INTERNATIONAL JOURNAL OF ENVIRONMENTAL SCIENCES Volume 2, No 4, 2012

Research article ISSN 0976 – 4402

Effect of synergies of $K_2Cr_2O_7$, K_2CrO_4, $NaNO_2$ and aniline inhibitors on the corrosion potential response of steel reinforced concrete in saline medium

Omotosho Olugbenga. A, Okeniyi Joshua. O, Ajayi Oluseyi. O, Loto Cleophas. A
Mechanical Engineering Department, Covenant University, P.M.B.1023, Ota, Nigeria
joshua.okeniyi@covenantuniversty.edu.ng
doi: 10.6088/ijes.00202030116

ABSTRACT

Studies involving performance of corrosion inhibitors had been identified as one of the critical research needs for improving the durability of concrete structures. This paper investigates the effect of synergy on the performance of potassium chromate, sodium nitrite and aniline as inhibitors on the corrosion of steel-rebar in concrete in sodium chloride medium. The corrosion monitoring technique of the open circuit potential was employed for specimens of steel-reinforced concrete, with different synergistic admixtures of $K_2Cr_2O_7$, K_2CrO_4, $NaNO_2$ and Aniline, partially immersed in the marine simulating environment. Interpretation of the statistical modelling of the experimental results, for each of the synergistic concentrations of inhibitor admixtures studied, was done using ASTM C876. The modelled ranking from these predicted the synergistic combination of 3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 4ml (0.274M) Aniline as exhibiting optimal inhibiting quality on the corrosion of steel-reinforced concrete in the chloride medium considered.

Keywords: Reinforced concrete durability, corrosion inhibitors, marine simulating environment, Normal distribution, Weibull distribution, Kolmogorov–Smirnov statistics.

1. Introduction

Collapse of building structures had been rampant in recent years in the coastal cities of Nigeria. Oni (2010) shows that these collapse had been on a steady increase, since the year 2004, in the metropolitan city of Lagos, a coastal city in Nigeria. Structural defects, dilapidation, deterioration of concrete structures had been identified as a major cause of many of these building disasters that had led to losses of human lives and material resources in the country (Oni, 2010; Burubai and Dagogo, 2007; Ayininuola and Olalusi, 2004; Akinpelu, 2002). There is need for research solutions geared towards forestalling these occurrences.

Corrosion damage of reinforcing steel bars (rebar) in concrete due to chloride ingress had been identified as the major militating factor against concrete durability in the coastal areas of the world (Junzhi et al, 2010; Robertson and Newtson, 2009; Burubai and Dagogo, 2007; Di Maio et al, 2004; Izquierdo et al, 2004). The chloride ingress is attributable to the transport mechanism whereby chloride ions from natural seawater penetrate into concrete by capillary suction into dry or partially dry concrete or by diffusion into water saturated concrete under a concentration gradient. This gradually builds up to the threshold level of the required chloride content to initiate depassivation of the concrete steel-rebar and, subsequently, activate the propagation of the rebar corrosion until unacceptable corrosion induced damage occur (Al-Gadhib et al, 2008; Shazali et al, 2008; Izquierdo et al, 2004).

Received on March 2012 Published on May 2012

Rusts, the product of the corrosion induced damage on reinforcement, are both weak in structural strength and expansive within the concrete structure. The progressive expansions culminate in cracks, delamination and spalling of the concrete structure; then loss of structural integrity of the structural member; and, if unchecked, outright collapse due to cumulative damage of the reinforced structure (Chidambaram and Thirugnanam, 2010 "a"; Chidambaram and Thirugnanam, 2010 "b"; Johnson and Thirugnanam, 2010; Arndt and Jalinoos, 2009; Burubai and Dagogo, 2007; Yoon et al, 2000). Incurred cost of repair and rehabilitation of these structures to prolong durability, effect restoration or forestall disaster constitutes major spending, of increasing magnitude annually, on infrastructure in many countries (Arndt and Jalinoos, 2009; Robertson and Newtson, 2009; Cook, 2005; Lee et al, 2000).

Preventing rebar corrosion is a major metallurgical challenge confronting world's engineering and scientific community (Akinyemi and Alamu, 2009). Several studies have been done with varying degrees of successes on different prevention and maintenance methods for addressing the problem of corrosion damage of reinforced concrete structures in corrosive chloride environments. Some of these include cathodic protection (Sekar et al, 2007; Chaudhary, 2002), surface coating of reinforcing bar (Chidambaram and Thirugnanam, 2010 "a"; Chidambaram and Thirugnanam, 2010 "b"; Selvaraj et al, 2009; Venkatesan et al, 2006), surface coating of concrete structure (Aguiar et al, 2008) and the use of corrosion inhibitors (Chidambaram and Thirugnanam, 2010 "a"; Chidambaram and Thirugnanam, 2010 "b"; Robertson and Newtson, 2009; Burubai and Dagogo, 2007). From these, the use of corrosion inhibitors as admixtures in concrete had been found to be one of the effective methods of controlling steel-rebar corrosion and improving durability of reinforced concrete structures (Saraswathy and Song, 2007).

