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INVESTIGATING CONCRETE STEEL REBAR DEGRADATION USING SOME SELECTED INHIBITORS IN MARINE AND MICROBIAL MEDIA

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ABSTRACT

Potential monitoring investigations were conducted on concrete steel rebar samples premixed with selected inhibitors accompanied by fixed amount of sodium chloride salt and partially immersed in sulphuric acid and sodium chloride solution. Varying concentration of potassium dichromate, potassium chromate and sodium nitrite inhibitors were used individually and synergistically in this study. The potential readings were taken in accordance with ASTM C 876 through the open circuit potential corrosion monitoring technique. Suppressive quality and dependability of the inhibitor was then assessed by the Weibull probability density distribution as an extreme value statistical modeling approach to study performance effectiveness and forecast the most effective inhibitor concentration in each media. Inhibitor effect on the compressive strengths of the reinforced concrete samples was also examined and reported. Results showed that 0.15M potassium chromate inhibitor had the best overall and individual performance in its inhibiting ability in the H_2SO_4 medium, while 0.68M sodium nitrite admixture was predicted as showing the lowest probability of corrosion risk in NaCl medium. Also, the best synergistic performance was shown by sample admixed with 0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4 and 0.27M $NaNO_2$ partially immersed in the NaCl medium. The compressive strength of concrete sample admixed with 0.03M $K_2Cr_2O_7$ and 0.10M K_2CrO_4 was the highest amongst samples admixed with inhibitor in both media, though the control sample partially immersed in the NaCl medium had the highest overall compressive strength value.

Keywords: Potential, concrete steel rebar corrosion, kolmogorov–smirnov statistics, compressive strength, Weibull distribution.

INTRODUCTION

Instances of building collapse have become an issue of concern in Lagos, South western-Nigeria with statistics from Lagos State Physical Planning and Development Authority showing Lagos Island has having the highest frequency of the incidences recorded. The high incidences of collapsed structures in Lagos Island may be connected with its proximity to the Atlantic where ample supply of salt is available (Omotosho, 2011). Corrosion of steel rebar in concrete is a phenomenon that has been linked to structural failure in concrete infrastructure. This phenomenon is prevalent in marine and sewage environments because of the presence of chloride and sulphate ions. These ions have the tendency of destroying the passive film on steel surface. The ever increasing Lagos population has also led to increased deposition of sewer waste in these water bodies, thereby increasing biogenic sulphuric acid attack (BSA) on concrete infrastructure.

The hydration reactions in cement components produce hydroxides which increase alkalinity within the pore structure of concrete by the formation of a passive film that protects the steel rebar from corrosion (Liu, 1996; Smith and Virmani, 2000). This buffer can be completely run-down by the entry of hostile electrochemical agents of corrosion in the form of carbonation, chloride contamination (Schiegg et al., 2000; Richard, 2002; NEA/CSNI, 2002 and Bertolini et al., 2004) and BSA on concrete in sewage environments (Hewayde et al., 2007). Carbonation hardens the concrete and reduces the alkalinity between steel and concrete, while the chloride ions breaks down the protective passive oxide layer which was originally produced by the passivating alkaline pore water on the embedded steel surface ((NEA/CSNI, 2002). The potency of BSA attack on concrete structure destroys hydration products of concrete changing it to gypsum and stimulates the formation of ettringite or hydrated calcium aluminium sulphate hydroxide. This is achieved through the dual mechanisms of sulphate reducing bacteria and sulphur oxidizing bacteria on concrete (Parande et al., 2006; Vollertsen et al., 2008).

However, several researchers Omotosho et al. (2010), Omotosho (2011), Omotosho et al. (2011) and Loto et al.

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Table 1. Composition of steel rebar employed for the experiment.

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

Table 2. List of Premixed Inhibitor Samples with fixed amount of NaCl in concrete.

S/N	Concrete Block Sample	Inhibitor Concentration
1	Concrete premixed with 0.1M NaCl (control sample).	None
2	Concrete premixed with 0.1M NaCl.	0.03M $K_2Cr_2O_7$
3	Concrete premixed with 0.1M NaCl.	0.06M $K_2Cr_2O_7$
4	Concrete premixed with 0.1M NaCl.	0.10M $K_2Cr_2O_7$
5	Concrete premixed with 0.1M NaCl.	0.13M $K_2Cr_2O_7$
6	Concrete premixed with 0.1M NaCl.	0.16M $K_2Cr_2O_7$
7	Concrete premixed with 0.1M NaCl.	0.19M $K_2Cr_2O_7$
8	Concrete premixed with 0.1M NaCl.	0.05M K_2CrO_4
9	Concrete premixed with 0.1M NaCl.	0.10M K_2CrO_4
10	Concrete premixed with 0.1M NaCl.	0.15M K_2CrO_4
11	Concrete premixed with 0.1M NaCl.	0.19M K_2CrO_4
12	Concrete premixed with 0.1M NaCl.	0.24M K_2CrO_4
13	Concrete premixed with 0.1M NaCl.	0.29M K_2CrO_4
14	Concrete premixed with 0.1M NaCl.	0.14M $NaNO_2$
15	Concrete premixed with 0.1M NaCl.	0.27M $NaNO_2$
16	Concrete premixed with 0.1M NaCl.	0.41M $NaNO_2$
17	Concrete premixed with 0.1M NaCl.	0.54M $NaNO_2$
18	Concrete premixed with 0.1M NaCl.	0.68M $NaNO_2$
19	Concrete premixed with 0.1M NaCl.	0.82M $NaNO_2$
20	Concrete premixed with 0.1M NaCl.	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4
21	Concrete premixed with 0.1M NaCl.	0.06M $K_2Cr_2O_7$, 0.05M K_2CrO_4
22	Concrete premixed with 0.1M NaCl.	0.03M $K_2Cr_2O_7$, 0.41M $NaNO_2$
23	Concrete premixed with 0.1M NaCl.	0.03M $K_2Cr_2O_7$, 0.14M $NaNO_2$
24	Concrete premixed with 0.1M NaCl.	0.05M K_2CrO_4, 0.27M $NaNO_2$
25	Concrete premixed with 0.1M NaCl.	0.10M K_2CrO_4, 0.14M $NaNO_2$
26	Concrete premixed with 0.1M NaCl.	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4, 0.41M $NaNO_2$
27	Concrete premixed with 0.1M NaCl.	0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4, 0.27M $NaNO_2$
28	Concrete premixed with 0.1M NaCl.	0.10M $K_2Cr_2O_7$, 0.05M K_2CrO_4, 0.14M $NaNO_2$

