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# Modelling the Performance of Sodium Nitrite and Aniline as Inhibitors in the Corrosion of Steel-reinforced Concrete

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#### ABSTRACT

The performances of sodium nitrite and aniline inhibitors on the corrosion of concrete steel rebar partially immersed in sodium chloride and sulphuric acid media were investigated in this study. The open circuit potential corrosion monitoring technique was employed for the marine and acidic simulating environments and potential readings were taken in accordance with ASTM C 876. Inhibiting quality and uniformity of the inhibitors were then analyzed using the Weibull probability density distribution as an extreme value statistical modelling approach to study performance effectiveness and predict the most efficient inhibitor in each media. In the statistically analyzed experimental results for each of the inhibitor concentrations employed, (0.679 M) sodium nitrite is identified as exhibiting the best inhibiting quality in sodium chloride while (0.137 M) aniline was predicted as showing the lowest probability of corrosion risk in sulphuric acid medium. The synergetic admixtures employed in the study performed poorly in inhibiting effectiveness compared to the control specimens in the two media considered. The overall probabilistic results predicted preferences of sodium nitrite as inhibitors in the sodium chloride medium simulating saline environments and aniline in sulphuric acidic medium simulating sewage or underground microbial environments.

**Key words:** Reinforced concrete, corrosion inhibitors, Weibull distribution, Kolmogorov-Smirnov statistics, saline/microbial environment

#### INTRODUCTION

Steel reinforced concrete is a very important item of construction, used for major portion of infrastructural developments that is vital to people's standard of living globally (Duffo et al., 2009; Ha et al., 2007), hence, its durability, safe functioning, serviceability and maintainability is essential for sustainable developments. However, the durability of reinforced concrete structures could be curtailed by premature or unexpected corrosion failure in the structures (Duffo et al., 2009) with debilitating costs of repair or replacement, which constitute major part of current spending on infrastructure (Duffo et al., 2009; Song and Saraswathy, 2007; Smith and Virmani, 2000).

Normally, due to the presence of sodium and potassium oxides, as well as calcium hydroxide produced in the hydration reactions of cement components, high alkaline solution within the pore structure of cement paste matrix enables formation of a passive film on steel rebar surface to protect it from further corroding (Smith and Virmani, 2000; Liu, 1996). However, this protection can be

completely depleted by aging of the structure (Bhargava et al., 2007), the ingress of aggressive electrochemical agents of corrosion in the form of carbonation, chloride contamination (Bertolini et al., 2004; Richard, 2002; NEA/CSNI, 2002; Schiegg et al., 2000) and the progressive Biogenic Sulphuric Acid (BSA) attack on concrete in sewage environments (Hewayde et al., 2007). Carbonation, not only hardens the concrete surface but also reduces the passifying alkalinity of the concrete rendering the embedded steel reinforcement unprotected (Bertolini et al., 2004). Concentration of chlorides sufficient for corrosion attack in concrete, is obtained from sodium chloride naturally present in sea water and marine atmospheres, or artificially introduced as deicing salts in highways and parking facilities in temperate countries (Bertolini et al., 2004; Broomfield, 2003; US Army Corps of Engineers, 1995). This actively breaks down the protective passive oxide layer, which was originally produced by the passivating alkaline pore water, on the embedded steel surface. BSA attack on concrete revert hydration products of concrete matrix to (CaSO<sub>4</sub>) and induce the formation of ettringite (3CaO.Al<sub>2</sub>O<sub>3</sub>.3CaSO<sub>4</sub>.31H<sub>2</sub>O or 3CaO.Al<sub>2</sub>O<sub>3</sub>.CaSO<sub>4</sub>.12H<sub>2</sub>O) through the combined mechanisms of sulphate reducing bacterial (e.g., Desulfovibrio) and sulphur oxidizing bacterial (e.g., Thiobacillus thiooxidans) on concrete (Vollertsen et al., 2008; Hewayde et al., 2007; Parande et al., 2006). Rust products from carbonation and chloride attack and gypsum and ettringite from BSA attack are all weak in structural strength even as they are also expansive within the restricted space of the concrete. As a result, expansive stresses are set up within the concrete which lead to cracking, delamination and subsequently spalling of the concrete cover. This leads to progressive exposure of the steel rebar to further corrosion, degradation of structural integrity and reduction of load bearing capacity, culminating eventually in catastrophic collapse of the concrete structure (Song and Saraswathy, 2007; Hewayde et al., 2007; Parande et al., 2006; Gaal, 2004). This therefore makes the need to combat this mode of concrete degradation essential.