Corrosion inhibitor is a chemical substance which, in the presence of corrosive agent, decreases the corrosion rate in a corroding system when used at suitable concentration (Al-Mehthel et al, 2009; Revie and Uhlig, 2008; Holloway et al, 2004). Studies, on the inhibitive effectiveness of different corrosion inhibitors, had not only linked corrosion mitigation to the concentrations of the inhibitors but also to the synergistic effects of the different inhibitor admixtures (Afolabi, 2007; Burubai and Dagogo, 2007). Authors of this work had studied the performance of different concentrations of potassium dichromate, potassium chromate, sodium nitrite and aniline on the corrosion of steel reinforcement in concrete both individually (Omotosho et al, 2011) and in some combinations of double synergies (Okeniyi et al, 2012, "b"; Omotosho, 2011; Omotosho et al, 2010). However, no study had been conducted on the effect of the multiple combinations of these inhibitors on the corrosion of reinforcing steel in concrete immersed in chloride medium. This paper, therefore, studies the synergistic effect of the multiple combinations of $K_2Cr_2O_7$, K_2CrO_4, $NaNO_2$ and Aniline ($C_6H_5NH_2$) as inhibitors on the corrosion of steel-rebar in concrete partially immersed in sodium chloride medium.

2. Materials and methods

2.1 Concrete blocks preparation

Concrete blocks used for the experiment were made, in accordance with literature (Burubai and Dagogo, 2007), using Portland cement, sand and gravel mixed with water at a mix ratio of 1:2:4 (cement, sand and gravel). The formulation used for each reinforced concrete specimen was: cement 320 kg/m^3, water 140 kg/m^3, sand 700 kg/m^3 and gravel 1150 kg/m^3. The water/cement (w/c) ratio was 0.44.

Ten blocks were used in the study, as specimens of reinforced concrete samples. These include a control specimen with which no inhibitor was admixed while each of the remaining nine specimen samples was admixed with different synergies of inhibitor concentrations. The quantity of each synergistic inhibitor admixtures, in the concrete specimens studied, by mass (and by concentration in mol/dm^3 (M)), were as shown in Table 1. All the concrete samples were also admixed with a fixed amount of 0.1M sodium chloride to accelerate corrosion. The specimens were then immersed in 3.5% sodium chloride (NaCl) medium to simulate marine/saline environments. All the chemicals used were of AnalaR reagent grade.

Table 1: Inhibitor admixed in specimens of reinforced concrete by mass and by concentration in mol/dm^3

Specimen No	Inhibitor Admixtures
0.	Control (no inhibitor)
1.	1.5g (0.032 M) $K_2Cr_2O_7$ + 3.0g (0.097M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$
2.	3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$
3.	4.5g (0.096 M) $K_2Cr_2O_7$ + 1.5g (0.048M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$
4.	1.5g (0.048M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 6ml (0.411M) Aniline
5.	4.5g (0.145M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$ + 4ml (0.274M) Aniline
6.	3.0g (0.097M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$ + 2ml (0.137M) Aniline
7.	1.5g (0.032 M) $K_2Cr_2O_7$ + 3.0g (0.097M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$ + 2ml (0.137M) Aniline
8.	3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 4ml (0.274M) Aniline
9.	4.5g (0.096 M) $K_2Cr_2O_7$ + 1.5g (0.048M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$ + 6ml (0.411M) Aniline

DIN-ST 60mm type of steel-rebar was used for the reinforcement. The steel was obtained from Oshogbo Steel Rolling Mill, Nigeria and its chemical composition was as shown in Table 2. The rebar were cut into several pieces each with a length of 160mm and 10mm diameter and embedded in the concrete. Abrasive grinder was used to remove the mill scales and rust stains on the steel specimens before each was placed in its concrete block. The protruded end of the block was painted to prevent atmospheric corrosion.

Table 2: Chemical composition of the steel rebar sample

Element	C	Si	Mn	P	S	Cu	Cr	Ni	Fe
% Composition	0.3	0.25	1.5	0.04	0.64	0.25	0.1	0.11	96.81

2.2 Experimental procedures

Each concrete block was partially immersed in the corrosive, sodium chloride, testing medium such that the liquid level was just below the exposed steel reinforcement but not making contact with it. Open circuit potential (OCP) readings (Chidambaram and

Thirugnanam, 2010 "a"; Chidambaram and Thirugnanam, 2010 "b"; Johnson and Thirugnanam, 2010; Al-Mehthel et al, 2009; Song and Saraswathy, 2007; Burubai and Dagogo, 2007) were obtained by placing a copper/copper sulphate electrode (CSE) firmly on the concrete block. One of the two lead terminals of a digital high impedance multimeter was connected to the copper/copper sulphate electrode (CSE) and the other to the exposed part of the embedded steel-rebar to make a complete electrical circuit. OCP for all the specimens were monitored over an exposure period of 32 days. The readings were taken at three different points on each concrete block directly over the embedded steel-rebar (Al-Mehthel et al, 2009) in 2-day intervals for the exposure period. The average of the three readings was computed and this was subjected to data analysis and interpretation based on ASTM C876-91 (Ha et al, 2007). All the experiments were performed under free corrosion potential and at ambient temperature.

2.3 Data analysis

The distribution functions used for analysing open circuit potential readings include the Normal distribution function, whose cumulative density function (CDF), F_N, is (Okeniyi et al, 2012 "a"; Soong, 2004; Montgomery and Runger, 2003; Roberge, 2003)

$$F_N\left(x\right)=\frac{1}{\sigma\sqrt{2\pi}}\int_{-\infty}^{x}\exp\left[-\left(\frac{x-\mu}{2\sigma^2}\right)^2\right]dx \tag{1}$$