(2011) have identified the use of corrosion inhibitors as a practicable means of combating the challenges associated with protecting concrete steel rebar from corrosion. Some of these articles worked on the use of individual inhibitors (Omotosho *et al*., 2011; Loto *et al*., 2011) while others used two inhibitors in synergy (Omotosho *et al*., 2010; Omotosho, 2011) but none has worked on the use of three inhibitors in synergy amongst the studies conducted so far. Of the articles examined, none has used potassium dichromate, potassium chromate and sodium nitrite as inhibitors in combined synergy on concrete steel rebar partially immersed in saline and sulphate media. Aside from this there is paucity of articles that has used a statistical means to analyze data emanating from open circuit potential (OCP) monitoring experiments because of the fluctuations experienced in potential readings taken.

Therefore, this paper focuses primarily on investigating the individual and synergistic effects of potassium dichromate, potassium chromate and sodium nitrite on concrete steel rebar degradation in saline and sulphate simulating environments by using a two-parameter Weibull distribution function to analyze the varying or fluctuating potential readings in order to be able to clarify data appropriately and to identify the most effective inhibitor concentration. Weibull analysis was also used to categorize inhibitor admixtures according to ASTM C 876. In addition, the concrete test samples used in the experiments were also subjected to compressive strength tests.

MATERIALS AND METHODS

A mix ratio of 1:2:4 consisting of mixtures of Portland cement (320kg/m³), sand (700kg/m³) and gravel (1150

kg/m^3) were used for preparing the experimental concrete blocks. All these were mixed with water (140kg/m^3) (Omotosho et al., 2010; Omotosho, 2011).

The first of the two sets of blocks was prepared for the sodium chloride and sulphuric acid media. This first set was made up of twenty eight blocks for each media but a total of fifty six for the two media. The blocks were cast with different inhibitor concentration premixed with fixed amount of sodium chloride. For each of the premixed inhibitor and the NaCl the percentages quoted were estimated based on every 10kg weight of the concrete from which the blocks were prepared. All reagents used were AnalaR grade. The composition of steel rebar used in the concrete and the list of the concrete blocks with premixed inhibitors is shown in tables 1 and 2 respectively. The 10mm diameter steel rebar inserted in the concrete block was cut into numerous pieces each with a length of 160mm. An abrasive grinder was used to remove mill scale and rust stains on the specimens before it was inserted in each concrete block. Only 140mm of the steel rebar was inserted in the block, the remaining 20mm stuck out at one end of the block and it was coated to prevent atmospheric corrosion. This part was connected to the multimeter. The test solutions used for the experiment with their concentration were; 3.5% NaCl solution and 0.5M dilute sulfuric acid. The reference electrode used in the experiment was the copper sulphate electrode (CSE).

The second set was made up of two concrete block samples with no premixed inhibitor in their formulation. They were intentionally made for determining strength under diverse curing conditions. One of the concrete blocks in the second group was cured in air for two weeks, and the other was cured in water for the same period (Omotosho et al., 2011).

The schematic diagram of the experimental set up can be obtained elsewhere (Omotosho et al., 2011; Loto et al., 2011). Electrochemical potential readings were obtained by positioning a copper/copper sulfate electrode (CSE) securely on the concrete sample. The two terminals of the digital multimeter were connected to the copper sulfate electrode and the visible part of the embedded steel rebar respectively. This was done to make an absolute electrical circuit. Record of the readings was taken at three separate locations on each concrete block directly over the embedded steel rebar (Omotosho et al., 2010; Omotosho et al., 2011). The mean of the three readings obtained was estimated as the potential reading for the steel rebar in two-day intervals for 32 days. The experiments were conducted under free corrosion potential and at ambient temperature of 25°C. The immersion of the sample blocks in the test medium was partial; the level of the test solution was just beneath the visible part of the steel rebar to prevent contact. Data examination and analysis of experimental readings was performed using the technique employed elsewhere (Omotosho et al., 2010; Omotosho et al., 2011) which involved the use of a two-parameter Weibull distribution function given by Equation 1.

$$F(x)=1-\exp\left(-\left(\frac{x}{j}\right)^1\right) \qquad (1)$$

Where l and j is the shape and scale parameter respectively.

