-rebar corrosion for model study of how the procedures [37] could be harnessed for tackling conflicting results of inhibitor effectiveness. Authors of this work are not aware of any other where this admixture had been used to study applicability for addressing results conflicts in inhibition studies. Therefore, it is opined that this kind of

work could engender the application of the methods of this standard, especially, for investigating other types of corrosion inhibitors that are not yet well known.

2 Materials and methods

2.1 Materials

2.1.1 Chemicals used

1) Solutions: Distilled water was used to prepare all solutions [27], except concrete mixing for which drinkable tap water was used [3, 15].

2) Inhibitor: Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7$, (Eurostar Scientific)

3) Aggressive agents: Sodium chloride, NaCl, (Eurostar Scientific); Sulphuric acid, H_2SO_4 , (Sigma-Aldrich)

4) Others: Acetone, $(\text{CH}_3)_2\text{CO}$, for degreasing (Sigma-Aldrich); iso-propyl alcohol, $\text{CH}_3\text{CHOHCH}_3$, for wetting fluid (J. T. Baker).

2.1.2 Reinforcing steel specimen

Steel reinforcement used in the work was obtained from Federated Steel Rolling Mills, Ota, Ogun State, Nigeria. The 12 mm diameter deformed rebar has the composition (mass fraction) of: 0.27% C, 0.40% Si, 0.78% Mn, 0.04% P, 0.04% S, 0.14% Cr, 0.11% Ni, 0.02% Mo, 0.24% Cu, 0.01% Co, 0.01% Nb, 0.01% Sn and the balance Fe. The steel rebar were cut into lengths of 190 mm for each rod of specimens. For these, surface preparation was maintained uniformly. Each deformed rebar was grinded with coarse and fine abrasive papers, pickled for 10 min in 10% H_2SO_4 [45], rinsed and cleaned in ultrasonic cleaner, degreased with acetone, dried with warm air stream and kept in desiccator prior to being used for the experiment [46–47].

2.1.3 Reinforced concrete blocks

Twenty-eight reinforced concrete block samples used for the experiment were produced as replicated blocks [36], each size of 100 mm×100 mm×200 mm. Embedded in each block was 150 mm length of the steel rebar which was symmetrically placed across the width of the block leaving 40 mm steel protrusion for electrochemical connections. Each of the concrete blocks was made of drinkable water and a mixture of Portland cement, clean natural sand [25, 48] from River Ogun in Nigeria and granite stones [23], of maximum size ≤ 19 mm, in a mix proportion (mass ratio) of 1:2:4 (C:S:G). The formulation used for the reinforced concrete specimens was 300.0 kg/m³ of cement, 149.7 kg/m³ of water, 890.6 kg/m³ of sand, and 1 106.3 kg/m³ of granite stones. The water-cement mass ratio was 0.499 [44–45]. Concrete blocks were batch mixed, moulded with wood covered with non-absorbent polyvinyl-chloride (PVC) material that is non-reactive with concrete, externally vibrated on an electric vibrator

(Matest equipment) and cured in a curing room for 28 d. All these were done in accordance with ASTM C192/192M-02 [49]. The departure from ASTM C192/192M-02 was that the specification maintained limitation of hand mixing volume to 0.007 m^3 , whereas a slightly higher volume of 0.008 m^3 had to be mixed in this work. This was done to ensure uniformity of admixture concentrations in each replicated sample for the two corrosive media being investigated which was such that each batch was made of four concrete specimen samples. The rebar protrusion was painted with glossy paint.

2.1.4 Inhibitor admixture

The $\text{Na}_2\text{Cr}_2\text{O}_7$ admixture concentrations in each specimen are presented in Table 1. For each batch of concrete mixing, the admixture was weighed on an

Table 1 Admixture concentrations in steel reinforced concrete samples

No.	Admixture concentration
1	0 g $\text{Na}_2\text{Cr}_2\text{O}_7$ (Control in NaCl)
2	0 g $\text{Na}_2\text{Cr}_2\text{O}_7$ (Control in H_2SO_4)
3	0 g $\text{Na}_2\text{Cr}_2\text{O}_7$ (Control in NaCl_Rep)
4	0 g $\text{Na}_2\text{Cr}_2\text{O}_7$ (Control in H_2SO_4 _Rep)
5	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl
6	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
7	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep
8	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
9	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl
10	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
11	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep
12	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
13	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl
14	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
15	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep
16	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
17	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl
18	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
19	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep
20	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
21	10 g (0.0318M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl
22	10 g (0.0318M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
23	10 g (0.0318M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep
24	10 g (0.0318M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
25	16 g (0.0509M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl
26	16 g (0.0509M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
27	16 g (0.0509M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep
28	16 g (0.0509M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep

analytical weighing balance (Adam equipment, PW 254, $250 \text{ g} \times 0.0001 \text{ g}$) and thoroughly mixed with some water before being made up to the required water volume for the concrete batch [49]. Concentrations varied from 0 g (for the control specimen replicates) in increments of 2 g (0.0064 mol) up to 10 g (0.0318 mol) of $\text{Na}_2\text{Cr}_2\text{O}_7$ for the reinforced samples. In addition, replicated samples with 16 g (0.0509 mol) of $\text{Na}_2\text{Cr}_2\text{O}_7$ were made to study the effect of high concentration of $\text{Na}_2\text{Cr}_2\text{O}_7$ admixture on the corrosion of steel-rebar in concrete. All these concentrations in mol/L (molarity) were computed from the inhibitor masses relative to the mixing water for each concrete batch. Hereafter, these are referred to by masses in the study.

2.2 Experimental procedures

2.2.1 Corrosion test setup

Steel reinforced concrete samples were partially immersed, longitudinally, in plastic bowls containing respective test solution of aggressive agent, Fig. 1. Each of the first replicated set of fourteen samples was partially immersed in 3.5% NaCl solution [50] while the second replicated set was partially immersed in 0.5M H_2SO_4 solution [51–52]. In each bowl, the test solution was made up to just below the reinforcing steel rebar but was not touching it. To prevent dryness and induce continuous system of corrosive environment, the test solutions were replenished every three weeks in the bowls [27].



Fig. 1 Corrosion test sample replicates

2.2.2 Electrochemical measurements

Non-destructive electrochemical measurements [21, 53–54] were taken from the experimental setup, first, in five days interval for forty days and thereafter in seven days interval for the following five weeks. This totals seventy-five days experimental period for this work. The electrochemical test methods used for evaluating inhibition performance of $\text{Na}_2\text{Cr}_2\text{O}_7$ concentrations include:

1) Half-cell potential (HCP) measurements of the reinforcing steel were measured through the

experimental period versus Cu/CuSO₄ electrode (CSE), Model 8-A (Tinker & Rasor), using a high impedance digital multimeter, Model DT-9205A, according to ASTM C876-91 R99 [55].

2) Electrochemical cell current (ECC) measurements in the concrete-test solution system were measured, versus the CSE, using zero resistance ammeter (ZRA), Model ZM3P (Corrosion Service) [3, 34, 56–57]. This was done for the measurement model of the reinforcing steel dissolution activity [56] in the aggressive test solution systems sharing porous partitioning with the Cu/CuSO₄, as implied in the Daniel cell description by BROOMFIELD [54]. This was premised on the concept that the porous partition by the semi-permeable membrane of the CSE would permit charge exchange, when reference and working electrodes are joined, while being impervious to ion movement. The zero resistance ammeter connection was, therefore, idealised to measure the current ensuing from the charge movement system of this Daniel cell model.

3) Corrosion rate (CR) measurements were obtained through direct instrument conversion to MPY [58] using the three-electrode LPR Data Logger, Model MS1500L (Metal Samples) [34]. As described by SONG and SARASWATHY [21] and BROOMFIELD [54], the three electrodes of this equipment were correspondingly connected to Ag/AgCl SCE reference electrode (EDT direct-ION double junction), brass plate auxiliary and the steel-rebar working electrode [59–60]. By this connection, the instrument, through a true potentiostatic circuit, null any residual potential difference between the reference electrode and the reinforcing steel working electrode after which current was made to flow between the auxiliary and the working electrode. This flowing current then increased until the potential of the working electrode was shifted by $\Delta E=10$ mV relative to the reference electrode. The current increase (ΔI) required to sustain the 10 mV potential (ΔE) was used to compute the polarisation resistance R_p which the instrument employed for direct readout of the corrosion rate in millimeter per year (mm/a).

Readings of the half-cell potential and the electrochemical cell current were taken at three different points on each concrete block, directly over the embedded reinforcement, and the average computed. The corrosion rate measurements were taken centrally on each concrete block specimen. To ensure good electrical contact for these electrochemical measurements, a water retentive conducting sponge was employed for the point of contact of the measuring probes and the reinforced concrete [21]. This sponge was wetted before measurements using contact solution consisting of drinkable tap water, small addition of iso-propyl alcohol and some local detergent, as prescribed in Ref. [55], to

improve the wetting characteristics of the conducting solution.

2.3 Data analysis

2.3.1 Probability distribution modelling

Each measured entity of electrochemical data was denoted as proceeding from system of independent and identically distributed (i.i.d.) random samples [61–62]. By this way, they were subjected to the statistical analysis of the normal and the Gumbel distribution functions [18, 61, 63–67]. The application of the normal distribution for modelling data had been described elsewhere [68]. This normal probability density function (PDF) modeling is especially useful for establishing normality conditions for many of the procedures of Ref. [37] because the condition of normality is usually, a requisite criterion for studying agreements, or otherwise, of central tendencies and variability of corrosion test measurements. However, the procedure of Ref. [37] could still be robustly applied even when normality condition could not be satisfied. Also, the Gumbel distribution is a type I extreme-value modelling distribution having PDF given by Refs. [64–66]:

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

where k is the scale parameter and c is the location parameter. Estimations of these parameters were obtained, for sample size n , from the solution of the simultaneous maximum likelihood equations [62, 67]:

$$\hat{k} + \hat{c} + \frac{1}{n} \sum_{i=1}^n x_i \exp\left\{-\frac{x_i - \hat{c}}{\hat{k}}\right\} - \frac{\hat{c}}{n} \sum_{i=1}^n \exp\left\{-\frac{x_i - \hat{c}}{\hat{k}}\right\} = \bar{x} \quad (2)$$

$$\sum_{i=1}^n \exp\left\{-\frac{x_i - \hat{c}}{\hat{k}}\right\} = n \quad (3)$$

For these, the combined fixed point iterative–Aitken Δ^2 procedures were employed [64, 69–70]. The unbiased estimated values of k and c , from these, were used to compute the Gumbel mean model from

$$\mu_G = c - k\Gamma'(1) \quad (4)$$

where $\Gamma'(1) = \gamma$ is Euler's constant and the value of

$$\frac{d\Gamma(n)}{dn} \text{ is evaluated at } n=1.$$

2.2.3 Goodness-of-fit test statistics

According to the dictates of Ref. [37], compatibility of each variable of electrochemical data to the normal and the Gumbel distribution functions were verified using the Kolmogorov–Smirnov (K-S) goodness-of-fit (GoF) test statistics [35, 65–66, 68, 71–75]. The K-S GoF method measures the absolute difference between empirical distribution function ($F^*(x)$) and theoretical