Where μ is the mean and σ is the standard deviation of the sample variable x. The other distribution function is the two-parameter Weibull distribution function with CDF, F_W, given by (Haynie, 2005; Murthy et al, 2004; Roberge, 2003)

$$F_W\left(x\right)=1-\exp\left(-\left(\frac{x}{c}\right)^k\right) \tag{2}$$

Where k is the shape parameter and c is the characteristic value or the scale parameter of the Weibull distribution function. Equation (2) can be expressed in linear form (Okeniyi et al, 2012 "b"; Murthy et al, 2004; Montgomery and Runger, 2003) to obtain

$$\ln\left[-\ln\left[1-F_W\left(x\right)\right]\right]=k\ln x-k\ln c \tag{3}$$

A threshold value x_0=0 had been assumed by using the two-parameter Weibull. In order to ensure the consistencies of the negative OCP values, especially, with the logarithmic nature of Equation (3), x values had been taken to be in negative millivolts versus copper/copper sulphate electrode, i.e. −mV (CSE). This approach finds similarity with the data presentation approach of Burubai and Dagogo (2007). Hence, positive values of x are used in the equations for the distribution functions. To model the quality and variability of the measured data using the Weibull distribution, Weibull predictions of the mean μ_W and the standard deviation σ_W were be obtained, respectively, from (Murthy et al, 2004; Montgomery and Runger, 2003)

$$\mu_W=c\Gamma\left(1+\frac{1}{k}\right) \tag{4}$$

$$\sigma_W = \sqrt{c^2 \left\{ \Gamma\left(1+\frac{2}{k}\right) - \left[\Gamma\left(1+\frac{1}{k}\right)\right]^2 \right\}} \qquad (5)$$

where $\Gamma(\cdot)$ is the gamma function of $(\cdot)$.

2.4 Goodness of Fit test

To ascertain the compatibility of the OCP data to each of the statistical distributions employed, the distribution free Kolmogorov−Smirnov (K-S) goodness of fit test (Okeniyi, et al, 2012, “a”; Okeniyi, et al, 2012, “b”; Okeniyi and Okeniyi, 2011; Fagbenle et al., 2011; Thas, 2010; Omotosho et al., 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 $F(x)$ through the statistics

$$d = d\left(x_1,\ldots,x_n\right) = \sqrt{n}\sup_{-\infty<x<\infty}\left|F^*(x) - F\left(x\right)\right| \qquad (6)$$

Where n is the number of analysed data points.

The value of d from Equation (6) is useful for ascertaining region of the level of significance (α) of the K-S goodness-of-fit from tables, using the condition $d_{computed} < c_{n,\alpha(tabulated)}$ (Soong, 2004; Zwillinger and Kokoska, 2000). In this study, however, the P-Value of the K-S goodness-of-fit test was computed directly from the d value and sample size n in Microsoft® Excel® using the method described in (Okeniyi and Okeniyi, 2011). From these considerations, a given set of data can be said to follow a particular distribution, at a significance level $\alpha = 0.05$, if the computed P-Value for the dataset satisfies the condition:

$$P \geq \alpha \qquad (7)$$

3. Results and discussions

Graphical plots of mean open circuit potential readings against time, obtained during the experiment for the ten specimens of reinforced concrete samples with admixed inhibitors, immersed in sodium chloride medium, are presented in Figure 1.

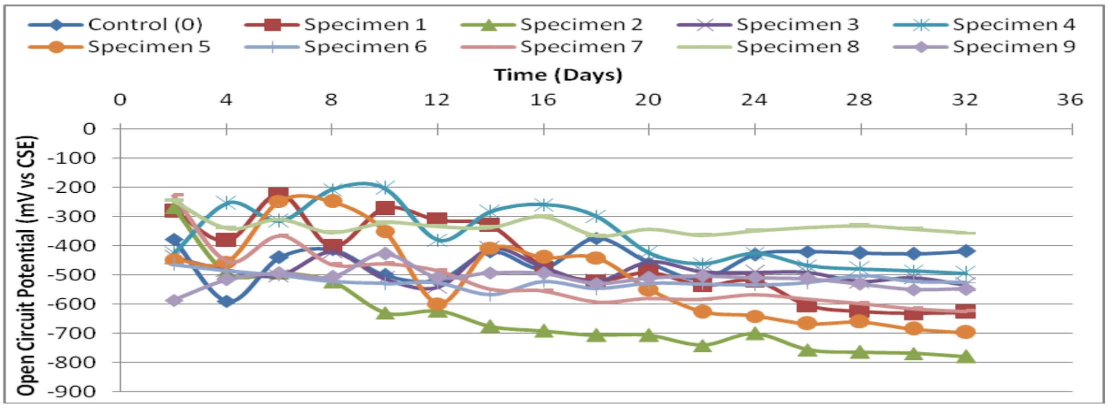
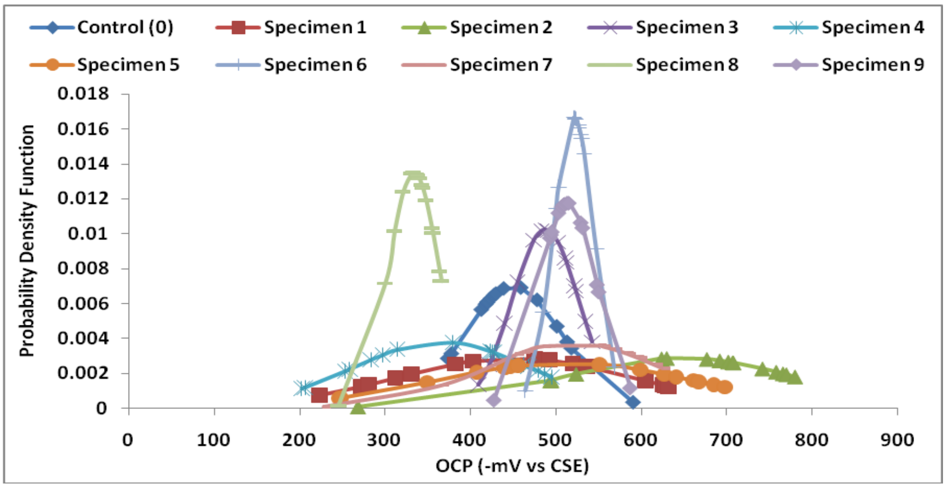
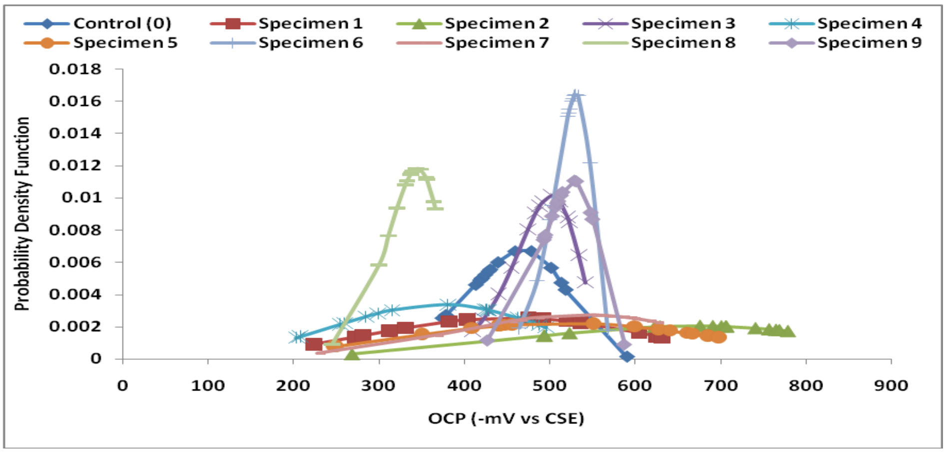