The quality of the data was also measured by a Weibull prediction of the mean μ (Omotosho et al., 2010):

$$\nu = j\Gamma(1+\frac{1}{l}) \qquad (2)$$

Where Γ ( ) is the gamma function of ( )

In a bid to ascertain the consistency of the OCP data to Weibull distribution, a goodness of fit test was conducted using the Kolmogorov-Smirnov (K-S) test (Omotosho et al., 2010; Omotosho et al., 2011). The K-S test was used to determine the contrast the empirical $F*$ and the theoretical distribution function F(x) (Omotosho et al., 2010; Omotosho et al., 2011).

$$d = d(x_1,...,x_n) = \sqrt{n} \sup_{-\infty<x<\infty} |F*(x) - F(x)| \qquad (3)$$

Where n is the number of the analyzed data points.

Subsequently, at a significant level of α = 0.05, the P-value of the K-S test is subjected to the hypothesis test:

$$S_o:P \geq \alpha$$
$$S_A:P \geq \alpha \qquad (4)$$

Where S_o and S_A is the null and alternative hypothesis such that the OCP data follow and does not follow the two-parameter Weibull distribution respectively (Omotosho et al., 2010; Omotosho et al., 2011). The influence of the inhibitors on the compressive strength of the test samples was established using the concrete samples in the second set of samples alluded to earlier. The completion of the electrochemical potential monitoring process was followed by the removal of steel-reinforced test samples from their test medium for the purpose of air-hardening them for seven days. Each block was subsequently subjected to weighing and compressive fracture test (Omotosho et al., 2011).

RESULTS AND DISCUSSION

Concrete samples premixed with potassium dichromate in sulfuric acid and sodium chloride medium

The plots of mean corrosion potential versus time for the control specimen in both sulphuric acid and NaCl medium are presented in figure 1. Potential reading of steel in the control specimen moved from the active region at -
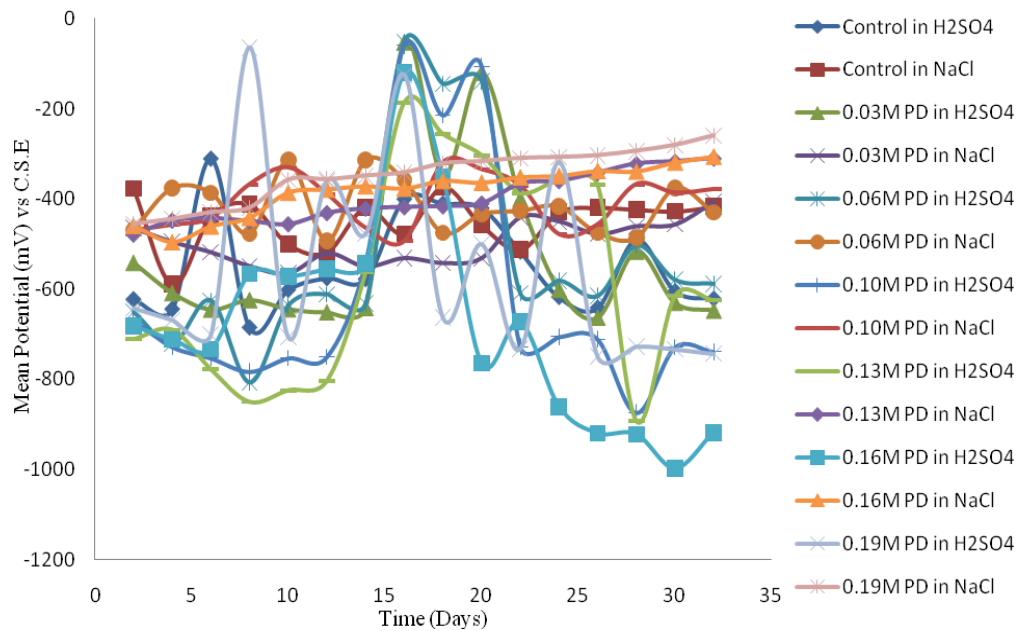
Fig. 1. Relationship of corrosion potential with time for test sample admixed with varying concentration of $K_2Cr_2O_7$ and 0.1M NaCl in H_2SO_4 and NaCl media.

620mV (CSE) to the passive region at -315mV (CSE) on the 7th day. This was because the sulphate ions in the medium had not reached the steel surface as a result of the protection provided by the alkaline pore solution of the concrete. Starting from the 8th to the 15th day, potential reading was in the active region, it then moved towards the passive region until the 20th day. The sulphate ions in the medium may have succeeded in destroying the alkaline barrier resulting in the active corrosion potential observed. Subsequently, the corrosion products suppressed the corrosion reaction and this led to the passive potential. Steel potential that became active after the 20th day is attributable to the dissolution of the corrosion products which exposed steel rebar surface.