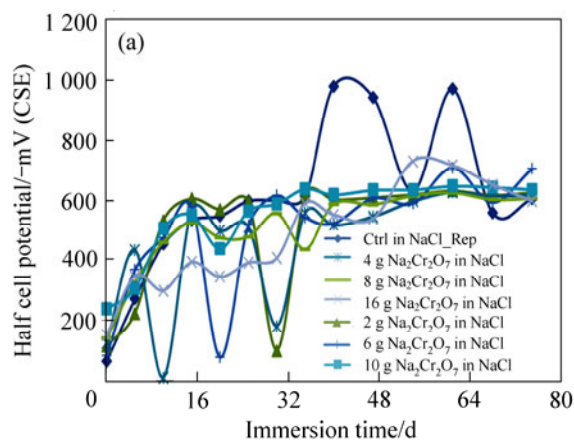
distribution function ($F(x)$), for n data points, through the statistics

$$D_n = D(x_1, \dots, x_n) = \sup_{-\infty < x < \infty} |F^*(x) - F(x)| \quad (5)$$

The D -value evaluation from Eq. (5) was used for direct computation of the K-S p -value using procedures that had been described in OKENIYI and OKENIYI [71]. By this approach, K-S p -value $< \alpha$ for a probability distribution model of corrosion test data indicates that such data were not scattered like that distribution while K-S p -value $\geq \alpha$ showed scattering of the test data like the distribution model. For all the statistical tests in this work, the significant level $\alpha=0.05$ was employed, which corresponds to 95% confidence interval [76].

2.3.6 Testing of statistical significance between steel-reinforced concrete samples

Differences between the corrosion test data of the replicated samples of each inhibitor admixtures, 0 g to 16 g, were studied for significance using student's t -test statistics. This includes the t -test with equal variance (EV) assumption (homoscedastic) and that with unequal variance (UV) assumption (heteroscedastic). Significance of differences of variability was investigated using one-way factorial analysis of variance, ANOVA [76]. Procedures, employed for these two statistical testing of significance, were as described in Ref. [37]. In furtherance of the factorial ANOVA, the Dunnett's test statistics was employed as the post hoc procedure for testing significance of variability between steel-reinforced concrete samples admixed with inhibitor and the control specimens without inhibitor [77]. These test methods find usefulness for indicating whether differences encountered in replicated samples (the t -test) or in the concrete samples with admixtures compared with the control (the factorial ANOVA) were due to chance (experimental error) and thus not significant or otherwise [76].



2.3.4 Inhibition efficiency

The Gumbel model of the mean corrosion rate (μ_G) was used for evaluating inhibition efficiency (η) of each replicate of admixture concentration employed, relative to each replicate of control sample, through the formula [51, 78–79]:

$$\eta = \frac{\mu_{G, \text{ctrl}} - \mu_{G, \text{inh}}}{\mu_{G, \text{ctrl}}} \times 100\% \quad (6)$$

3 Results and discussion

3.1 Measured experimental data

Plots of the measured data of non-destructive corrosion tests through the seventy-five days experimental period are presented for the half-cell potential (HCP), the electrochemical cell current (ECC) and the corrosion rate (CR) measurements from Fig. 2 to Fig. 7. In Figs. 2 and 3, the plots of the HCP test data are presented for reinforced concrete samples in NaCl medium and in H_2SO_4 medium, respectively. Plots of the ECC test data are presented for these media in Figs. 4 and 5 while that of the CR test data for the media are presented in Figs. 6 and 7. In each of these figures, the test data of replicates of the reinforced concrete specimens studied were plotted separately in order to aid good view of the graphical plots. These plots show that the corrosion test results were well attended with experimental scatter or variability that could make interpretation difficult. This necessitates needs for employing statistical tools for the analysis of the measured data to aid result interpretation for each steel-reinforced concrete specimen.

3.2 Corrosion test data modeling and analyses

Results of the corrosion test data models by the normal and the Gumbel distribution functions are presented in Table 2 for samples immersed in NaCl medium and in Table 3 for samples in H_2SO_4 medium.

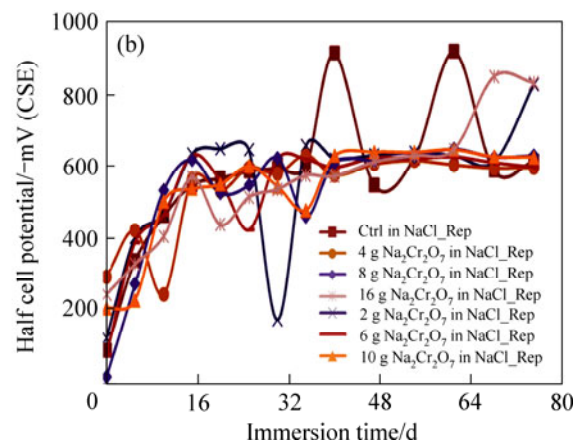


Fig. 2 Measurements of half-cell potential (HCP) test data for steel-reinforced concrete samples partially immersed in NaCl medium: (a) Concrete samples; (b) Replicates of concrete samples

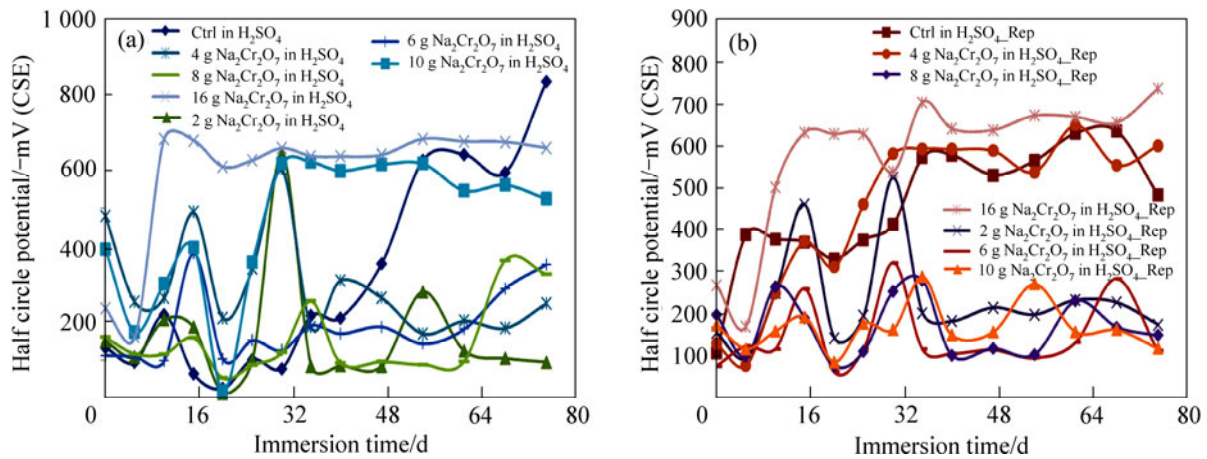


Fig. 3 Measurements of half-cell potential (HCP) test data for steel-reinforced concrete samples partially immersed in H₂SO₄ medium: (a) Concrete samples; (b) Replicates of concrete samples

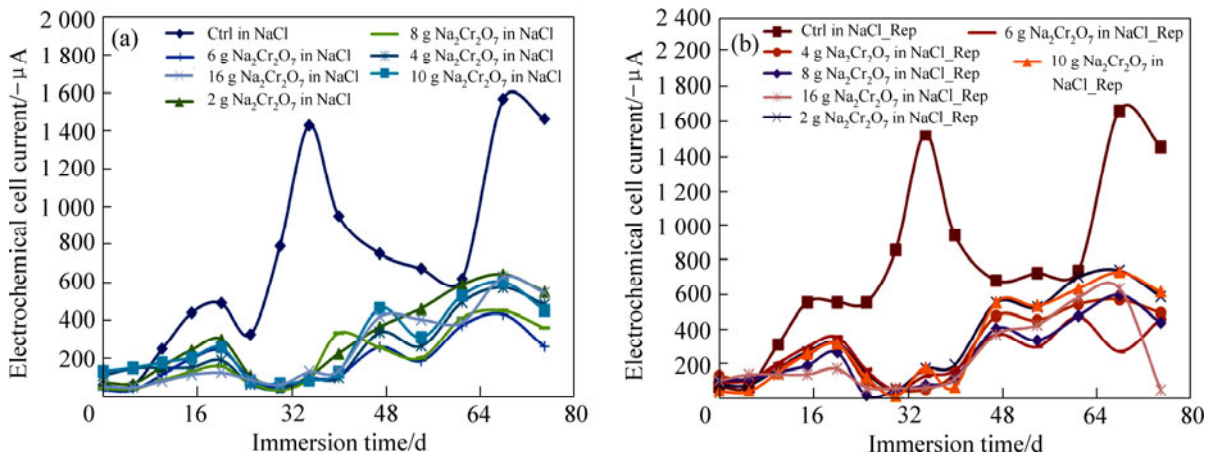


Fig. 4 Measurements of electrochemical cell current (ECC) data for steel-reinforced concrete samples partially immersed in NaCl medium: (a) Concrete samples; (b) Replicates of concrete samples

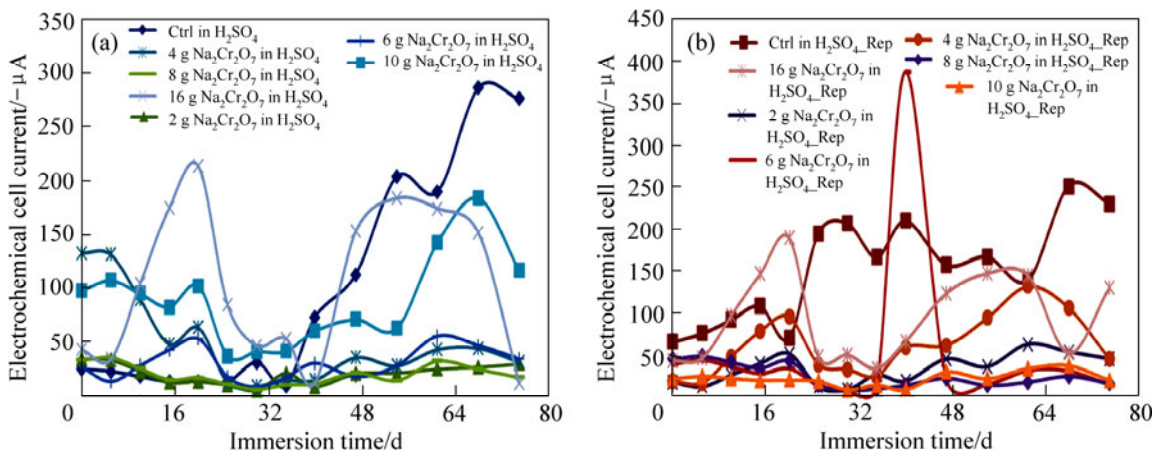


Fig. 5 Measurements of electrochemical cell current (ECC) data for steel-reinforced concrete samples partially immersed in H₂SO₄ medium: (a) Concrete samples; (b) Replicates of concrete samples