The use of corrosion inhibitor, amongst others has been recognised in studies as a viable means of protecting steel reinforced concrete from corrosion in potentially corrosive environments (Song and Saraswathy, 2007; Hewayde et al., 2007; Parande et al., 2006; Smith and Virmani, 2000; Schiegg et al., 2000). Several authors have worked on the effectiveness of inhibitors in various environments many of which studied the inhibitors individually and in synergies (Burubai and Dagogo, 2007; Afolabi, 2007; Saraswathy and Ha-Won, 2007; Hewayde et al., 2007; Loto, 1992), employing the OCP technique. This technique which only determines inhibitor effectiveness is found to have a major shortcoming in the form of fluctuations of potential readings during experiments (Burubai and Dagogo, 2007). These fluctuations make data interpretation difficult and sometimes impossible. Apart from the fact that, there is a dearth of studies that employed the statistical approach of the extreme value distribution, the use of sodium nitrite (NaNO<sub>2</sub>) and aniline in synergy have not been reported elsewhere, though they have been used individually and in synergy with other inhibitors (Burubai and Dagogo, 2007; Afolabi, 2007; Saraswathy and Ha-Won, 2007; Loto, 1992). This study therefore focuses on the evaluation of the performance of sodium nitrite and aniline inhibitors on the corrosion of steel reinforced concrete using statistical method of the extreme value distribution. The synergetic effects of the combination of the two inhibitors in comparison with their individual effects were also studied. The study specifically employed the Weibull Probability Distribution Function (PDF), as an extreme value statistical modelling tool (Roberge and Klassen, 2003), to analyse the quality, reliability and uniformity of inhibitor performance in investigating the comparative effectiveness of the inhibitors.

#### MATERIALS AND METHODS

Concrete blocks used for the experiment were made, in accordance with literatures (Ha et al., 2007; Burubai and Dagogo, 2007), using Portland cement, sand and gravel mixed with water at a mix ratio of 1:2:4. The formulation used for the reinforced concrete specimens for cement, water, sand and gravel, respectively was 320, 140, 700 and 1150 all in kg m<sup>-3</sup>. The water/cement (w/c) ratio was 0.44. Thirty concrete blocks, in two-sets of fifteen block specimens were used in the study. Each of the specimens was admixed with different concentrations of inhibitors and with a fixed amount of 0.1 M sodium chloride. The first sets of fifteen specimens were immersed in 3.5% sodium chloride (NaCl) medium to simulate marine/saline environments while the second sets were immersed in 0.5 M dilute sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) medium to simulate microbial (sewage) environment. All chemicals used were of AnalaR reagent grade. Concrete samples were premixed with NaNO<sub>2</sub> and aniline inhibitors concentration that include (1.5 g) 0.136 M, (3.0 g) 0.272 M, (4.5 g) 0.408 M, (6.0 g) 0.544 M, (7.5 g) 0.679 M, (9.0 g) 0.815 M and (1 mL) 0.069 M, (2 mL) 0.137 M, (3 mL) 0.206 M, (4 mL) 0.274 M, (5 mL) 0.343 M, (6 mL) 0.411 M, respectively. The synergetic combinations include concrete specimen admixed with 0.136 M NaNO<sub>2</sub> and 0.274 M aniline and 0.272 M NaNO<sub>2</sub> and 0.069 M aniline, respectively.