Figure 1: Plots of open circuit potential readings vs. time for specimens of steel-reinforced

From the open circuit potential readings shown in the graphical plots of Figure 1, fluctuations, in the form of spikes of varying amplitudes could be observed for each concentration of inhibitors presented. These oscillatory drifts between the active and passive regions are referred to, in studies, as corrosion response due to a form of "electrochemical noise" by the corroding system (Kuang et al, 2010; Afolabi et al, 2009). The fluctuating spikes can be attributed to constant corrosion damage of the protective film by the notorious corrosive medium and subsequent inhibition by the constantly formed protective layer of applied inhibitor admixture which re-passivate the reinforcing steel (Okeniyi, et al 2012, "b"; Omotosho et al, 2010; Afolabi et al, 2009). By these, ranking of inhibiting effectiveness by the varying concentrations of admixed inhibitor using the observed data can be difficult, especially, when these types of fluctuations are well pronounced. These constitute the need for the use of statistical modelling tools for the analysis and prediction of the effectiveness of inhibitor performance in the corrosive medium (Okeniyi et al, 2012 "b"; Omotosho et al, 2010).



(a)



(b)

Figure 2: Probability distribution function (PDF) plots for steel-reinforced concrete samples (a) Normal PDF plots (b) Weibull PDF plots

The probability density function (PDF) plots for the Normal distribution and the Weibull distribution functions are presented in Figure 2 for the reinforced concrete samples. Results of analytical modelling of the mean OCP data using the Normal distribution and the Weibull distribution fittings are presented in Table 3 for the reinforced concrete samples with admixed inhibitors immersed in sodium chloride medium.

Table 3: Normal distribution and Weibull distribution modelling of the open circuit potential readings for reinforced concrete samples

Specimen No	Inhibitor Admixture in Reinforced Concrete	Normal Distribution			Weibull Distribution						
		μ (-mV (CSE))	σ	*P*-Value (K-S)	*k*	*c*	μ_W (-mV (CSE))	σ_W	Prob(μ_W)	Prob(μ)	*P*-Value (K-S)
0.	Control (no inhibitor)	450.19	56.86	0.4700	8.72	475.48	449.62	61.52	0.4588	0.4625	0.3042
1.	1.5g (0.032 M) $K_2Cr_2O_7$ + 3.0g (0.097M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$	452.31	139.23	0.9288	3.36	505.13	453.49	149.06	0.5016	0.4986	0.9542
2.	3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$	645.13	138.31	0.4063	3.90	719.12	650.90	186.73	0.4922	0.4804	0.2098
3.	4.5g (0.096 M) $K_2Cr_2O_7$ + 1.5g (0.048M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$	487.31	39.01	0.9469	13.90	504.99	486.44	42.81	0.4482	0.4563	0.9876
4.	1.5g (0.048M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 6ml (0.411M) Aniline	366.81	104.71	0.4413	3.58	408.41	367.92	114.02	0.4974	0.4937	0.6227
5.	4.5g (0.145M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$ + 4ml (0.274M) Aniline	510.44	151.37	0.8131	3.32	571.80	513.04	170.42	0.5024	0.4966	0.9415
6.	3.0g (0.097M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$ + 2ml (0.137M) Aniline	520.69	23.96	0.2092	23.70	532.12	520.06	27.33	0.4406	0.4500	0.3243
7.	1.5g (0.032 M) $K_2Cr_2O_7$ + 3.0g (0.097M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$ + 2ml (0.137M) Aniline	519.25	106.06	0.2740	4.14	576.03	523.12	142.35	0.4889	0.4784	0.2345
8.	3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 4ml (0.274M) Aniline	333.25	29.51	0.3705	11.14	348.31	332.83	36.15	0.4526	0.4573	0.6132
9.	4.5g (0.096 M) $K_2Cr_2O_7$ + 1.5g (0.048M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$ + 6ml (0.411M) Aniline	513.75	33.96	0.4376	15.91	530.33	513.05	39.66	0.4459	0.4530	0.3597