From these tables, the modeled values by the two distribution functions instil better form of order to the corrosion test results than the stochastic scatter of the measured data. By these, models of the corrosion potential by the HCP, the steel-rebar dissolution activity through the ECC and the corrosion rate (CR) could be

ascertained for each replicates of admixtures in their corrosive test environments. The corrosion rate (CR), mm/a, modelled for the control (Ctrl) sample ($\mu_N=2.549$; $\mu_G=2.650$) and that for its replicate (Rep) sample ($\mu_N=2.554$; $\mu_G=2.656$) in the saline/marine simulating environment (Table 2) find comparison with the

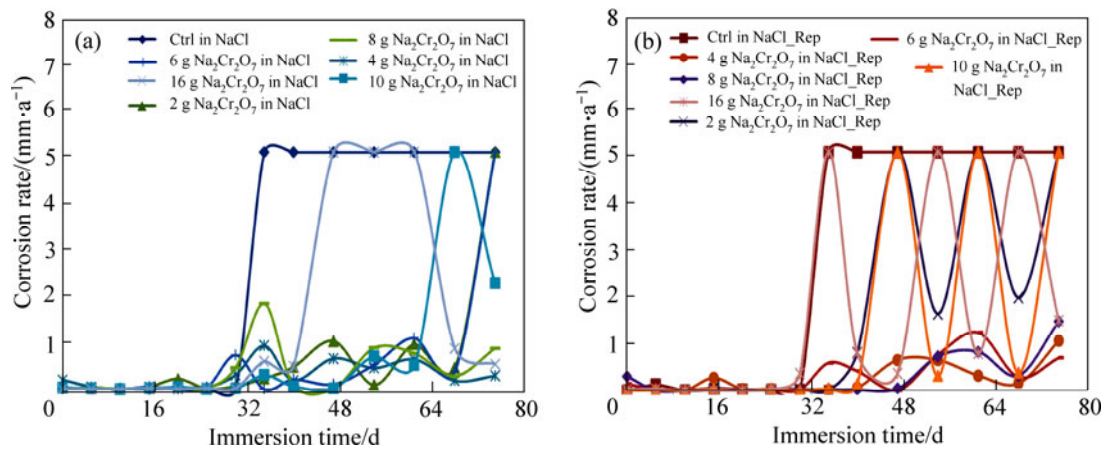


Fig. 6 Measurements of corrosion rate (CR) test data for steel-reinforced concrete samples partially immersed in NaCl medium: (a) Concrete samples; (b) Replicates of concrete samples

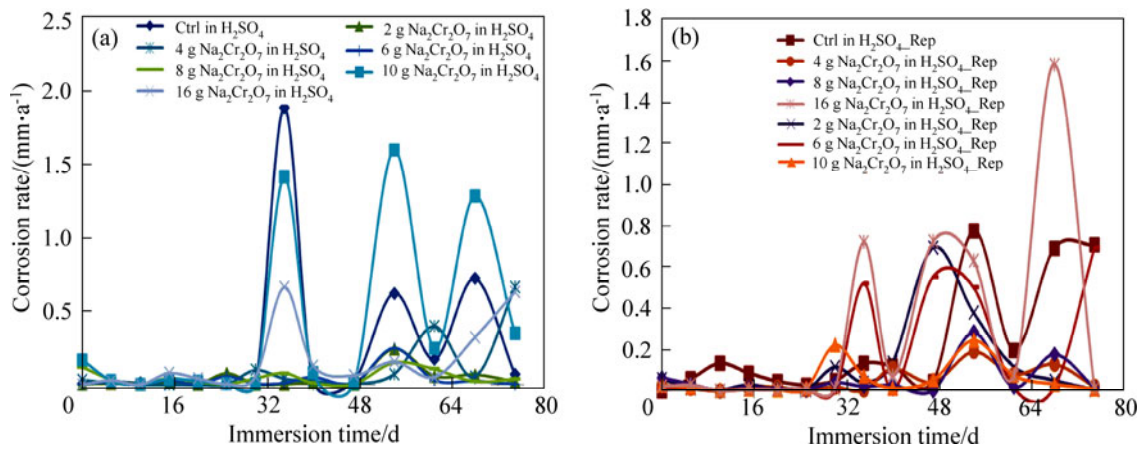


Fig. 7 Measurements of corrosion rate (CR) test data for steel-reinforced concrete samples partially immersed in H₂SO₄ medium: (a) Concrete samples; (b) Replicates of concrete samples

Table 2 Mean of corrosion test data by normal and Gumbel PDF models for samples in NaCl medium

No.	Inhibitor concentration admixed in concrete	Normal distribution			Gumbel distribution		
		$\mu_{N-HCP} / -mV$	$\mu_{N-ECC} / -\mu A$	$\mu_{N-CR} / (mm \cdot a^{-1})$	$\mu_{G-HCP} / -mV$	$\mu_{G-ECC} / -\mu A$	$\mu_{G-CR} / (mm/a^{-1})$
1	0 g Na ₂ Cr ₂ O ₇ (Ctrl) in NaCl	597.83	705.25	2.549	635.31	728.38	2.650
2	0 g Na ₂ Cr ₂ O ₇ (Ctrl) in NaCl_Rep	570.93	764.11	2.554	608.87	794.70	2.656
3	2 g Na ₂ Cr ₂ O ₇ in NaCl	504.31	280.54	0.619	541.26	285.35	0.541
4	2 g Na ₂ Cr ₂ O ₇ in NaCl_Rep	550.98	329.25	1.413	588.15	334.26	1.343
5	4 g Na ₂ Cr ₂ O ₇ in NaCl	457.43	228.06	0.281	494.83	228.05	0.283
6	4 g Na ₂ Cr ₂ O ₇ in NaCl_Rep	531.33	278.10	0.234	557.26	284.36	0.223
7	6 g Na ₂ Cr ₂ O ₇ in NaCl	498.67	176.41	0.591	537.91	180.23	0.510
8	6 g Na ₂ Cr ₂ O ₇ in NaCl_Rep	532.29	245.37	0.298	575.96	252.75	0.292
9	8 g Na ₂ Cr ₂ O ₇ in NaCl	501.07	190.99	0.374	533.53	193.71	0.359
10	8 g Na ₂ Cr ₂ O ₇ in NaCl_Rep	525.02	238.52	0.276	573.26	242.94	0.256
11	10 g Na ₂ Cr ₂ O ₇ in NaCl	545.74	259.44	0.648	572.59	261.24	0.557
12	10 g Na ₂ Cr ₂ O ₇ in NaCl_Rep	531.86	303.81	1.161	562.45	310.48	1.027
13	16 g Na ₂ Cr ₂ O ₇ in NaCl	478.60	231.57	1.271	497.91	229.61	1.159
14	16 g Na ₂ Cr ₂ O ₇ in NaCl_Rep	553.55	217.50	1.367	572.33	212.42	1.274

Table 3 Mean of corrosion test data by normal and Gumbel PDF models for samples in H₂SO₄ medium

No	Inhibitor concentration admixed in concrete	Normal distribution			Gumbel distribution		
		$\mu_{N-HCP} /$ -mV	$\mu_{N-ECC} /$ - μ A	$\mu_{N-CR} /$ (mm·a ⁻¹)	$\mu_{G-HCP} /$ -mV	$\mu_{G-ECC} /$ - μ A	$\mu_{G-CR} /$ (mm/a ⁻¹)
1	0 g Na ₂ Cr ₂ O ₇ (Ctrl) in H ₂ SO ₄	298.52	91.81	0.256	298.30	89.91	0.224
2	0 g Na ₂ Cr ₂ O ₇ (Ctrl) in H ₂ SO _{4_Rep}	453.83	152.51	0.218	481.67	157.20	0.206
3	2 g Na ₂ Cr ₂ O ₇ in H ₂ SO ₄	161.12	19.91	0.035	157.51	20.73	0.032
4	2 g Na ₂ Cr ₂ O ₇ in H ₂ SO _{4_Rep}	230.05	32.10	0.118	229.48	33.09	0.107
5	4 g Na ₂ Cr ₂ O ₇ in H ₂ SO ₄	300.10	49.85	0.101	298.86	49.66	0.089
6	4 g Na ₂ Cr ₂ O ₇ in H ₂ SO _{4_Rep}	449.10	60.28	0.049	477.72	61.64	0.047
7	6 g Na ₂ Cr ₂ O ₇ in H ₂ SO ₄	184.67	29.61	0.035	183.79	30.38	0.032
8	6 g Na ₂ Cr ₂ O ₇ in H ₂ SO _{4_Rep}	142.48	50.11	0.167	140.69	43.59	0.155
9	8 g Na ₂ Cr ₂ O ₇ in H ₂ SO ₄	151.31	19.27	0.047	149.47	19.73	0.047
10	8 g Na ₂ Cr ₂ O ₇ in H ₂ SO _{4_Rep}	164.60	24.79	0.050	167.36	25.15	0.046
11	10 g Na ₂ Cr ₂ O ₇ in H ₂ SO ₄	452.76	88.56	0.375	487.39	90.36	0.346
12	10 g Na ₂ Cr ₂ O ₇ in H ₂ SO _{4_Rep}	166.52	21.22	0.056	169.64	22.00	0.053
13	16 g Na ₂ Cr ₂ O ₇ in H ₂ SO ₄	589.38	102.82	0.159	630.94	106.55	0.149
14	16 g Na ₂ Cr ₂ O ₇ in H ₂ SO _{4_Rep}	577.43	94.04	0.279	614.70	95.59	0.257

corrosion rate of 2.088 mm/a reported for mild steel in the USA [80]. The CR, mm/a, modeled in the industrial/microbial simulating environment for the control sample ($\mu_N=0.256$; $\mu_G=0.224$) and its replicate ($\mu_N=0.218$; $\mu_G=0.206$), in Table 3, compare well with 0.206 mm/a indicated for mild steel in Sweden [80]. Compared to the normal PDF, the Gumbel PDF overestimated the mean test data for many of the results while it underestimated these for the remainders except for the sample with 8 g Na₂Cr₂O₇, in H₂SO₄ medium, where $\mu_{N-CR}=\mu_{G-CR}=0.047$ (correct to 3 decimal places). However, according to Refs. [65–66], the study of how well the fitted corrosion test data from each admixture concentration follow any of these distribution function requires the use of a goodness of fit (GoF) analysis such as the Kolmogorov-Smirnov (K-S) test statistics.