DIN-ST 60 mm type of steel rebar was used for the reinforcement. The steel was obtained from Oshogbo Steel Rolling Mill, Nigeria and its chemical composition include: 0.3% C, 0.25% Si, 1.5% Mn, 0.04% P, 0.64% S, 0.25% Cu, 0.1% Cr, 0.11% Ni and the remainder Fe. The rebar were cut into several pieces each with a length of 160 and 10 mm 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 (Burubai and Dagogo, 2007).

Each concrete block was partially immersed in their respective test medium such that the liquid level was just below the exposed steel reinforcement but not making contact with it. Open Circuit Potential (OCP) readings were then obtained, by placing a Copper/copper Sulphate Electrode (CSE) firmly on the concrete block. One of the two lead terminals of a high impedance multimeter was connected to the CSE and the other to the exposed part of the embedded steel reinforcement 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 reinforcement (Saraswathy and Ha-Won, 2007; Burubai and Dagogo, 2007) in 2-day intervals for the exposure period. All the experiments were performed under free corrosion potential and at ambient temperature. The average of the three readings was computed and this was subjected to data analysis and interpretation based on the standards of American Society for Testing and Materials, ASTM C876-91 R99 (Ha et al., 2007; Song and Saraswathy, 2007; ASTM, 2007). Curves of mean corrosion potential readings against exposure time, obtained during the experiment are presented in Fig. 1 for the first set of specimens with inhibitor admixtures in NaCl medium, while the curves for the second set of specimen with inhibitor admixtures in H<sub>2</sub>SO<sub>4</sub> medium are presented in Fig. 2.

**Data analysis:** The two-parameter Weibull distribution function used is given by Haynie (2005), Murthy *et al.* (2004) and Montgomery and Runger (2003):

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

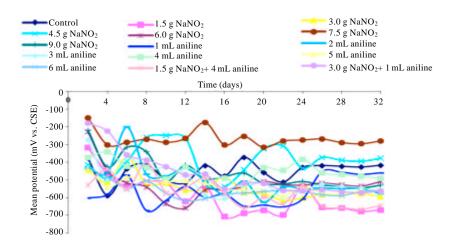


Fig. 1: Curves of mean potential vs. time for concrete sample admixed with varying concentrations of sodium nitrite and aniline in NaCl medium

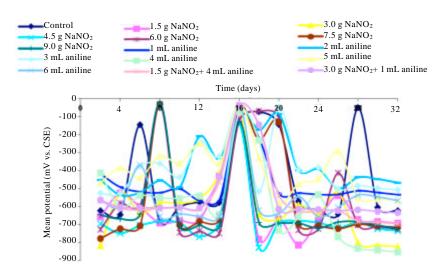


Fig. 2: Curves of mean potential vs. time for concrete sample admixed with varying concentrations of sodium nitrite and aniline in  $H_2SO_4$  medium

where, k is the shape parameter and c is the characteristic value or the scale parameter. Equation can be expressed in linear form (Haynie, 2005; Murthy  $et\ al.$ , 2004) to obtain:

$$\ln\left[-\ln\left[1-F(x)\right]\right] = k\ln x - k\ln c \tag{2}$$

A threshold value  $x_0 = 0$  had been assumed by using the two-parameter Weibull (Murthy *et al.*, 2004). For this, the consistencies of the negative OCP values with the logarithmic nature of Eq. 2 had been ensured by taking x values 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 equation. For measurement of quality for the data, a Weibull prediction of the mean  $\mu$  is given by Haynie (2005) and Murthy *et al.* (2004):