The corrosion potential of the control test sample in the NaCl medium as shown in figure 1 drifted from the passive region of -348mV(CSE) to the active region of -605mV(CSE) in the first 5 days of the experiment. After the 5th day, potential readings increased gradually to -400mV (CSE) on the 14th day indicating that the alkaline barrier between steel rebar and the chloride ions in the matrix was capable of reducing corrosion. This trend was sustained until the experiment ended except for the fluctuation on the 25th day.

The potential versus time curves for concrete steel rebar admixed with varying amounts of potassium dichromate partially immersed in H_2SO_4 and NaCl media are presented in the figure 1. An observation of the potassium dichromate potential curves for the two media shows that

the inhibitor was more effective in the NaCl environment. Generally, a decrease in the negative potential of steel was shown by the NaCl medium throughout the experiment. It was also observed that higher inhibitor concentration produced improved inhibition for both media but it was not prolonged in the H_2SO_4 medium. The phenomenon of passsivation (surface film formation), depassivation and repassivation was fluctuating throughout the experiment in both media, but was milder in the H_2SO_4 medium. In addition, it was observed that the inhibitor did not totally prevent corrosion but only reduced or delayed its commencement in a corrosive environment. The inhibition effectiveness observed in the NaCl medium as concentration increased may be as a result of anions becoming inhibitive or acting in such a way as to seal holes in the passive film. The sulphate ions in the H_2SO_4 media did not permit the anions to become effectual rather it stifled their action which may have resulted in the fluctuating depassivation and repassivation phenomenon that was observed throughout the experiment.

Samples premixed with potassium chromate in sulfuric acid and sodium chloride medium
The plots of potential readings against time obtained for the concrete test samples partially immersed in sulphuric acid and sodium chloride are presented in figure 2. It is obvious from the curves obtained that the potential readings demonstrated upward and downward shift from the beginning of the experiment to the end in the two test media, though this incessant spikes and unsteadiness of
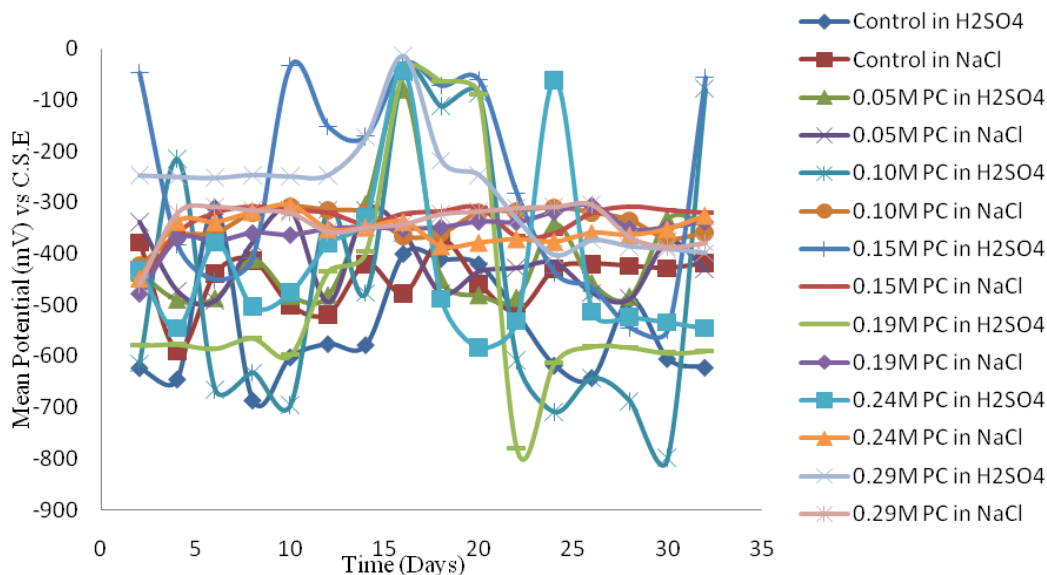
Fig. 2. Relationship of corrosion potential with time for test sample admixed with varying concentration of K_2CrO_4 and 0.1M NaCl in H_2SO_4 and NaCl media.

the readings were less in the NaCl medium indicating that there may be a correlation between the OCP readings and action of NaCl environment. Fundamentally, the shift of the readings towards the passive region infers that the inhibitors were able to protect steel rebar from corrosion through the formation of a thin passive film on the surface of the steel whereas the drift into the active region shows that the aggressive ions present in the medium succeeded in destroying the passive film on the steel rebar as was the case for most of the samples in the sulphuric acid medium. In certain instances, as observed in the curves in figure 2 the destruction of the film was short-lived, while in other instances it was prolonged. This phenomenon of repeated destruction and repair of the passive film on the steel rebar led to persistent and frequent fluctuations. This unsteadiness of the readings may have occurred because of the continued contest between the alkaline environment around steel rebar in the concrete test samples and the acidic environment of the sulphuric acid or the chloride ions in the NaCl medium. The complex steel-concrete-inhibitor-media reaction may be another reason for these fluctuations. Hence, the H_2SO_4 medium was more aggressive because of the presence of sulphate ions and therefore fluctuations became more repeated, continuous, erratic and apparent, whereas the samples in the NaCl medium showed fewer fluctuations.