The modelling of the OCP data by the Normal distribution function, Figure 2(a), compares very well with that by the two-parameter Weibull distribution function, Figure 2(b), for all the reinforced concrete samples in the NaCl medium considered, as shown, also, in Table 3. The predicted Weibull mean models, though with just slight differences, exhibit equalities of Weibull probabilities of obtaining both the Weibull mean and the sample mean correct to two decimal places, for all the samples. The Normal probability of obtaining the Normal mean was not tabulated because it is equal to 0.5 for all samples. The *P*-Values from the Kolmogorov−Smirnov (K−S) goodness of fit test show that the measured OCP data, for all these concrete samples, follow both the Normal and the two-parameter Weibull distribution functions. These *P*-Values were all greater than the significant values of α (i.e. P>0.05) thus satisfying the condition imposed by Equation (7). Also, the large shape parameter values (k: $k > 1$) of the Weibull model of these samples imply small scatter of the OCP data employed for the modelling, which thus translate to good uniformity of the measured OCP data.

To investigate the performance prediction of the specimens of reinforced concrete samples with inhibitor admixtures, the sample mean and the Weibull mean models were subjected to the corrosion classification standard of ASTM C876 with reference to copper/copper sulphate electrode (CSE). These corrosion classification conditions, obtained based on the standard, are presented in Table 4 for concrete samples immersed in NaCl medium.

Table 4: Comparative prediction of corrosion condition for concrete samples

Specimen No	Inhibitor Admixture in Reinforced Concrete	μ	Predicted Corrosion Condition (Normal PDF Modelling)	μ_W	Predicted Corrosion Condition (Weibull PDF Modelling)
0.	Control (no inhibitor)	450.19	High (> 90% risk of Corrosion)	449.62	High (> 90% risk of Corrosion)
1.	1.5g (0.032 M) $K_2Cr_2O_7$ + 3.0g (0.097M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$	452.31	High (> 90% risk of Corrosion)	453.49	High (> 90% risk of Corrosion)
2.	3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$	645.13	Severe Corrosion	650.9	Severe Corrosion
3.	4.5g (0.096 M) $K_2Cr_2O_7$ + 1.5g (0.048M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$	487.31	High (> 90% risk of Corrosion)	486.44	High (> 90% risk of Corrosion)
4.	1.5g (0.048M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 6ml (0.411M) Aniline	366.81	High (> 90% risk of Corrosion)	367.92	High (> 90% risk of Corrosion)
5.	4.5g (0.145M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$ + 4ml (0.274M) Aniline	510.44	Severe Corrosion	513.04	Severe Corrosion
6.	3.0g (0.097M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$ + 2ml (0.137M) Aniline	520.69	Severe Corrosion	520.06	Severe Corrosion
7.	1.5g (0.032 M) $K_2Cr_2O_7$ + 3.0g (0.097M) K_2CrO_4 + 1.5g (0.136M) $NaNO_2$ + 2ml (0.137M) Aniline	519.25	Severe Corrosion	523.12	Severe Corrosion

Specimen No	Inhibitor Admixture in Reinforced Concrete	μ	Predicted Corrosion Condition (Normal PDF Modelling)	μ_W	Predicted Corrosion Condition (Weibull PDF Modelling)
8.	3.0g (0.064 M) $K_2Cr_2O_7$ + 4.5g (0.145M) K_2CrO_4 + 3.0g (0.272M) $NaNO_2$ + 4ml (0.274M) Aniline	333.25	Intermediate Corrosion risk	332.83	Intermediate Corrosion risk
9.	4.5g (0.096 M) $K_2Cr_2O_7$ + 1.5g (0.048M) K_2CrO_4 + 4.5g (0.408M) $NaNO_2$ + 6ml (0.411M) Aniline	513.75	Severe Corrosion	513.05	Severe Corrosion

The predicted corrosion condition for concrete samples immersed in NaCl medium, presented in Table 4, based on ASTM C876 by the Normal PDF modelling agree with that by the Weibull PDF modelling.

The performance rankings of inhibiting quality modelled by the two distribution functions are presented in Figure 3 for the reinforced concrete samples considered in this study.