$$\mu = c\Gamma\left(1 + \frac{1}{k}\right) \tag{3}$$

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

Goodness of fit test: To study how well the OCP data follow the Weibull distribution, the Kolmogorov-Smirnov (K-S) goodness of fit test (GoF) (Izquierdo et al., 2004; Murthy et al., 2004; Roberge, 2003; Roberge, 1999) was employed. This GoF criteria measures the absolute difference between the empirical distribution function  $F^*(x)$  and the theoretical distribution function F(x) (Okeniyi and Okeniyi, 2011; Polyanin and Manzhirov, 2007; Soong, 2004) using the expression:

$$d = d(x_1, ..., x_n) = \sqrt{n} \sup_{-\infty < x < \infty} |F^*(x) - F(x)|$$
(4)

where, n is the sample size. The value of d from Eq. 4 is useful for ascertaining region of the level of significance ( $\alpha$ ) of the K-S goodness-of-fit from tables, using the condition  $d_{computed} < c_{n,\alpha(tabulated)}$  (Soong, 2004; Gibbons and Chakraborti, 2003). 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). Thus, based on  $\alpha = 0.05$ , level of significance, the computed p-value, could be subjected to test the hypotheses:

$$\begin{array}{l} H_{_{0}}\colon P \geq \alpha \\ H_{_{A}}\colon P < \alpha \end{array} \tag{5}$$

Where:

H<sub>0</sub> = Null hypothesis that the measured gas emission data follow the Weibull distribution

H<sub>A</sub> = Alternative hypothesis that the measured gas emission data does not follow the Weibull distribution

## RESULTS AND DISCUSSION

Observation of the plots of the potential readings in Fig. 1 and 2 show that these readings fluctuate from the beginning to the end of the experiment, for each concentration of inhibitors presented. These fluctuations occur in the form of spikes of varying amplitudes and make interpretation of observed data difficult. Although, the concrete admixed with 0.679 M NaNO<sub>2</sub> could be deduced from Fig. 1 to monotonically lead the stack in inhibition effectiveness in the NaCl medium, in spite of the fluctuations in the OCP plots, it is almost impossible however to identify which concentration exhibited such optimal effectiveness of inhibition in the sulphuric acid medium from the fluctuating curves in Fig. 2. These fluctuations could be due to reactions between the inhibitor, alkaline pore solution, steel rebar and the medium resulting in complex formations which accounted for sharp oscillatory drifts between the active and passive regions. For these fluctuations in the OCP readings for each admixed inhibitor, the Weibull distribution modelling tool was

employed to study the underlying characteristics, especially of inhibiting quality and effectiveness, with subsequent GoF analysis using the K-S GoF criteria. The results from these analyses are presented in Table 1 and 2 for admixed inhibitors in NaCl and H<sub>2</sub>SO<sub>4</sub> media, respectively.

From Table 1, the p-values from the K-S goodness of fit test shows that the measured OCP data for all the reinforced concrete samples immersed in NaCl medium followed the two-parameter Weibull distribution. For the statistical modelling for these inhibitors, using the Weibull PDF, the p-values is greater than the significant values of  $\alpha$  (i.e., p>0.05) thus satisfying the null hypothesis in Eq. 5. Also, the large values of shape parameters (k) of the Weibull modelling of the admixed inhibitors imply small scatters of OCP data and these translate to good uniformity of the measured data.

Table 2 shows that the p-values of the K-S GoF for the reinforced concrete admixed inhibitors in  $H_2SO_4$  medium are not only lower than that obtained in NaCl medium but also that p<0.05 for

Table 1: Results of Weibull distribution modelling of aniline and NaNO<sub>2</sub> admixtures in reinforced concrete samples immersed in NaCl medium