Samples premixed with sodium nitrite in sulfuric acid and sodium chloride medium
The curves of potential versus time for concrete steel rebar premixed with varying concentration of sodium nitrite partially immersed in NaCl and H_2SO_4 media are

presented in figure 3. Clearly the $NaNO_2$ inhibitor was not so effective in the H_2SO_4 medium. Throughout the experimental period fluctuating corrosion potential was displayed and most of the potential reading was in the active corrosion region. In the NaCl medium, it is observed that the $NaNO_2$ inhibitor is more effective as more passivating potential was experienced showing that the H_2SO_4 medium produced sulphate ions that suppressed the activity of the inhibitor throughout the experimental period. Nitrite is an anodic inhibitor that offers only single action inhibitive effect on the steel as revealed in figure 3 in the case of concrete steel rebar in the NaCl medium. The inhibitive effect also increased with increase in nitrite additions in the NaCl medium which indicates that a higher amount of this inhibitor is required to promote anodic passivity. However, the phenomenon of fluctuating corrosion potential was more pronounced in the sulphuric acid medium throughout the duration of the experiment.

Samples premixed with synergetic combination of inhibitors in sulfuric acid and sodium chloride medium
Figures 4 and 5 show the curves of potential against time for concrete steel rebar premixed with synergetic combination of two and three inhibitors respectively in sulphuric acid and sodium chloride medium. The behavior displayed by these synergetic combinations is not so different from the individual use of the inhibitors. Worthy of note is the fact that some of the synergetic combinations showed improved performance in the NaCl medium when compared to the sulphuric acid medium. It
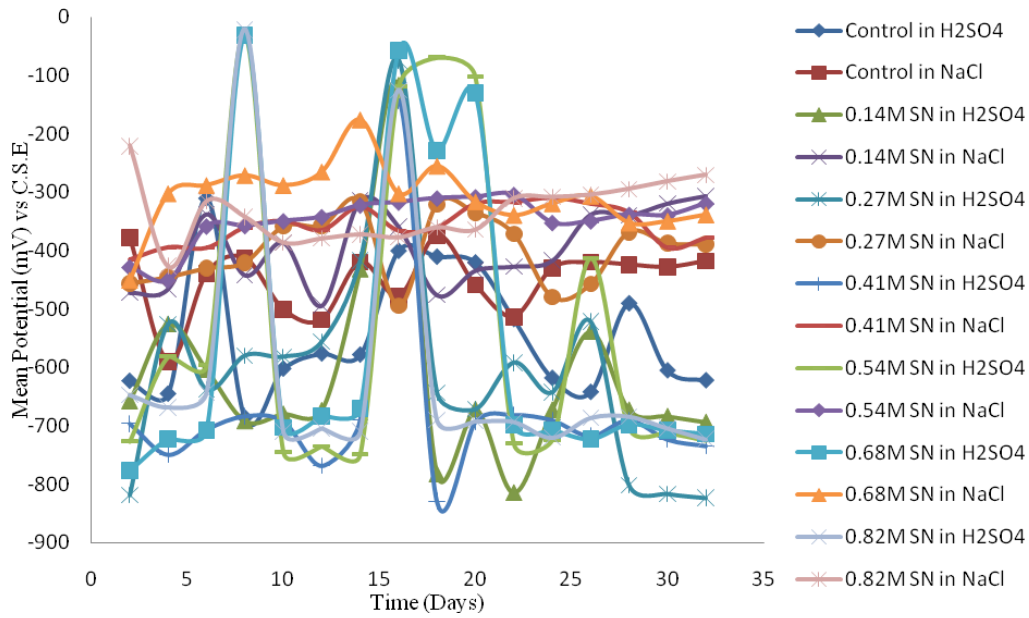
Fig. 3. Relationship of corrosion potential with time for test sample admixed with varying concentration of NaNO$_2$ and 0.1M NaCl in H$_2$SO$_4$ and NaCl media.
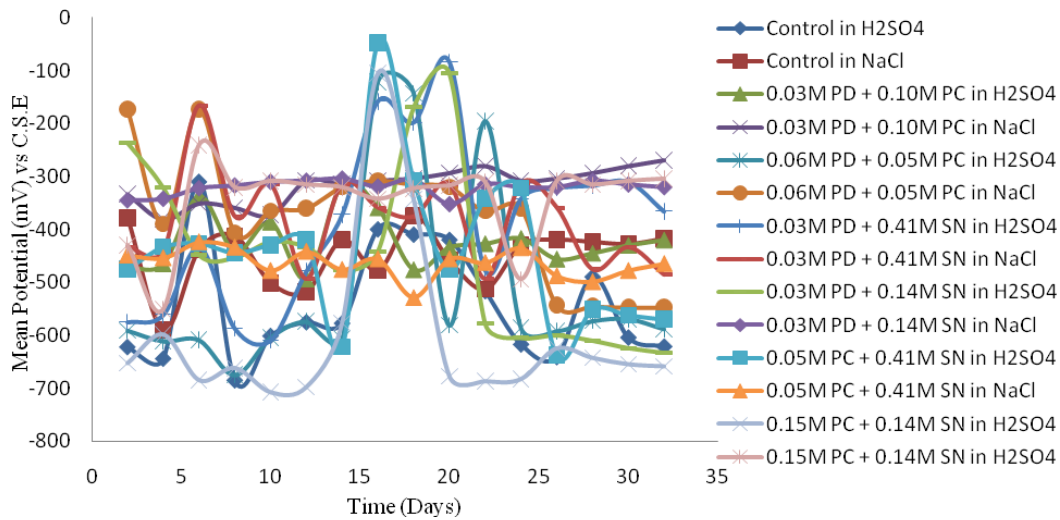
Fig. 4. Relationship of corrosion potential with time for test sample admixed with varying concentration of two inhibitors per sample and 0.1M NaCl in H$_2$SO$_4$ and NaCl media.