3.2.1 Kolmogorov-Smirnov goodness-of-fit

The *p*-values of the K-S GoF test results are plotted in Fig. 8. The results for samples in NaCl medium are plotted in Fig. 8(a) and those for samples in H₂SO₄ medium are in Fig. 8(b). In each of the figures, the significant level $\alpha=0.05$ is shown for direct identification of test data which follow, or did not follow, each of the modelling distribution functions according to the Kolmogorov-Smirnov GoF criteria. From these, it could be observed that many of the test data scattered like normal and Gumbel pdf. In the NaCl medium, three test data did not follow the normal PDF while two did not scatter like the Gumbel, out of the forty-two data groups fitted in each medium. In the acidic medium, five test

data, four of which in PDF agreements were from the same samples, did not follow normal and Gumbel PDF model.

In the NaCl medium, the corrosion test data of a replicate Na₂Cr₂O₇ sample each of 6 g HCP, 8 g and 10 g CR did not scatter like the Gumbel PDF while the same replicate sample of 10 g CR with that of 16 g CR did not scatter like normal PDF. In the H₂SO₄ medium, the test data of the CR of the control, a replicate each of 6 g and 16 g as well as the ECC of the same replicate of 6 g and the HCP of the other 16 g did not follow the Gumbel distribution function. Also, in the acidic medium, the corrosion test data of the CR of the 4 g, the same replicate of 6 g and the same replicate of 16 g as well as the ECC of the same 6 g replicate and the HCP of the other 16 g failed to scatter like the normal distribution function. It is worth noting that all these samples having their corrosion test data not following the normal PDF and those not following the Gumbel have the test data of their other replicate sample with the same concentration of admixed inhibitor following these distribution functions.

3.2.2 Student's *t*-test of significance between replicates

The use of replicated samples had portrayed very sparse result agreements even within the distribution model of the test data of samples with the same admixed inhibitor concentrations. Interpretation from randomised assignment of one of the replicate samples, from each unit of admixture concentrations, say, to another researcher in a nearby laboratory, sharing the same

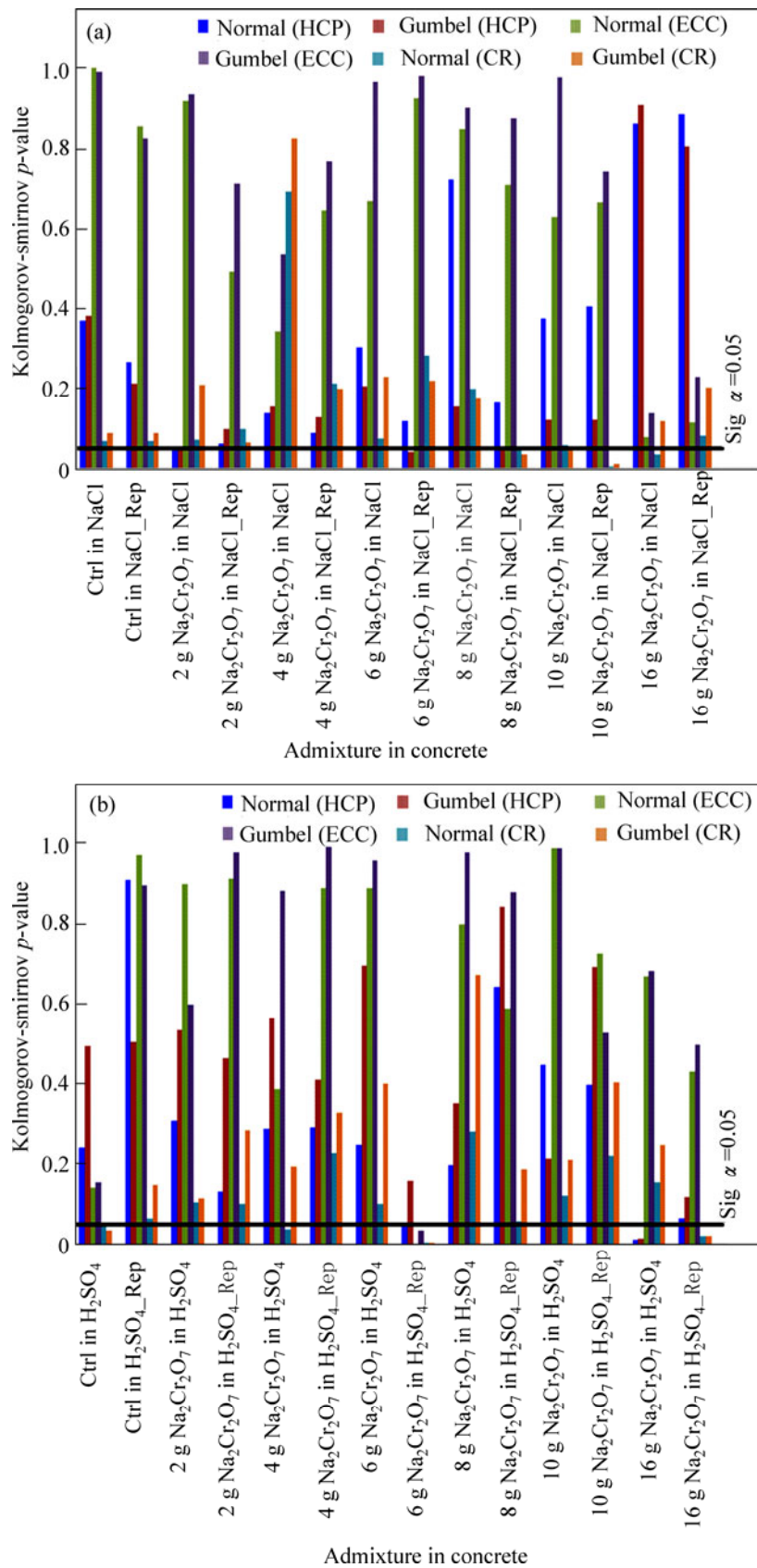


Fig. 8 Goodness of fit test results for reinforced concrete samples in NaCl medium (a) and H₂SO₄ medium (b)

instrument and experimental conditions, would definitely culminate in contradictory reports. From Table 2, in NaCl medium for example, the corrosion rate of 0.281

(normal) or 0.283 (Gumbel) modelled for 4 g Na₂Cr₂O₇ sample would be greater than 1.413 (normal) or 1.343 (Gumbel) results of the replicate with 2 g Na₂Cr₂O₇ in

one lab. In the nearby lab, 0.234 (normal) or 0.223 (Gumbel) of the replicate with 4 g $\text{Na}_2\text{Cr}_2\text{O}_7$ would be less than 0.619 (normal) or 0.541 (Gumbel) of the other 2 g $\text{Na}_2\text{Cr}_2\text{O}_7$ sample. It is of interest to investigate where these encountered discrepancies originated from whether they are due to chance or complexities of rebar corrosion not accounted for in the present experimental design or whether they are significant difference in the test data of each replicated sample. In order to ascertain whether these differences, within the same replicates of admixture concentration, were due to chance or if they were otherwise significant, the applications of the student's t -test statistics would be required, according to the specifications of ASTM G16.

Results of the statistical tests of significance, using the student's t -test statistics are presented, graphically, in Fig. 9, for each replicated admixture concentration in the

NaCl medium, Fig. 9(a), and in the H_2SO_4 medium, Fig. 9(b). The graphical plots include the t -test with equal variance (EV) assumed as well as that for unequal variance (UV) assumption. The significant level $\alpha=0.05$ is also indicated on each plot for direct identification of significant differences.

From Fig. 9(a), it could be observed that all the differences encountered in the corrosion test data of each of the admixture concentrations replicated in the NaCl medium were due to chance or unaccounted complexities in the rebar corrosion attacks, but were not significant.

However, in the H_2SO_4 medium, Fig. 9(b), differences encountered from the ECC test data models of the replicates of 2 g samples and those encountered in the HCP test data models of the replicates of 4 g samples were not due to chance but significant. Also in the medium, the replicates of 10 g samples only had the CR

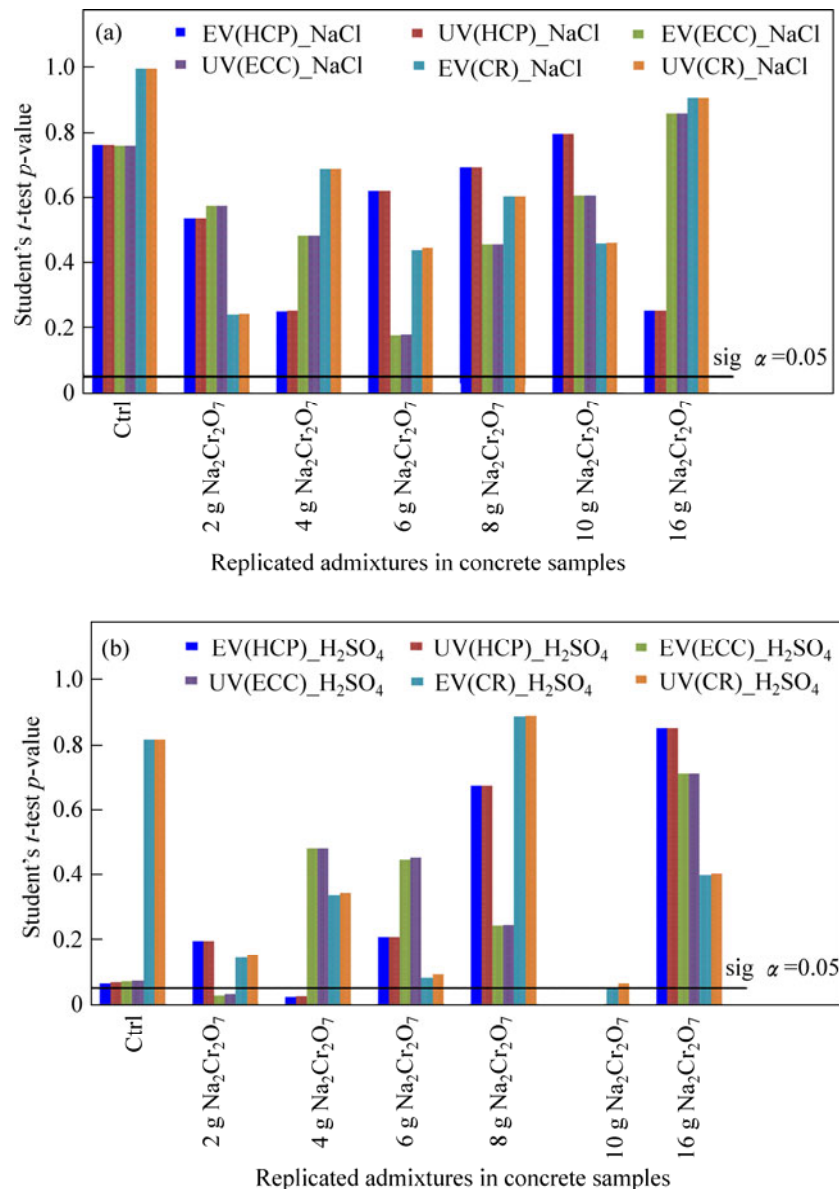


Fig. 9 Models of student's t -test of statistical significance, with equal variance (EV) and unequal variance (UV) assumed, between replicated concrete samples in NaCl medium (a) and H_2SO_4 medium (b)

test data having differences that were not significant while the differences encountered in their ECC and HCP test data were significant according to the student's *t*-test criteria. All of these test results agreed in the *t*-tests with equal variance assumed (EV) and the tests with unequal variance (UV) assumption.