Admixed inhibitor	k	c	$\mu_{\mathbb{W}}\left(\text{-mV}\left(CSE\right)\right)$	$\operatorname{Prob}\left(\mu_{\mathbb{W}}\right)$	$\mu_{\text{actual}} \left( \text{-mV} \left( CSE \right) \right)$	$Prob \ (\mu_{\text{actual}})$	p-value (K-Stest)
Control	8.72	475.48	449.62	0.4588	450.19	0.4625	0.3556
$1.5\mathrm{g}\mathrm{NaNO}_2$	5.20	644.75	593.30	0.4775	592.38	0.4748	0.5814
$3.0~\mathrm{g~NaNO_2}$	8.52	574.17	542.35	0.4595	543.06	0.4632	0.8201
$4.5~{ m g~NaNO}_2$	4.69	422.55	386.53	0.4824	386.75	0.4833	0.9778
$6.0~{ m g~NaNO}_2$	4.10	582.81	529.00	0.4894	521.81	0.4704	0.0847
$7.5~{ m g~NaNO}_2$	5.14	293.70	270.10	0.4780	268.88	0.4701	0.2359
9.0 g NaNO <sub>2</sub>	4.35	507.36	462.08	0.4862	459.75	0.4788	0.2599
1 mL aniline	7.54	603.15	566.35	0.4632	566.94	0.4658	0.7925
2 mL aniline	3.87	561.33	507.85	0.4927	501.13	0.4751	0.2851
3 mL aniline	5.41	548.13	505.55	0.4757	505.06	0.4739	0.7217
4 mL aniline	9.78	470.42	447.12	0.4557	448.00	0.4621	0.9486
5 mL aniline	13.90	555.49	535.10	0.4482	536.00	0.4559	0.9785
6 mL aniline	12.06	581.46	557.30	0.4509	558.13	0.4568	0.4707
$1.5 \mathrm{gNaNO_2} + 4 \mathrm{mL}$ aniline	7.56	608.94	571.88	0.4631	572.88	0.4675	0.9268
$3.0 \text{ g NaNO}_2 + 1 \text{ mL aniline}$	3.09	532.23	475.88	0.5073	468.50	0.4906	0.1544

Table 2: Results of Weibull distribution modelling of aniline and  $NaNO_2$  admixtures in reinforced concrete samples immersed in  $H_2SO_4$  medium

Admixed inhibitor	k	c	$\mu_{\mathbb{W}}\left(\text{-mV}\left(CSE\right)\right)$	Prob (μ <sub>W</sub> )	μ <sub>actual</sub> (-mV (CSE))	Prob (µactual)	p-value (K-Stest)
Control	1.14	553.00	527.96	0.6127	455.69	0.5517	0.0575
$1.5\mathrm{gNaNO_2}$	2.08	752.26	666.32	0.5403	619.75	0.4875	0.0982
$3.0~\mathrm{g~NaNO_2}$	1.66	760.92	679.98	0.5637	605.75	0.4955	0.0755
$4.5\mathrm{gNaNO_2}$	1.93	854.12	757.54	0.5476	680.13	0.4748	0.0085
$6.0~\mathrm{g~NaNO_2}$	1.00	657.74	659.04	0.6328	529.13	0.5530	0.0748
$7.5~\mathrm{g~NaNO_2}$	0.98	723.07	729.38	0.6353	560.00	0.5409	0.0357
$9.0~\mathrm{g~NaNO_2}$	0.91	898.80	937.47	0.6463	613.69	0.5061	0.0040
1 mL aniline	1.72	593.03	528.65	0.5597	472.50	0.4913	0.0135
2 mL aniline	1.58	448.40	402.60	0.5699	371.63	0.5247	0.2084
3 mL aniline	1.26	489.81	455.21	0.5981	384.69	0.5215	0.0564
4 mL aniline	1.68	716.18	639.54	0.5626	585.88	0.5101	0.1922
5 mL aniline	1.41	512.11	466.22	0.5835	399.50	0.5057	0.1047
6 mL aniline	1.24	763.82	712.19	0.6001	556.00	0.4901	0.0045
$1.5\mathrm{gNaNO_2} + 4\mathrm{mL}$ aniline	1.21	732.58	688.10	0.6043	547.56	0.5053	0.0154
$3.0 \text{ g NaNO}_2 + 1 \text{ mL aniline}$	1.15	728.73	693.90	0.6114	534.31	0.5036	0.0060