was also observed that fluctuations also reduced when the inhibitors were synergistically combined and in fact reduced more in the NaCl medium, but these fluctuations did not disappear.

However, the inference that could be drawn from figures 1 to 5 is that data became difficult to understand and it also became almost impossible to identify the most efficient inhibitor concentration. Therefore, it became imperative that a tool having the capacity to analyze data satisfactorily would be needed to interpret and establish

the most effective inhibitor concentration. A two-parameter Weibull distribution function was therefore utilized to perform the task. By engaging a statistical tool to determine the quality and the reliability of inhibitions in the respective media, a clear interpretation of the inhibitions in the test media could be obtained irrespective of the fluctuations displayed by the admixed inhibitors. Subsequently, Weibull distribution fittings to the OCP measurements for the premixed inhibitor were made. The aptness and dependability of the fittings were then investigated using the K–S goodness of fit test in a bid to
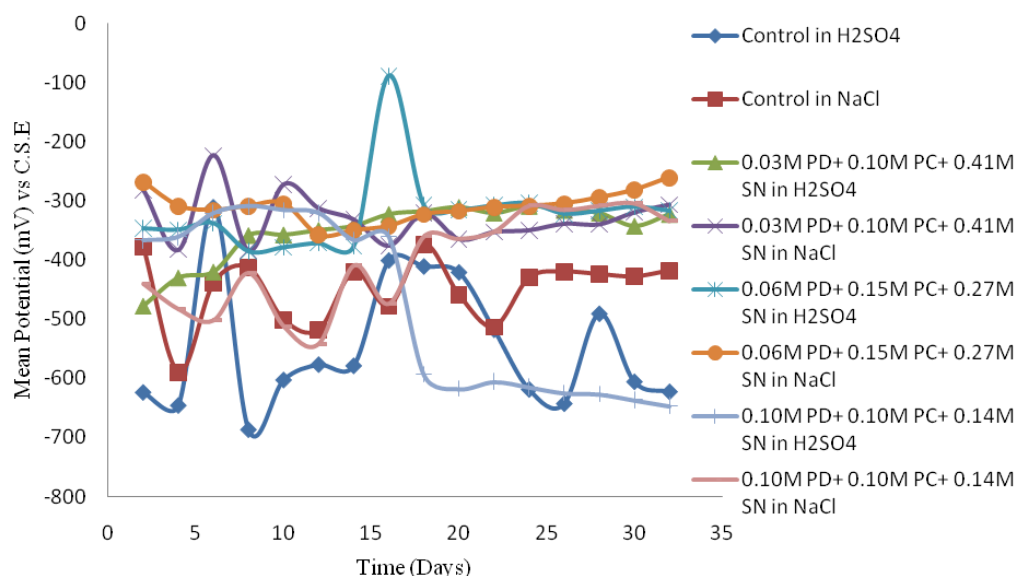
Fig. 5. Relationship of corrosion potential with time for test sample admixed with varying concentration of three inhibitors per sample and 0.1M NaCl in H_2SO_4 and NaCl media.
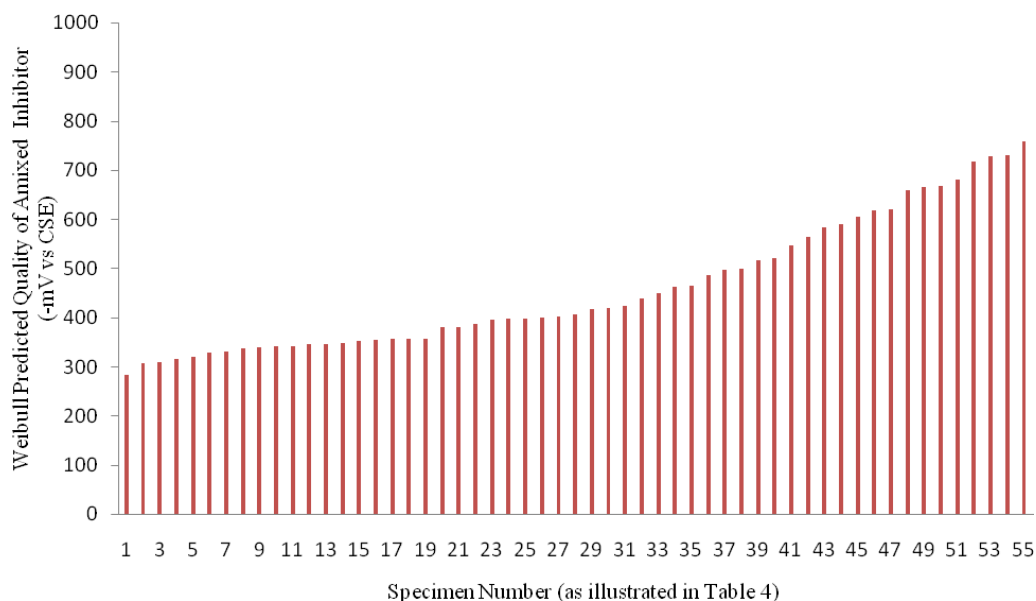
Fig. 6. Performance ranking of inhibiting quality of premixed inhibitor based on prediction by the Weibull distribution.

determine the consistencies of the OCP measurements for each admixed inhibitor with the Weibull distribution fittings. The results obtained are shown in table 3.