3.2.3 Analysis of variance among different inhibitor concentrations

The results of the one-way factorial ANOVA in each corrosion test data of samples with different inhibitor concentrations are presented in Table 4 for HCP test data, Table 5 for ECC test data and Table 6 for CR test data. Each of these tables are appropriately partitioned to contain the results of factorial ANOVA for samples in NaCl medium and the factorial ANOVA results for samples in H₂SO₄ medium. The results from Table 4 shows that the differences encountered in the HCP test data of all the samples admixed with inhibitor concentrations in NaCl medium should be considered as chance, stochastic HCP responses, which were not statistically significant, at *p*=0.849 3. For samples admixed with inhibitor concentrations in H₂SO₄ medium, however, Table 4 also shows that the differences

encountered in the HCP test data were not due to chance but were significant, *p*<0.000 1.

The ECC test data ANOVA showed that differences in ECC test data were significant, *p*<0.000 1 for the samples in NaCl medium and *p*<0.000 1 for the samples in H₂SO₄ medium, see Table 5. Also, the CR test data ANOVA, presented in Table 6, depicted that the differences in CR test data were also significant, *p*=0.000 2 for the samples in NaCl medium and *p*=0.023 for the samples in H₂SO₄ medium.

3.2.4 Dunnett's post hoc test

Post hoc test results from the application of Dunnett's statistics for comparing corrosion test data of concrete samples with inhibitor admixtures versus the control samples are presented in Fig. 10, for the HCP test data, Fig. 10(a), ECC test data, Fig. 10(b) and CR test data Fig. 10(c). The minimum significant difference criteria of this post hoc test method was used, such that negative values of the Dunnett's statistics would indicate inhibitor concentration admixed in concrete with corrosion test data that were significantly less than that of the control specimen. Such negative value translates to significant inhibition by that sample relative to the

Table 4 Results of one-way factorial analyses of variance (ANOVA) of half-cell potential (HCP) test data for concrete samples in NaCl medium and in H₂SO₄ medium

HCP ANOVA Source of variations	Degree of freedom	Sample in NaCl medium				Sample in H ₂ SO ₄ medium			
		Sum of square	Mean square	<i>F</i>	<i>p</i> -value	Sum of square	Mean square	<i>F</i>	<i>p</i> -value
Treatment	13	249 549.91	19 196.15	0.603 5	0.849 3	4 892 100.49	376 315.42	17.238 0	0.0000
Residual	182	5 788 816.10	31 806.68	—	—	3 973 162.79	21 830.56	—	—
Total	195	6 038 366.01	—	—	—	8 865 263.28	—	—	—

Table 5 Results of one-way factorial analyses of variance (ANOVA) of electrochemical cell current (ECC) test data for concrete samples in NaCl medium and in H₂SO₄ medium

ECC ANOVA Source of variations	Degree of freedom	Sample in NaCl medium				Sample in H ₂ SO ₄ medium			
		SS	MS	<i>F</i>	<i>p</i> -value	SS	MS	<i>F</i>	<i>p</i> -value
Treatment	13	6 008 324.37	462 178.80	6.903 3	0	298 070.57	22 928.51	8.558 5	0
Residual	182	12 185 036.63	66 950.75	—	—	487 584.05	2 679.03	—	—
Total	195	18 193 361.00	—	—	—	785 654.62	—	—	—

Table 6 Results of one-way factorial analyses of variance (ANOVA) of corrosion rate (CR) test data for concrete samples in NaCl medium and in H₂SO₄ medium

CR ANOVA Source of variations	Degree of freedom	Sample in NaCl medium				Sample in H ₂ SO ₄ medium			
		SS	MS	<i>F</i>	<i>p</i> -value	SS	MS	<i>F</i>	<i>p</i> -value
Treatment	13	114.20	8.78	3.272 1	0.000 2	2.12	0.16	1.999 4	0.023 0
Residual	182	488.62	2.68	—	—	14.82	0.08	—	—
Total	195	602.83	—	—	—	16.93	—	—	—

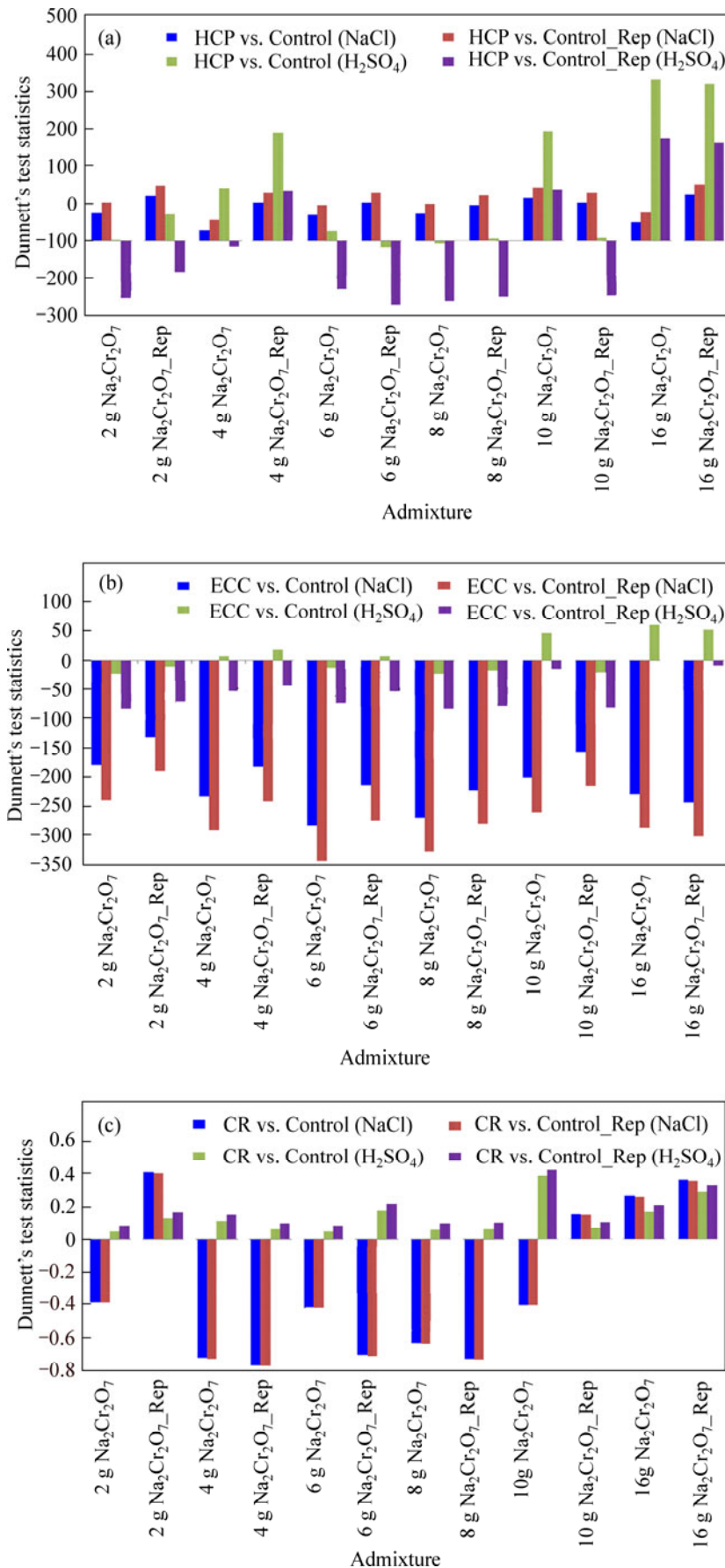


Fig. 10 Dunnett's post hoc statistics test for concrete steel-rebar corrosion model—the negative ordinate indicate region of significant difference vs control: (a) Half-cell potential model; (b) Electrochemical cell current model; (c) Corrosion rate model

control.

Figure 10(a) shows that all HCP test data in NaCl medium compared with any of the control specimen replicates were not significantly less than the HCP test data of the control. This confirmed the ANOVA test results. In the H₂SO₄ medium, only the 6 g replicate sample and the 8 g sample had HCP test data significantly less than the control sample. Compared with the control replicate sample, however, the HCP test data of the 4 g Na₂Cr₂O₇ sample, the 10 g replicate sample and each of the two replicated samples of the 2 g, 6 g and 8 g admixtures were significantly less than that of the control replicate sample in the H₂SO₄ medium.

The 6 g replicate sample, the 10 g sample and the two replicate samples each of the 4 g and the 16 g admixtures bear the exceptions that their ECC test data were either not less than or not significantly less than that of the control sample in H₂SO₄ medium, see Table 3 and Fig. 10(b). All other ECC test data of admixtures the NaCl and H₂SO₄ media were significantly less than that of the control sample and than that of the control replicate, according to the Dunnett's post hoc test statistics. This bears suggestions of possible suitability of the ECC data for inhibition effectiveness evaluation for the admixture concentrations, especially, as a measure of the corrosion component originating from the reduction activities at the reference electrode. However, restraint had been exercised against this, so as to heed the caution from Ref. [11] on the use of HCP and ECC test data for indicating absolute corrosion activity.

The Dunnett's test results in Fig. 10(c) shows that the CR test data of the 2 g, 10 g, each of the two replicates of the 4 g, 6 g and 8 g admixture samples were significantly less than that of the control sample and than that of the control replicate in the NaCl medium. However, in the H₂SO₄ medium, the CR test data of all the concentrations of inhibitor admixtures studied were either not less than or not significantly less than both that of the control sample and that of the control replicate, as seen in Table 3 and Fig. 10(c). The comparison of these Dunnett's test results with that of the CR ANOVA in Table 6, where $p=0.023 \Rightarrow$ significant CR test data difference for samples in H₂SO₄, indicates that the significant differences analysed for the samples were not absolutely relative to the control samples. This bears suggestion of the need for other types of multiple comparison post hoc test procedures for conducting full pair-wise comparisons among the samples, in the bid to ascertain the samples bearing significant difference of CR test data with one another. However, these multiple comparison methods are not applied in this work because they are not within the set-out scope of this research in which control samples had been predetermined in the experimental design.

3.3 Inhibition effectiveness modelling

The inhibition efficiency, η , for studying the effectiveness of each inhibitor admixture in mitigating concrete steel-rebar corrosion was evaluated using the modelled Gumbel mean, μ_G of corrosion rate (CR) test data computed in Eq. (4) and Eq. (6). The results obtained from this were subjected to inhibition ranking effectiveness models and these are presented in Fig. 11, for replicates of steel reinforced concrete samples with Na₂Cr₂O₇ admixtures in NaCl medium, Fig. 11(a) and for those in H₂SO₄ medium, Fig. 11(b).