seven of these fifteen specimens. By this, while we fail to reject the null hypothesis that the measured OCP data follow the two-parameter Weibull PDF for the remaining eight admixed inhibitors having p>0.05, there is need to reject the null hypothesis for the other seven concrete admixed inhibitors. The reason for this kind of result could be due to the large scatter of OCP data, derivable from the smallness of the shape parameter (k), which is a measure of the uniformity of the measured data, predominant with these inhibitors in the highly corroding  $H_2SO_4$  medium. Such large scatter in measured OCP data populations, in corrosion sense, might have resulted from initiations of pitting corrosion occurring when sulphate ions in ample concentration hit the steel rebar surface (Hausmann, 2004).

To further investigate performance prediction of the admixed inhibitors in reinforced concrete, the mean values obtained from the Weibull model were subjected to the corrosion classification standard of ASTM C 876 with reference to CSE. Corrosion classification conditions obtained based on the standard are presented in Table 3 and 4 for admixed inhibitors in NaCl and  $\rm H_2SO_4$  media, respectively.

Table 3: Corrosion condition prediction for admixed inhibitor in NaCl medium

Admixed inhibitor	μ	Predicted corrosion condition
Control (no inhibitor)	449.62	High (>90% risk of corrosion)
$1.5\mathrm{g}\mathrm{NaNO}_2$	593.30	Severe corrosion
$3.0~{ m g~NaNO}_2$	542.35	Severe corrosion
4.5 g NaNO₂	386.53	High (>90% risk of corrosion)
$6.0~{ m g~NaNO}_2$	529.00	Severe corrosion
7.5 g NaNO₂	270.10	Intermediate corrosion risk
$9.0~{ m g~NaNO}_2$	462.08	High (>90% risk of corrosion)
1 mL aniline	566.35	Severe corrosion
2 mL aniline	507.85	Severe corrosion
3 mL aniline	505.55	Severe corrosion
4 mL aniline	447.12	High (>90% risk of corrosion)
5 mL aniline	535.10	Severe corrosion
6 mL aniline	557.30	Severe corrosion
$1.5~{ m g~NaNO_2} + 4~{ m mL}$ aniline	571.88	Severe corrosion
$3.0 \text{ g NaNO}_2 + 1 \text{ mL aniline}$	475.88	High (>90% risk of corrosion)

Table 4: Corrosion condition prediction for admixed inhibitor in H<sub>2</sub>SO<sub>4</sub> medium

Admixed inhibitor	μ	Predicted corrosion condition
Control (no inhibitor)	527.96	Severe corrosion
1.5 g NaNO <sub>2</sub>	666.32	Severe corrosion
3.0 g NaNO₂	679.98	Severe corrosion
$4.5~{ m g~NaNO}_2$	757.54	Severe corrosion
6.0 g NaNO <sub>2</sub>	659.04	Severe corrosion
7.5 g NaNO₂	729.38	Severe corrosion
9.0 g NaNO <sub>2</sub>	937.47	Severe corrosion
1 mL aniline	528.65	Severe corrosion
2 mL aniline	402.60	High (>90% risk of corrosion)
3 mL aniline	455.21	High (>90% risk of corrosion)
4 mL aniline	639.54	Severe corrosion
5 mL aniline	466.22	High (>90% risk of corrosion)
6 mL aniline	712.19	Severe corrosion
$1.5 \mathrm{gNaNO_2} + 4 \mathrm{mL}$ aniline	688.10	Severe corrosion
$3.0 \text{ g NaNO}_2 + 1 \text{ mL aniline}$	693.90	Severe corrosion

The performance ranking of inhibiting quality based on Weibull model prediction is presented in Fig. 3 and 4 for admixed inhibitors in NaCl and  $H_2SO_4$  media, respectively.