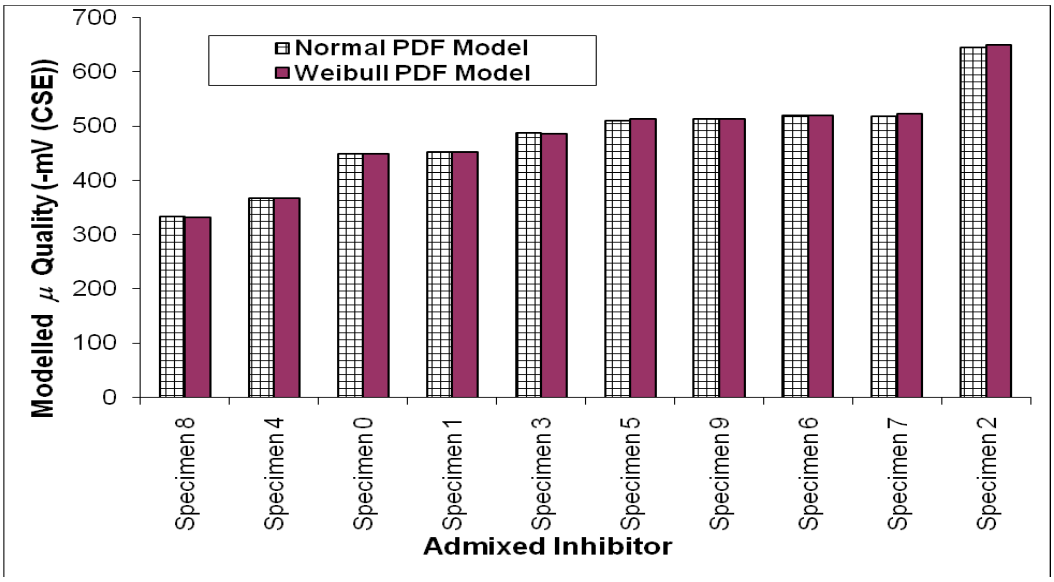


Figure 3: Performance rankings of modelled inhibiting quality of specimens of concrete samples

The performance ranking in Figure 3 identified the reinforced concrete sample with the synergistic admixture of 3.0g $K_2Cr_2O_7$, 4.5g K_2CrO_4, 3.0g $NaNO_2$ and 4ml Aniline as exhibiting optimal inhibiting quality in the corrosive sodium chloride medium. The corrosion potential for this sample was predicted as exhibiting inhibiting quality μ=−333.25 mV (CSE) at a variability of 29.51, K-S *P*-Value=0.3705 by the Normal PDF modelling, Table 3, and by the Weibull PDF modelling, the inhibiting quality μ=−332.83 mV (CSE) at σ = 36.15. The reliability of the Weibull model for this inhibiting quality equals 45.26% and K-S *P*-Value=0.6132. By subjecting the modelled quality for this sample to ASTM C876 standard, the corrosion condition of this sample was modelled by both the Normal and the Weibull PDFs' to be within the "intermediate corrosion risk" range, see Table 4. This sample exhibited improvement over the control sample (without inhibitor) with modelled quality μ=−450.19 mV (CSE), by Normal PDF, or μ=−449.62 mV (CSE), by Weibull PDF, both of which interprets to the "high (> 90% risk of corrosion)" range by ASTM C876.

Also modelled as exhibiting better inhibiting performance than the control specimen include the specimens admixed with the synergistic admixture of 1.5g K_2CrO_4, 3.0g $NaNO_2$ and 6ml Aniline with Normal μ=−366.81 mV (CSE) and Weibull μ=−367.92 mV (CSE). All the other concrete samples with synergistic inhibitor admixtures considered in this work exhibited poor performance compared to the control specimen according to the Normal PDF and the Weibull PDF models. The highest risk of corrosion potential response was exhibited by the reinforced concrete sample admixed with 3.0g $K_2Cr_2O_7$, 4.5g K_2CrO_4 and 3.0g $NaNO_2$.

The ranked results of corrosion potential responses of the synergistic inhibitor admixtures in concrete considered in this work portrayed the effect of combining different concentrations of inhibitors on the improvement or retrogression of inhibition effectiveness in NaCl medium. These results bear serious implications on the responsible application of corrosion inhibiting admixtures. From these, a major implication that could be deduced from this study is that the application of inhibitor concentrations, one with another, for the expectation of synergetic performance, can rather increase susceptibility to corrosion damage, rather than effect corrosion inhibition. This, consequently, can militate against the durability of the reinforced concrete to which such retrogressive substance has been applied in the semblance of corrosion inhibitor. The foregoing, therefore, uphold the need for appropriate research involving testing, monitoring and requisite analysis for ascertaining the effect of selected concentrations of inhibitor admixtures on corrosion performance. This, when done adequately for reinforced concrete, in their given medium or environment of application, will abate corrosion damage and promote the durability of the concrete structure.

4. Conclusions

The effect of synergy on the performance of $K_2Cr_2O_7$, K_2CrO4, $NaNO_2$ and Aniline on the corrosion of steel-rebar in concrete, in NaCl medium, has been studied using the statistical modelling tools of the Normal and the Weibull probability distribution functions. From the results in the study, the following conclusions can be drawn:

1. The open circuit potential (OCP) readings of all the ten specimens (including the control specimen) of reinforced concrete considered, in NaCl medium, follow both the Normal PDF and the Weibull PDF, according to the Kolmogorov-Smirnov (K-S) goodness of fit criteria. The predictions of the corrosion conditions and performance effectiveness rankings in the medium by the two distributions were in agreement for all the concentrations of inhibitor admixtures in reinforced concrete studied.
2. Steel-reinforced concrete sample with the synergistic combination of 3.0g $K_2Cr_2O_7$, 4.5g K_2CrO_4, 3.0g $NaNO_2$ and 4ml Aniline inhibitor admixture exhibited optimal performance in the saline corrosive medium studied by both statistical modelling tools employed.
3. This synergistic admixture in concrete exhibited modelled result which moderated OCP quality from μ=−450.19 mV (CSE) for the control specimen to μ=−333.25 mV (CSE), by the Normal PDF model; and from μ=−449.62 mV (CSE) to μ=−332.83 mV (CSE), by the Weibull PDF model. The Normal PDF was modelled at K-S *P*-Value=0.6132 while the Weibull PDF was modelled at K-S *P*-Value=0.3705 goodness of fit criteria. This modelled synergy of inhibiting quality interprets to the “intermediate corrosion risk” classification of ASTM C876.
4. Also, while other synergistic combinations of inhibitor admixtures showed poor performance, compared with the control sample, the concrete sample with the

synergistic admixture of 1.5g K_2CrO_4, 3.0g $NaNO_2$ and 6ml Aniline exhibited better inhibiting quality, Normal μ=−366.81 mV (CSE) and Weibull μ=−367.92 mV (CSE), than the control specimen, though its OCP response, according to ASTM C876, interprets to the “high (> 90% risk of corrosion)” range.