In the NaCl medium, the replicate sample of reinforced concrete with 4 g Na₂Cr₂O₇ (Rep) admixture exhibited optimal inhibition effectiveness relative to the control samples by having inhibition efficiency, $\eta=91.58\%$ and $\eta_{(rep)}=91.60\%$, where η is the inhibitor efficiency relative to the control and $\eta_{(rep)}$ is the inhibition efficiency relative to the control replicate. This 4 g Na₂Cr₂O₇ (Rep) was modelled with CR of 0.223 mm/a with reduced rebar dissolution activity of 284.36 μ A and more anodic corrosion potential of 557.26 mV (CSE) compared with the control samples, see Table 2. This optimum sample was followed, in order, by the reinforced concrete samples with 8 g (Rep), 4 g, 6 g (Rep), 8 g and then 6 g Na₂Cr₂O₇ admixture concentrations such that the least of these (the 6 g admixture Na₂Cr₂O₇) had $\eta=80.74\%$ and $\eta_{(rep)}=80.79\%$. These six admixture concentrations, the 4 g, 6 g and 8 g Na₂Cr₂O₇, had very high inhibition effectiveness model, $\eta>80\%$, which bear good agreements with that of their replicate samples and which were obtained from test data having sound statistical inferences of significance. It is, however, worthy noting that all the other concentrations of Na₂Cr₂O₇ admixed in concrete also had positive inhibition efficiencies in the NaCl medium, whereby 2 g Na₂Cr₂O₇ admixture exhibited least effectiveness by having $\eta=49.33\%$ and $\eta_{(rep)}=49.44\%$.

The sample with 6 g Na₂Cr₂O₇ admixture which was modeled, in Fig. 7(b), with the optimal inhibition effectiveness in the H₂SO₄ medium did not exhibit the type of good agreements, as that obtained for the optimal sample in NaCl medium, with its replicate sample. While the 6 g Na₂Cr₂O₇ sample exhibited optimal inhibition efficiency of $\eta=85.88\%$ and $\eta_{(rep)}=84.62\%$ its replicate sample with similar Na₂Cr₂O₇ concentration had $\eta=30.60\%$ and $\eta_{(rep)}=24.43\%$. By this, the 6 g Na₂Cr₂O₇ replicate sample had the least effectiveness, the 10th just before the control samples which are the 11th and 12th, in the acidic medium. Also, the sample with 2 g Na₂Cr₂O₇ had $\eta=85.82\%$ and $\eta_{(rep)}=84.56\%$, thus coming second behind the optimal 6 g Na₂Cr₂O₇ in effectiveness, while its replicate sample had $\eta=52.01\%$ and $\eta_{(rep)}=47.74\%$ which made it ranked as the 8th, just

before the penultimate sample in positive effectiveness. These effectiveness models are conflicting. It is opined that the reason for this could be linked to the lack of statistical significance, compared with the control samples, which had been observed in the CR test data of samples in the H_2SO_4 medium by the Dunnett's post hoc test statistics.

Since the differences observed in the CR test data of each of the replicated $Na_2Cr_2O_7$ concentrations in concrete samples were found to be due to chance, or experimental error, it is of interest to see how such error averaged out between the replicate samples [36, 51]. By these, the averaged inhibitor efficiency models are presented, also in ranking order, in Fig. 12(a) for samples in NaCl medium and in Fig. 12(b) for samples in H_2SO_4

medium.

It could be observed from Fig. 12(a) that the order of optimal inhibition effectiveness was retained in the NaCl medium as the 4 g, 8 g and 6 g $Na_2Cr_2O_7$ concentrations. These have the averaged model of inhibition efficiency $\eta=(90.46\pm 1.30)\%$ for the 4 g admixture; $\eta=(88.41\pm 2.24)\%$ for the 8 g admixture and $\eta=(84.87\pm 4.74)\%$ for the 6g admixture in the saline/marine simulating environment. All other admixture concentrations in NaCl medium retained their positive inhibition, in this averaged model, even as the 2 g $Na_2Cr_2O_7$ ranked as the penultimate, $\eta=(64.50\pm 23.07)\%$, while the 16 g $Na_2Cr_2O_7$ was confirmed with the lowest in effectiveness, $\eta=(54.15\pm 2.51)\%$, in the medium. The deduction from these includes the

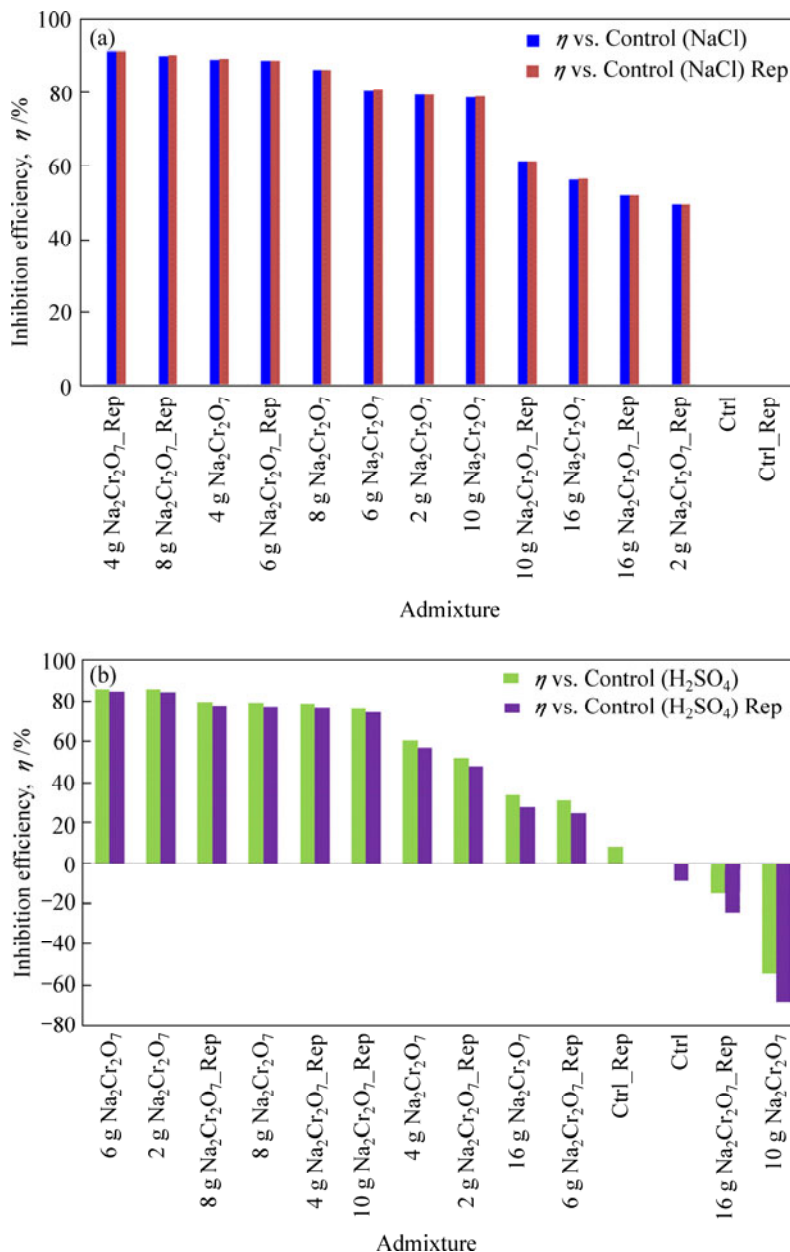


Fig. 11 Ranking of inhibition efficiency for modelling inhibitor admixture effectiveness vs. each replicate of control samples: (a) Replicates in NaCl medium; (b) Replicates in H_2SO_4 medium

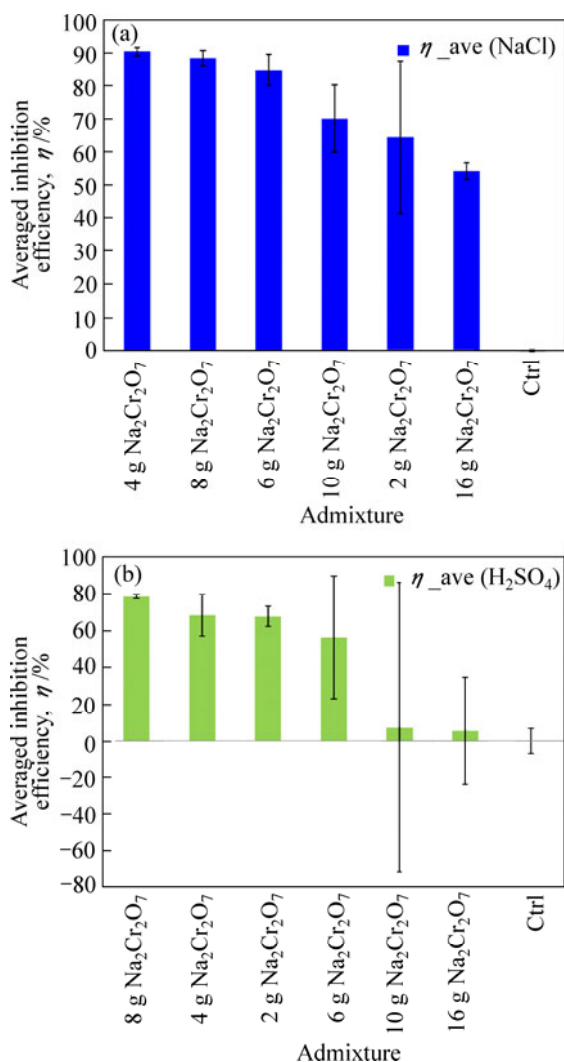


Fig. 12 Ranking of averaged inhibition efficiency model for samples in NaCl medium (a) and H₂SO₄ medium (b)

implications that the 16 g Na₂Cr₂O₇ could be too much and the 2 g Na₂Cr₂O₇ could be too little Na₂Cr₂O₇ concentrations, in the concrete samples studied, for effecting comparable inhibition effectiveness in the NaCl medium.

In the H₂SO₄ medium, Fig. 12(b), the averaged inhibition efficiency model identified the 8 g Na₂Cr₂O₇ concentration which had $\eta=(78.44\pm 1.10)\%$ with optimal inhibition effectiveness in the medium. It could be noted, from Fig. 11(b), that the two replicate samples admixed with this 8 g Na₂Cr₂O₇ concentration ranked as the 3rd and 4th, directly following the first two samples in the medium, the 6 g and the 2 g Na₂Cr₂O₇, in effectiveness, in that replicated samples model. By that, the 8 g Na₂Cr₂O₇ replicate samples were the only two replicate samples with such following order of agreements in inhibition efficiency other than the control samples in the H₂SO₄ effectiveness ranking model in Fig. 11(b).