Figure 3 identified 7.5 g NaNO<sub>2</sub> admixture in steel reinforced concrete as exhibiting optimum inhibiting effectiveness in NaCl medium, according to the performance ranking of the Weibull model prediction. This inhibiting effectiveness is valued at a quality of -270.10 mV (CSE), from Table 1, representing a slight over-prediction compared to its actual mean OCP of -268.88 mV (CSE) from measured data. The reliability of this modelled quality stands at a probability of 47.80% bearing good comparison with the probability of observing its measured actual mean OCP data valued at 47.01%. This optimal inhibiting quality predicted for 7.5 g NaNO<sub>2</sub> admixture moderated the corrosion condition to the intermediate corrosion risk range from high (i.e., greater than 90% probability that corrosion will occur) modelled for the control specimen (Table 3) according to ASTM C876-91 R99.

Also identified by the Weibull prediction modelling presented in Fig. 3 as exhibiting good inhibiting effectiveness in NaCl medium compared to the control specimen is 4.5 g NaNO<sub>2</sub> admixture followed, in order of predicted effectiveness, by 4 mL aniline admixture in steel reinforced concrete. The quality of inhibition predicted for 4.5 g NaNO<sub>2</sub> admixture in Table 1 is valued at-386.53 mV (CSE) at a reliability of 48.24% probability, also representing good model prediction compared to a measured actual mean value of -386.75 mV (CSE) at 48.33% probability of observation. Predicted for 4 mL aniline admixture, from Table 1, include the modelled quality of -447.12 mV (CSE) at a reliability of 45.57% probability from measured OCP data with the mean of -448.00 mV (CSE) observed at a probability of 46.21%.

Compared to the control specimen having no admixed inhibitor, all other concentrations of admixed inhibitors studied in this work are predicted as exhibiting poor corrosion inhibition in NaCl medium. This model prediction of the Weibull probability density distribution, though giving more perceptible interpretations than that from the OCP data curves in Fig. 1, finds good agreement with performance rankings deducible. In Fig. 1, for instance, 7.5 g NaNO<sub>2</sub> had been

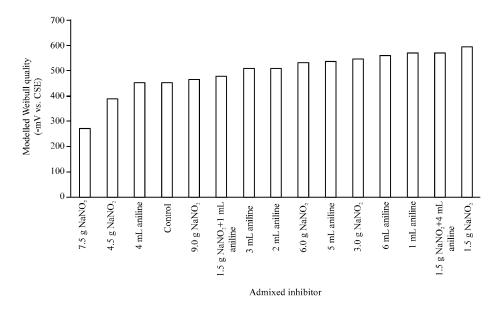


Fig. 3: Performance ranking of inhibiting quality of admixed inhibitors in NaCl medium based on Weibull model prediction

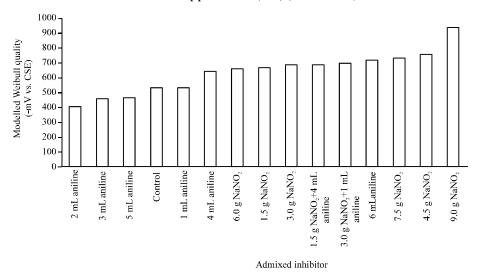


Fig. 4: Performance ranking of inhibiting quality of admixed inhibitors in H<sub>2</sub>SO<sub>4</sub> medium based on Weibull model prediction

observed as leading the stack even as  $1.5 \,\mathrm{g}$  NaNO<sub>2</sub> could be identified as exhibiting lowest mean corrosion potential performance as confirmed by the Weibull rankings of performance prediction presented in Fig. 3.