5. By the foregoing, it could be deduced that while the right combinations of inhibitor concentrations as admixtures in concrete could synergistically improve inhibition performance some other inappropriate combinations inhibitor concentrations would rather increase susceptibility of the reinforced concrete to corrosion damage.
6. For this reason, adequate research involving testing, monitoring and requisite analysis is recommended for ascertaining the effect of selected combinations of inhibitor concentrations on corrosion performance of reinforced concrete. This approach, when carried out adequately, will both meliorate corrosion damage and promote the durability of concrete structure in their given medium or environment of application.

5. References

1. Afolabi A.S., (2007), Synergistic inhibition of potassium chromate and sodium nitrite on mild steel in chloride and sulphide media, Leonardo electronic journal of practices and technologies, 11, pp 143−154.

2. Afolabi A.S., Alaneme K.K., Bada S.O., (2009). Corrosion Behavior of Austenitic and Duplex Stainless Steels in Lithium Bromide, Leonardo Electronic Journal of Practices and Technologies, 14, pp. 1−10.

3. Aguiar J.B., Camões A., Moreira P.M., (2008), Performance of concrete in aggressive environment, International journal of concrete structures and materials, 2(1), pp 21−25.

4. Akinpelu J.A., (2002), The need for code of conduct, building regulations and by-laws for the building industry in Nigeria, The professional builder, journal of the Nigerian institute of building, pp 11–14.

5. Akinyemi O.O., Alamu O.J., (2009), Effect of 0.05M NaCl on corrosion of coated reinforcing steels in concrete, The pacific journal of science and technology, 10(1), pp 462−471.

6. Al-Gadhib A.H., Shazali M.A., Rahman M.K., Baluch M.H., (2008), Confluence of diffusivity influence functions on chloride ingress in concrete structures, paper presented at the international conference on construction and building technology, ICCBT 2008 – A – (35), June 26 – 30, 2008, Kuala Lumpur, Malaysia, pp 389−400.

7. Al-Mehthel M., Al-Dulaijan S., Al-Idi S.H., Shameem M., Ali M.R. Maslehuddin, M., (2009), Performance of generic and proprietary corrosion inhibitors in chloride-contaminated silica fume cement concrete, construction and building materials, 23, pp 1768–1774.

8. Arndt R., Jalinoos F., (2009), NDE for corrosion detection in reinforced concrete structures – a benchmark approach, Paper presented at the 7th international symposium on non-destructive testing in civil engineering - NDTCE'09, June 30 –July 03 2009. Nantes, France.

9. Ayininuola G.M., Olalusi O.O., (2004), Assessment of building failures in Nigeria. Lagos and Ibadan case study, African journal of science and technology (AJST) science and engineering series, 5(1), pp 73–78.

10. Burubai W., Dagogo G., (2007), Comparative study of inhibitors on the corrosion of mild steel reinforcement in Concrete, agricultural engineering international, the CIGRE journal, manuscript BC 06 008, IX, pp 1−10.

11. Chaudhary Z., (2002), Built-in corrosion prevention systems for new reinforced concrete seawater pits, 6th Saudi engineering conference, KFUPM, Dhahran, 3, pp 203−216.

12. Chidambaram R.S., Thirugnanam G.S., (2010, "a"), Performance evaluation of protective coatings on angle specimens for corrosion resistance, International journal of civil and structural engineering, 1(1), pp 13–26.

13. Chidambaram R.S., Thirugnanam G.S., (2010, "b"), Performance evaluation of protective coatings on corrosion resistance in transmission line tower foundations, International journal of applied engineering research, Dindigul, 1(1), pp 1–14.

14. Cook D.C., (2005), Spectroscopic identification of protective and non-protective corrosion coatings on steel structures in marine environments, Corrosion Science, 47, pp 2550–2570.

15. Di Maio A.A., Lima L.J., Traversa L.P., (2004), Chloride profiles and diffusion coefficients in structures located in marine environment, Structural concrete, 5(1), pp 1−4.

16. Fagbenle R.O., Katende J., Ajayi O.O., Okeniyi J.O., (2011), Assessment of wind energy potential of two sites in North-East, Nigeria. Renewable energy 36, pp 1277–1283.

17. Ha T.–H., Muralidharan S., Bae J.–H., Ha Y.–C., Lee, H.–G., Park, K.–W., Kim, D.–K., (2007), Accelerated short-term techniques to evaluate the corrosion performance of steel in fly ash blended concrete, building and environment, 42, pp 78–85.

18. Haynie F.H., (2005), Statistical treatment of data, data interpretation, and reliability, In: Baboian, R., (ed.), corrosion tests and standards – application and interpretation, 2nd Edition, ASTM international, West Conshohocken, PA, pp 83−88.

19. Holloway L., Nairn K., Forsyth M., (2004), Concentration monitoring and performance of a migratory corrosion inhibitor in steel-reinforced concrete, cement and concrete research, 34, pp 1435–1440.

20. Izquierdo D., Alonso C., Andrade C., Castellote M., (2004), Potentiostatic determination of chloride threshold values for rebar depassivation. Experimental and statistical study, Electrochimica Acta, 49, pp 2731–2739.

21. Johnson S.C., Thirugnanam G.S., (2010), Experimental study on corrosion of transmission line tower foundation and its rehabilitation, International journal of civil and structural engineering, 1(1), pp 27–34.