Weibull result and evaluation
In table 3 the value of l for all inhibitor amounts show that the data spread exhibits good consistency with relatively small scatter. Most of the samples comply with the null hypothesis which shows that the OCP data came from a two-parameter Weibull distribution based on the P-value of the K-S test from ($P \geq 0.05$). The null hypothesis was

not satisfied by certain samples in table 3, this samples identified with their numbers are 25, 30, 36, 40, 44, 46, 47, 49, 53 and 55.

The sudden increase in the negative corrosion potential in the first 12 days of the experiment may have been the reason why the specimen did not satisfy the null hypothesis. The increased negative potential could also have led to pitting corrosion because of the presence of sulphate and chloride ions in which the specimens were partially immersed.

Table 3. Weibull distribution fitting results of inhibitor admixtures in reinforced concrete samples.

S/N	Admixture	Medium	l	j	ν	Prob (μ)	P-value (K-S) test
1	Control	NaCl	8.723	475.482	449.621	0.459	0.356
2	0.03M $K_2Cr_2O_7$	NaCl	11.628	518.347	496.135	0.452	0.936
3	0.06M $K_2Cr_2O_7$	NaCl	7.593	446.035	418.971	0.463	0.896
4	0.10M $K_2Cr_2O_7$	NaCl	7.643	432.697	406.577	0.463	0.552
5	0.13M $K_2Cr_2O_7$	NaCl	7.821	423.742	398.616	0.462	0.787
6	0.16M $K_2Cr_2O_7$	NaCl	7.688	405.138	380.792	0.463	0.263
7	0.19M $K_2Cr_2O_7$	NaCl	6.415	372.313	346.669	0.469	0.495
8	0.05M K_2CrO_4	NaCl	7.049	445.544	416.931	0.465	0.852
9	0.10M K_2CrO_4	NaCl	11.290	357.148	341.455	0.452	0.277
10	0.15M K_2CrO_4	NaCl	7.969	357.002	336.141	0.461	0.059
11	0.19M K_2CrO_4	NaCl	9.841	374.249	355.799	0.456	0.164
12	0.24M K_2CrO_4	NaCl	11.893	371.702	356.077	0.451	0.816
13	0.29M K_2CrO_4	NaCl	8.574	361.505	341.570	0.459	0.259
14	0.14M $NaN0_2$	NaCl	6.573	423.549	394.890	0.468	0.755
15	0.27M $NaN0_2$	NaCl	7.829	423.156	398.083	0.462	0.816
16	0.41M $NaN0_2$	NaCl	11.898	371.516	355.904	0.451	0.955
17	0.54M $NaN0_2$	NaCl	9.020	365.539	346.188	0.458	0.089
18	0.68M $NaN0_2$	NaCl	5.544	332.708	307.296	0.475	0.594
19	0.82M $NaN0_2$	NaCl	6.802	354.613	331.222	0.467	0.914
20	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4	NaCl	10.358	331.764	316.090	0.454	0.253
21	0.06M $K_2Cr_2O_7$, 0.05M K_2CrO_4	NaCl	3.120	425.566	380.698	0.507	0.674
22	0.03M $K_2Cr_2O_7$, 0.41M $NaNO_2$	NaCl	3.966	426.939	386.792	0.491	0.587
23	0.03M $K_2Cr_2O_7$, 0.14M $NaNO_2$	NaCl	22.941	327.499	319.851	0.441	0.075
24	0.05M K_2CrO_4, 0.27M $NaNO_2$	NaCl	19.090	476.672	463.494	0.443	0.799
25	0.10M K_2CrO_4, 0.14M $NaNO_2$	NaCl	4.550	379.141	346.216	0.484	0.024
26	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4, 0.41M $NaNO_2$	NaCl	8.018	347.528	327.319	0.461	0.984
27	0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4, 0.27M $NaNO_2$	NaCl	13.065	321.094	308.648	0.449	0.683
28	0.10M $K_2Cr_2O_7$, 0.05M K_2CrO_4, 0.14M $NaNO_2$	NaCl	5.342	435.931	401.786	0.476	0.659
29	Control	H_2SO_4	4.985	595.688	546.846	0.479	0.572
30	0.03M $K_2Cr_2O_7$	H_2SO_4	1.378	662.188	605.050	0.586	0.027
31	0.06M $K_2Cr_2O_7$	H_2SO_4	1.311	670.344	618.112	0.593	0.087
32	0.10M $K_2Cr_2O_7$	H_2SO_4	0.365	515.080	2251.364	0.820	0.049
33	0.13M $K_2Cr_2O_7$	H_2SO_4	2.338	658.847	583.803	0.529	0.925
34	0.16M $K_2Cr_2O_7$	H_2SO_4	2.056	808.576	716.289	0.541	0.360
35	0.19M $K_2Cr_2O_7$	H_2SO_4	1.475	686.007	620.583	0.578	0.076
36	0.05M K_2CrO_4	H_2SO_4	2.115	494.230	437.718	0.539	0.022
37	0.10M K_2CrO_4	H_2SO_4	1.142	545.374	520.091	0.612	0.316
38	0.15M K_2CrO_4	H_2SO_4	1.009	283.942	282.882	0.631	0.691
39	0.19M K_2CrO_4	H_2SO_4	1.104	611.594	589.469	0.617	0.103
40	0.24M K_2CrO_4	H_2SO_4	1.254	555.679	517.198	0.599	0.044
41	0.29M K_2CrO_4	H_2SO_4	1.171	373.278	353.410	0.609	0.054
42	0.14M $NaN0_2$	H_2SO_4	2.079	752.258	666.323	0.540	0.098
43	0.27M $NaN0_2$	H_2SO_4	1.664	760.920	679.979	0.564	0.075
44	0.41M $NaN0_2$	H_2SO_4	1.932	854.119	757.543	0.548	0.008
45	0.54M $NaN0_2$	H_2SO_4	0.995	657.743	659.043	0.633	0.075
46	0.68M $NaN0_2$	H_2SO_4	0.980	723.070	729.378	0.635	0.036
47	0.82M $NaN0_2$	H_2SO_4	0.915	898.800	937.469	0.646	0.004