In H<sub>2</sub>SO<sub>4</sub> medium, the performance prediction model of the Weibull distribution, presented in Fig. 4, identified 2 mL aniline admixed inhibitor in steel reinforced concrete as exhibiting optimal inhibition effectiveness, compared to the control specimen with no admixed inhibitor. At a predicted inhibiting quality of -402.60 mV (CSE) (Table 2) and reliability of 56.99% probability, this modelling, however, represents a wide margin of over-prediction in comparison with the actual mean OCP of -371.63 mV (CSE) observed at a probability of 52.47%. Though obtained at a good K-S goodness of fit which confirms the null hypothesis, this margin of quality over-prediction is, however, wider than that obtainable with any of the admixed inhibitors in NaCl medium. It could also be observed that the reliability obtained as probability percentage in this medium (H<sub>2</sub>SO<sub>4</sub>) is higher than any obtainable in NaCl medium. Furthermore, the H<sub>2</sub>SO<sub>4</sub> medium was confirmed in this study as a harsh corroding environment to steel reinforced concrete even as observed in literatures (Hewayde et al., 2007; Parande et al., 2006). At this, the optimal inhibiting quality favouring 2 mL aniline admixture in steel reinforced concrete was only able to assuage the predicted corrosion condition to the range of high (>90%) risk that corrosion will occur from the severe corrosion range modelled for the control specimen, according to ASTM C876-91 R99, in Table 4. However, the 3 and 5 mL admixtures closely followed the 2 mL inhibitor concentration in order of effectiveness with quality/reliability of -455.21 mV (CSE)/59.81% and -466.22 mV (CSE)/58.35%, respectively, compared to measured OCP mean/probability of -384.69 mV (CSE)/52.15% and -399.50 mV (CSE)/50.57%, as shown in Table 2. The other inhibitor admixture concentrations appeared (in no particular order) to come after the control in effectiveness, revealing that no specific relationship exists between increasing concentrations and inhibitor effectiveness.

All the synergetic inhibitor admixtures considered in this study are modelled as exhibiting poor inhibiting performance both in NaCl and  $\rm H_2SO_4$  media. Of these, only the synergetic combination of  $3.0~\rm g~NaNO_2 + 1~mL$  aniline admixtures in NaCl medium could be considered as somewhat close

to the control specimen as to be suggestive of the need for further studies involving optimal increase of the concentrations of the inhibitor combinations needed for effective inhibition in that medium.

#### CONCLUSION

The performance of sodium nitrite and aniline as inhibitors on the corrosion of steel reinforced concrete has been modelled in this study using the Weibull PDF and the Kolmogorov-Smirnov statistics for the goodness of fit test of the modelled data. From the study the following conclusions could be drawn:

- Of the two-sets of fifteen specimens of inhibitor admixture in steel reinforced concrete tested, all the fifteen specimens in NaCl medium followed the fittings of the Weibull distribution model along with eight out of the fifteen specimens in H<sub>2</sub>SO<sub>4</sub> medium. The remaining seven specimens in H<sub>2</sub>SO<sub>4</sub> medium were characterised with large scatter of measured data in the harsh sulphate corrosive environment and thus did not follow the Weibull model fittings according to the K-S criteria
- The statistical model identified 7.5 g (0.679 M) NaNO<sub>2</sub> inhibitor admixture in steel reinforced concrete as exhibiting optimal performance of inhibition effectiveness in NaCl medium with Weibull quality modelling of -270.10 mV (CSE) at 47.80% probability, followed, in order, by 4.5 g NaNO<sub>2</sub> and 4 mL aniline admixtures
- In the H<sub>2</sub>SO<sub>4</sub> medium, 2 mL (0.137 M) aniline inhibitor admixture in steel reinforced concrete
  was modelled as exhibiting optimum performance of inhibition effectiveness, with Weibull
  quality of -402.60 mV (CSE) at 56.99% probability
- All the synergetic admixtures employed in the study performed poorly in inhibiting effectiveness compared to the control specimens in the two media considered
- The Weibull modelling of corrosion potential for each concrete samples have enabled interpretation of the OCP data in accordance with ASTM C876-91 R99

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