22. Junzhi Z., Jianze W., Deyu K., (2010), Chloride diffusivity analysis of existing concrete based on Fick's second law, journal of Wuhan university of technology-mater. Sci. Ed., 25(1), pp 142−146.

23. Kuang F., Zhang J., Zou C., Shi T., Wang Y., Zhang S., Xu H., (2010), Electrochemical methods for corrosion monitoring. A survey of recent patents, recent patents on corrosion science, 2, pp 34−39.

24. Lee C., Bonacci J.F., Thomas M.D.A., Maalej M., Khajehpour S., Hearn N., Pantazopoulou S., Sheikh S., (2000), Accelerated corrosion and repair of reinforced concrete columns using carbon fibre reinforced polymer sheets, Can. J. Civ. Eng., 27, pp 941−948.

25. Montgomery D.C., Runger G.C., (2003), Applied statistics and probability for engineers, 3rd edition, John Wiley & Sons, Inc.

26. Murthy D.N.P., Xie M., Jiang R., (2004), Weibull models, John Wiley & Sons, Inc., Hoboken, New Jersey.

27. Okeniyi J.O., Okeniyi E.T., (2011), Implementation of Kolmogorov-Smirnov P-Value computation in Visual Basic®. Implication for Microsoft Excel® library function, Journal of Statistical Computation and Simulation, doi:101080/009496552011593035.

28. Okeniyi J.O., Obiajulu U.E., Ogunsanwo A.O., Odiase N.W., Okeniyi, E.T, (2012, "a"), CH_4 emission model from the waste of sus domesticus and gallus domesticus in Nigerian local farms. Environmental implications and prospects, mitigation and adaptation of strategies for global change, DOI: 10.1007/s11027-012-9365-7, published as online first March 20, 2012 at http://www.springerlink.com/openurl.asp?genre=article&id=doi:10.1007/s11027-012-9365-7.

29. Okeniyi, J.O., Omotosho, O.A., Ajayi, O.O., James, O.O., Loto C.A, (2012, "b"), Modelling the performance of sodium nitrite and aniline as inhibitors in the corrosion of steel-reinforced Concrete, Asian journal of applied sciences, 5(3), pp 132–143.

30. Omotosho O.A., (2011), Assessing the performance of potassium dichromate and aniline on concrete steel rebar deterioration in marine and microbial media, Research journal of applied sciences, 6(3), pp 143–149.

31. Omotosho O.A., Okeniyi J.O., Ajayi O.O., (2010), Performance evaluation of potassium dichromate and potassium chromate inhibitors on concrete steel rebar corrosion, Journal of failure analysis and prevention, 10(5), pp 408–415.

32. Oni A.O., (2010), Analysis of incidences of collapsed buildings in Lagos metropolis, Nigeria, International journal of strategic property management, 14, pp 332–346.

33. Revie R.W., Uhlig H.H., (2008), Corrosion and corrosion control, 4th Edition, John Wiley & Sons, Inc, Hoboken, New Jersey.

34. Roberge P.R., (2003), Statistical Interpretation of Corrosion Test Results, In: Cramer, S.D., Covino, B.S., Corrosion: Fundamentals, Testing, and Protection, ASM Handbook, Vol. 13A, ASM International), pp. 425−429.

35. Robertson I.N., Newtson C., (2009), Performance of corrosion inhibitors in concrete exposed to marine environment, In: Alexander, M.G., Beushausen, H.-D., Dehn, F., Moyo, P., (eds), Concrete Repair, Rehabilitation and Retrofitting II, Taylor & Francis Group, London), pp 901−906.

36. Saraswathy V., Song H.-W., (2007), Improving the durability of concrete by using inhibitors, Building and environment, 42, pp 464–472.

37. Sekar A.S.S., Saraswathy V., Parthiban G.T., (2007), Cathodic protection of steel in concrete using conductive polymer overlays, International Journal of Electrochemical Science, 2(7)**,** pp 872−882.

38. Selvaraj R., Selvaraj M., Iyer S.V.K., (2009), Studies on the evaluation of the performance of organic coatings used for the prevention of corrosion of steel rebars in concrete structures, Progress in Organic Coatings, 64, pp 454–459.

39. Shazali M.A., Al-Gadhib A.H., Rahman M.K., Baluch M.H., (2008), Modeling ingress and binding behavior of chlorides in unsaturated concrete, paper presented at the international conference on Construction and Building Technology, ICCBT 2008 – A – (35), June 26 – 30, 2008, Kuala Lumpur, Malaysia, pp 401−410.

40. Song H.–W., Saraswathy V., (2007), Corrosion monitoring of reinforced concrete structures – A review, International Journal of Electrochemical Science, 2, pp 1–28.

41. Soong T.T., (2004), Fundamentals of probability and statistics for engineers, John Wiley & Sons Ltd, England.

42. StatPoint, Inc., (2005), Distribution Fitting (Uncensored Data), StatPoint, Inc.

43. Thas O., (2010) Comparing Distributions, Springer Science+Business Media, LLC.

44. Venkatesan P., Palaniswamy N., Rajagopal K., (2006), Corrosion performance of coated reinforcing bars embedded in concrete and exposed to natural marine environment, Progress in Organic Coatings, 56, pp 8–12.

45. Yoon S., Wang K., Weiss W.J., Shah S.P., (2000), Interaction between loading, corrosion, and serviceability of reinforced concrete, ACI Materials Journal, 97(6), pp 637−644.

46. Zwillinger D., Kokoska S., (2000), CRC standard probability and statistics tables and formulae, Chapman & Hall/CRC.