The averaged inhibition efficiency model in the H₂SO₄ medium, Fig. 12(b), also showed that the 4 g

Na₂Cr₂O₇ concentration with $\eta=(68\pm 11.34)\%$ followed the 8 g Na₂Cr₂O₇ in effectiveness. The 2 g Na₂Cr₂O₇ concentration followed this order with $\eta=(67.53\pm 5.48)\%$, by which it now surpassed the 6 g Na₂Cr₂O₇ concentration which had $\eta=(56.38\pm 33.43)\%$ averaged inhibition efficiency model in the medium. The averaged inhibition effectiveness model in Fig. 12(b) also showed that the 10 g Na₂Cr₂O₇ ($\eta=(7.02\pm 79.23)\%$) and the 16 g Na₂Cr₂O₇ ($\eta=(5.30\pm 29.34)\%$) concentrations could both relapse into negative inhibition that could translate into corrosion aggravation for steel-rebar. This suggests that the admixtures exhibit the tendency, by the variability in their inhibition efficiency (η), to be extended in their concrete steel-rebar corrosion aggravations beyond that obtained in the control. This bears implication that the 10 g Na₂Cr₂O₇ and the 16 g Na₂Cr₂O₇ concentrations admixed in the reinforced concretes were too high admixture concentrations and were thus not suitable inhibitor for reinforcing steel corrosion, in the studied H₂SO₄ test environment.

4 Conclusions

1) The stochastic scatter of the corrosion test data measurements of steel reinforced concrete samples with Na₂Cr₂O₇ admixtures make interpretation of inhibition effectiveness difficult, in both studied test environments, thus making the use of statistical modeling functions required for fitting and instilling order in the test data, by this, the modelled corrosion rate (CR) test data by the normal and Gumbel distribution for the uninhibited control samples, in both media of environments, compared well with that obtained in literature for selected locations in the world.

2) Although, many fittings of the modeled test data scattered like the probability distribution functions studied, according to the Kolmogorov-Smirnov test criteria, result discrepancies are observed even in replicated samples with similar admixture concentrations that could generate conflicting interpretations of effectiveness, for these, the student's *t*-tests and one-way ANOVA applications, according to ASTM G16-95 R04, identified differences that were significant/not significant among the corrosion test data models while the Dunnett's post hoc test statistics further identified differences that are significant/not significant compared to the control samples;

3) From the foregoing statistical basis, 4 g (0.012 7 mol) Na₂Cr₂O₇ admixture concentration exhibits optimal model of inhibition effectiveness ($\eta=(90.46\pm 1.30)\%$), followed by the 8 g (0.025 4 mol) Na₂Cr₂O₇ admixture ($\eta=(88.41\pm 2.24)\%$) and then by the 6 g (0.019 1 mol) Na₂Cr₂O₇ admixture ($\eta=(84.87\pm 4.74)\%$) concentrations in the NaCl medium.

4) The 8 g (0.025 4 mol) $\text{Na}_2\text{Cr}_2\text{O}_7$ admixture concentration, in H_2SO_4 medium, is also identified with the optimal model of inhibition effectiveness ($\eta = 78.44 \pm 1.10\%$), the replicated reinforced concrete samples with this admixture concentration exhibit better agreements of inhibition efficiency than samples with other concentrations.

5) The 16 g (0.050 9 mol) and the 2 g (0.006 4 mol) $\text{Na}_2\text{Cr}_2\text{O}_7$ admixture concentrations have the lowest and the penultimate effectiveness, respectively, in the NaCl medium, while the 16 g (0.050 9 mol) and the 10 g (0.031 8 mol) $\text{Na}_2\text{Cr}_2\text{O}_7$ admixture concentrations are modeled with the lowest and the penultimate effectiveness, respectively. In the H_2SO_4 medium, these later admixture concentrations exhibit tendency to aggravate concrete steel-rebar corrosion in the acidic test environment.

References

- [1] SHI X, XIE N, FORTUNE K, GONG J. Durability of steel reinforced concrete in chloride environments: An overview [J]. *Construction and Building Materials*, 2012, 30: 125–138.
- [2] OMOTOSHO O A, LOTO C A, AJAYI O O, OKENIYI J O. Aniline effect on concrete steel rebar degradation in saline and sulfate media [J]. *Agricultural Engineering International: CIGR Journal*, 2011, 13(2): 1–10.
- [3] ABDELAZIZ G E, ABDELALIM A M K, FAWZY Y A. Evaluation of the short and long-term efficiencies of electro-chemical chloride extraction [J]. *Cement and Concrete Research*, 2009, 39: 727–732.
- [4] EL-REEDY M A. *Advanced materials and techniques for reinforced concrete structures* [M]. Boca Raton, CRC Press/Taylor & Francis, 2009.
- [5] HOLLOWAY L, NAIRN K, FORSYTH M. Concentration monitoring and performance of a migratory corrosion inhibitor in steel-reinforced concrete [J]. *Cement and Concrete Research*, 2004, 34: 1435–1440.
- [6] SCHWEITZER, P A. *Fundamentals of corrosion: mechanisms, causes, and preventative methods* [M]. Boca Raton, FL: CRC Press/Taylor & Francis, 2010.
- [7] YU H, SHI X, HARTT W H, LU B. Laboratory investigation of reinforcement corrosion initiation and chloride threshold content for self-compacting concrete [J]. *Cement and Concrete Research*, 2010, 40: 1507–1516.
- [8] TANG Y M, MIAO Y F, ZUO Y, ZHANG G D, WANG C L. Corrosion behavior of steel in simulated concrete pore solutions treated with calcium silicate hydrates [J]. *Construction and Building Materials*, 2012, 30: 252–256.
- [9] NÜRNBERGER, U. Corrosion of metals in contact with mineral building materials [M]. In: RAUPACH M, ELSENER B, POLDER R, MIETZ J. (eds.) *Corrosion of reinforcement in concrete: Mechanisms, monitoring, inhibitors and rehabilitation techniques*. England: Woodhead Publishing and Maney Publishing on behalf of Institute of Materials, Minerals and Mining, 2007.
- [10] ZHANG Y L, LI Q L. Electrochemical study on semiconductive properties of the passive film on rebar in concrete [J]. *Journal of Zhejiang University: Science A*, 2006, 7(8): 1447–1452.
- [11] BERKE N S, HICKS M C. Predicting long-term durability of steel reinforced concrete with calcium nitrite corrosion inhibitor [J]. *Cement & Concrete Composites*, 2004, 26: 191–198.
- [12] TRABANELLI G, MONTICELLI C, GRASSI V, FRIGNANI A. Electrochemical study on inhibitors of rebar corrosion in carbonated concrete [J]. *Cement and Concrete Research*, 2005, 35: 1804–1813.
- [13] ZHANG X G, ZHAO Y G, XING F, LU Z H. Coupling effects of influence factors on probability of corrosion initiation time of reinforced concrete [J]. *Journal of Central South University Technology*, 2011, 18: 223–229.
- [14] TITTARELLI F, MORICONI G. The effect of silane-based hydrophobic admixture on corrosion of reinforcing steel in concrete [J]. *Cement and Concrete Research*, 2008, 38: 1354–1357.
- [15] BATIS G, PANTAZOPOULOU P, ROUTOULAS A. Corrosion protection investigation of reinforcement by inorganic coating in the presence of alkanolamine-based inhibitor [J]. *Cement & Concrete Composites*, 2003, 25: 371–377.
- [16] TOMMASSELLI M A G, MARIANO N A, KURI S E. Effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components [J]. *Construction and Building Materials*, 2009, 23: 328–333.
- [17] HUNTING E R, KAMPFRAATH, A A. Contribution of bacteria to redox potential (E_h) measurements in sediments [J]. *International Journal of Environmental Science and Technology*, 2012, doi:10.1007/s13762–012–0080–4.
- [18] ROBERGE P R. *Corrosion engineering: Principles and practice* [M]. New York: The McGraw-Hill Companies, Inc., 2008.
- [19] HEWAYDE E, NEHDI M L, ALLOUCHE E, NAKHLA G. Using concrete admixtures for sulphuric acid resistance [C]// *Proceedings of the Institution of Civil Engineers Construction Materials*, 2007, 160: 25–35.
- [20] PARANDE A K, RAMSAMY P L, ETHIRAJAN S, RAO C R K, PALANISAMY N. Deterioration of reinforced concrete in sewer environments [J]. *Proceedings of the Institution of Civil Engineers-Municipal Engineer*, 2006, 159(1): 11–20.
- [21] SONG H W, SARASWATHY V. Corrosion monitoring of reinforced concrete structures: A review [J]. *International Journal of Electrochemical Science*, 2007, 2: 1–28.
- [22] LEE C, BONACCI J F, THOMAS M D A, MAALEJ M, KHAJEHPUR S, HEARN N, PANTAZOPOULOU S, SHEIKH S. Accelerated corrosion and repair of reinforced concrete columns using carbon fibre reinforced polymer sheets [J]. *Canadian Journal of Civil Engineering*, 2000, 27: 941–948.
- [23] AGUIAR J B, CAMOES A, MOREIRA P M. Performance of concrete in aggressive environment [J]. *International Journal of Concrete Structures and Materials*, 2008, 2(1): 21–25.
- [24] BURUBAI W, DAGOGO G. Comparative study of inhibitors on the corrosion of mild steel reinforcement in concrete [J]. *Agricultural Engineering International: CIGR Journal*, 2007, 9: 1–10.
- [25] SARASWATHY V, SONG H W. Improving the durability of concrete by using inhibitors [J]. *Building and Environment*, 2007, 42: 464–472.
- [26] FRANCIŠKOVIĆ J, MIKŠIĆ B, ROGAN I, TOMIČIĆ M. Protection and repair of reinforced concrete structures by means of mci-inhibitors and corrosion protective materials [C]// *Structural Engineering Conferences: International Conference on Bridges*, Dubrovnik, Croatia: SEC, 2006: 553–560.
- [27] MURALIDHARAN S, SARASWATHY V, MERLIN NIMA S P, PALANISWAMY N. Evaluation of a composite corrosion inhibiting admixtures and its performance in Portland pozzolana cement [J]. *Materials Chemistry and Physics*, 2004, 86: 298–306.
- [28] CHAUDHARY Z. Built-in corrosion prevention systems for new reinforced concrete seawater pits [C]// *The 6th Saudi Engineering Conference, KFUPM, Dhahran: SEC*, 2002, 3: 203–216.
- [29] FENG L, YANG H, WANG F. Experimental and theoretical studies for corrosion inhibition of carbon steel by imidazoline derivative in

- 5% NaCl saturated Ca(OH)₂ solution [J]. *Electrochimica Acta*, 2011, 58: 427–436.
- [30] SÖYLEV T A, RICHARDSON M G. Corrosion inhibitors for steel in concrete: State-of-the-art report [J]. *Construction and Building Materials*, 2008, 22: 609–622.
- [31] SIDERIS K K, SAVVA A E. Durability of mixtures containing calcium nitrite based corrosion inhibitor [J]. *Cement & Concrete Composites*, 2005, 27: 277–287.
- [32] JAMIL H E, MONTEMOR M F, BOULIF R, SHRIRI A, FERREIRA M G S. An electrochemical and analytical approach to the inhibition mechanism of an amino-alcohol-based corrosion inhibitor for reinforced concrete [J]. *Electrochimica Acta*, 2003, 48: 3509–3518.
- [33] VAYSBURD A M, EMMONS P H. Corrosion inhibitors and other protective systems in concrete repair: Concepts or misconceptions [J]. *Cement & Concrete Composites*, 2004, 26: 255–263.
- [34] SASTRI V S. *Green corrosion inhibitors: Theory and practice* [M]. Hoboken: John Wiley & Sons, Inc., 2011.
- [35] OMOTOSHO O A, OKENIYI J O, AJAYI O O. Performance evaluation of potassium dichromate and potassium chromate inhibitors on concrete steel rebar corrosion [J]. *Journal of Failure Analysis and Prevention*, 2010, 10: 408–415.
- [36] HAYNIE F H. Statistical treatment of data, data interpretation, and reliability [M]// BABOIAN R. (ed.) *Corrosion Tests and Standards: Application and Interpretation—second edition*, West Conshohocken, PA: ASTM International, 2005: 83–88.
- [37] ASTM G16-95 R04. Standard guide for applying statistics to analysis of corrosion data [S].
- [38] CASTRELLON-URIBE J, CUEVAS-ARTEAGA C, TRUJILLO-ESTRADA A. Corrosion monitoring of stainless steel 304L in lithium bromide aqueous solution using transmittance optical detection technique [J]. *Optics and Lasers in Engineering*, 2008, 46(6): 469–476.
- [39] CUEVAS-ARTEAGA C. Corrosion study of HK-40m alloy exposed to molten sulfate/vanadate mixtures using the electrochemical noise technique [J]. *Corrosion Science*, 2008, 50(3): 650–663.
- [40] CICEK V, AL-NUMAN B. *Corrosion chemistry* [M]. Salem, Massachusetts: John Wiley & Sons, Inc. 2011.
- [41] LOTO C A, OMOTOSHO O A, POPOOLA A P I. Inhibition effect of potassium dichromate on the corrosion protection of mild steel reinforcement in concrete [J]. *International Journal of the Physical Sciences*, 2011, 6(9): 2275–2284.
- [42] LOTO C A, ADELEKE A H. The effect of potassium dichromate inhibitor on the corrosion of stainless steels in sulphuric acid mixed with sodium chloride [J]. *Corrosion Prevention & Control*, 2004, 51: 61–69.
- [43] KRÓLIKOWSKI A, KUZIĄK J. Impedance study on calcium nitrite as a penetrating corrosion inhibitor for steel in concrete [J]. *Electrochimica Acta*, 2011, doi:10.1016/j.electacta.2011.01.069.
- [44] ORMELLESE M, BERRA M, BOLZONI F, PASTORE T. Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures [J]. *Cement and Concrete Research*, 2006, 36: 536–547.
- [45] ASTM G109-99a. Standard test method for determining the effects of chemical admixtures on the corrosion of embedded steel reinforcement in concrete exposed to chloride environments [S].
- [46] LOTO C A, POPOOLA A P I. Effect of tobacco and kola tree extracts on the corrosion inhibition of mild steel in acid chloride [J]. *International Journal of Electrochemical Science*, 2011, 6: 3264–3276.
- [47] NGALA V T, PAGE C L, PAGE M M. Corrosion inhibitor systems for remedial treatment of reinforced concrete. Part 1: Calcium nitrite [J]. *Corrosion Science*, 2002, 44: 2073–2087.
- [48] VENKATESAN P, PALANISWAMY N, RAJAGOPAL K. Corrosion performance of coated reinforcing bars embedded in concrete and exposed to natural marine environment [J]. *Progress in Organic Coatings*, 2006, 56: 8–12.
- [49] ASTM C192/192M-02. Standard practice for making and curing concrete test specimens in the laboratory [S].
- [50] ZHOU X, YANG H, WANG F. Investigation on the inhibition behavior of a pentaerythritol glycoside for carbon steel in 3.5% NaCl saturated Ca(OH)₂ solution [J]. *Corrosion Science*, 2012, 54: 193–200.
- [51] OBOT I B, OBI-EGBEDI N O. 2,3-Diphenylbenzoquinoxaline: A new corrosion inhibitor for mild steel in sulphuric acid [J]. *Corrosion Science*, 2010, 52: 282–285.
- [52] MORETTI G, GUIDI F, GRION G. Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid [J]. *Corrosion Science*, 2004, 46: 387–403.
- [53] ZAFEIROPOULOU T, RAKANTA E, BATHIS G. Performance evaluation of organic coatings against corrosion in reinforced cement mortars [J]. *Progress in Organic Coatings*, 2011, 72: 175–180.
- [54] BROOMFIELD J P. *Corrosion of steel in concrete: Understanding, investigation and repair* [M]. New York: Taylor & Francis, 2003.
- [55] ASTM C876-91 R99. Standard test method for half-cell potentials of uncoated reinforcing steel in concrete [S].
- [56] MCCARTER W J, VENNESLAND Ø. Sensor systems for use in reinforced concrete structures [J]. *Construction and Building Materials*, 2004, 18: 351–358.
- [57] JÄGGI S, BOHNI H, ELSENER B. Macrocell corrosion of steel in concrete: Experimental and numerical modelling [C]// *Proceeding of Eurocorr 2001*, Riva di Garda, Italy: Associazione Italiana Metallurgia (AIM), 2001
- [58] ABOSRRA L, ASHOUR A F, YOUSEFFI M. Corrosion of steel reinforcement in concrete of different compressive strengths [J]. *Construction and Building Materials*, 2011, 25: 3915–3925.
- [59] KAHLERT H. Reference Electrodes [M]// SCHOLZ F. (ed.) *Electroanalytical Methods: Guide to Experiments and Applications*, 2nd Edition. Berlin Heidelberg: Springer-Verlag, 2010, 291–308.
- [60] STOJEK Z. Experimental Setup [M]// SCHOLZ F. (ed.) *Electroanalytical Methods: Guide to Experiments and Applications*, 2nd Edition. Berlin Heidelberg: Springer-Verlag, 2010, 331–335.
- [61] LOVRIC M. *International encyclopedia of statistical science* [M]. Berlin, Heidelberg: Springer-Verlag, 2011.
- [62] KVAM P, LU J C. *Statistical reliability with applications* [M]// PHAM, H. (ed.) *Springer handbook of engineering statistics*. London: Springer-Verlag, 2006: 49–61.
- [63] KARIAN Z A, DUDEWICZ E J. *Handbook of fitting statistical distributions* [M]. Boca Raton: Taylor and Francis Group, LLC, 2011.
- [64] WALDEMAR D P. *Numerical methods, algorithms, and tools in C#* [M]. Boca Raton: Taylor and Francis Group, LLC, 2010.
- [65] ROBERGE P R. Computer based data organization and computer applications [M]// Baboian, R. (ed.) *Corrosion Tests and Standards: Application and Interpretation—second edition*, West Conshohocken, PA: ASTM International, 2005: 89–104.
- [66] ROBERGE P R. Statistical interpretation of corrosion test results [M]// Cramer, S. D, Covino, Jr. B. S. (eds.) *Corrosion: fundamentals, testing, and protection*, Vol 13A, ASM Handbook, Materials Park, OH: ASM International, 2003: 425–429.
- [67] KOTZ S, NADARAJAH S. *Extreme value distributions: theory and applications* [M]. London: Imperial College Press, 2000.
- [68] OKENIYI J O, OBIJULU U E, OGUNSANWO A O, ODIASE N W, OKENIYI E T. CH₄ emission model from the waste of *Sus Domesticus* and *Gallus Domesticus* in Nigerian local farms: environmental implications and prospects [J]. *Mitigation and Adaptation Strategies for Global Change*, 2013, 18(3): 325–335, doi: 10.1007/s11027-012-9365-7.

- [69] LANGE K. Numerical analysis for statisticians [M]. 2nd ed. New York: Springer Science+Business Media, LLC, 2010.
- [70] HOFFMAN J D. Numerical methods for engineers and scientists [M]. 2nd ed. New York: Marcel Dekker, Inc., 2001.
- [71] OKENIYI J O, OKENIYI E T. Implementation of Kolmogorov-Smirnov p-value computation in Visual Basic®: Implication for Microsoft Excel® library function [J]. *Journal of Statistical Computation and Simulation*, 2012, 82(12): 1727–1741, doi:10.1080/00949655.2011.593035.
- [72] FAGBENLE R O, KATENDE J, AJAYI O O, OKENIYI J O. Assessment of wind energy potential of two sites in North-East, Nigeria [J]. *Renewable Energy*, 2011, 36: 1277–1283.
- [73] AJAYI O O, FAGBENLE R O, KATENDE J, OKENIYI J O. Availability of wind energy resource potential for power generation at Jos, Nigeria [J]. *Frontiers of Energy*, 2011, 5(4): 376–385.
- [74] THAS O. Comparing distributions [M]. New York: Springer Science+Business Media, LLC, 2010.
- [75] SHABRI A, JEMAIN A A. Application of multi criteria method to identify the best-fit statistical distribution [J]. *Journal of Applied Sciences*, 2006, 6(4): 926–932.
- [76] AGUILAR C A, MONTALVO C, RODRÍGUEZ L, CERÓN J G, CERÓN R M. American oyster (*Crassostrea virginica*) and sediments as a coastal zone pollution monitor by heavy metals [J]. *International Journal of Environmental Science and Technology*, 2012, doi: 10.1007/s13762-012-0078-y.
- [77] HINKELMANN K, KEMPTHORNE O. Design and analysis of experiments: Introduction to experimental design [M]. 2nd ed. Hoboken, New Jersey: John Wiley & Sons, Inc., 2008.
- [78] BEHPOUR M, GHOREISHI S M, GANDOMI-NIASAR A, SOLTANI N, SALAVATI-NIASARI M. The inhibition of mild steel corrosion in hydrochloric acid media by two Schiff base compounds [J]. *Journal of Materials Science*, 2009, 44: 2444–2453.
- [79] ETTEYEB N, DHOUBI L, TAKENOUTI H, ALONSO M C, TRIKI E. Corrosion inhibition of carbon steel in alkaline chloride media by Na_3PO_4 [J]. *Electrochimica Acta*, 2007, 52: 7506–7512.
- [80] NATESAN M, VENKATACHARI G, PALANISWAMY N. Kinetics of atmospheric corrosion of mild steel, zinc, galvanized iron and aluminium at 10 exposure stations in India [J]. *Corrosion Science*, 2006, 48: 3584–3608.

(Edited by DENG Lü-xiang)