Table 3 continue…

S/N	Admixture	Medium	l	j	ν	Prob (μ)	P-value (K-S) test
48	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4	H_2SO_4	8.878	446.556	422.611	0.458	0.745
49	0.06M $K_2Cr_2O_7$, 0.05M K_2CrO_4	H_2SO_4	1.713	631.568	563.233	0.560	0.020
50	0.03M $K_2Cr_2O_7$, 0.41M $NaNO_2$	H_2SO_4	2.100	448.440	397.180	0.539	0.667
51	0.03M $K_2Cr_2O_7$, 0.14M $NaNO_2$	H_2SO_4	2.147	522.428	462.667	0.537	0.415
52	0.05M K_2CrO_4, 0.27M $NaNO_2$	H_2SO_4	1.594	556.566	499.171	0.569	0.142
53	0.10M K_2CrO_4, 0.14M $NaNO_2$	H_2SO_4	1.877	748.442	664.410	0.551	0.010
54	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4, 0.41M $NaNO_2$	H_2SO_4	7.223	374.595	350.978	0.465	0.115
55	0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4, 0.27M $NaNO_2$	H_2SO_4	2.549	381.087	338.295	0.522	0.027
56	0.10M $K_2Cr_2O_7$, 0.05M K_2CrO_4, 0.14M $NaNO_2$	H_2SO_4	3.198	542.575	485.944	0.505	0.259

Table 4. Predicted Corrosion Condition.

S/N	Admixture	Medium	ν	Predicted Corrosion condition
1	0.15M K_2CrO_4	H_2SO_4	282.882	Intermediate corrosion risk
2	0.68M $NaNO_2$	NaCl	307.296	Intermediate corrosion risk
3	0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4, 0.27M $NaNO_2$	NaCl	308.648	Intermediate corrosion risk
4	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4	NaCl	316.090	Intermediate corrosion risk
5	0.03M $K_2Cr_2O_7$, 0.14M $NaNO_2$	NaCl	319.851	Intermediate corrosion risk
6	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4, 0.41M $NaNO_2$	NaCl	327.319	Intermediate corrosion risk
7	0.82M $NaNO_2$	NaCl	331.222	Intermediate corrosion risk
8	0.15M K_2CrO_4	NaCl	336.141	Intermediate corrosion risk
9	0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4, 0.27M $NaNO_2$	H_2SO_4	338.295	Intermediate corrosion risk
10	0.10M K_2CrO_4	NaCl	341.455	Intermediate corrosion risk
11	0.29M K_2CrO_4	NaCl	341.570	Intermediate corrosion risk
12	0.54M $NaNO_2$	NaCl	346.188	Intermediate corrosion risk
13	0.10M K_2CrO_4, 0.14M $NaNO_2$	NaCl	346.216	Intermediate corrosion risk
14	0.19M $K_2Cr_2O_7$	NaCl	346.669	Intermediate corrosion risk
15	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4, 0.41M $NaNO_2$	H_2SO_4	350.978	Intermediate corrosion risk
16	0.29M K_2CrO_4	H_2SO_4	353.410	High (>90% risk of corrosion)
17	0.19M K_2CrO_4	NaCl	355.799	High (>90% risk of corrosion)
18	0.41M $NaNO_2$	NaCl	355.904	High (>90% risk of corrosion)
19	0.24M K_2CrO_4	NaCl	356.077	High (>90% risk of corrosion)
20	0.06M $K_2Cr_2O_7$, 0.05M K_2CrO_4	NaCl	380.698	High (>90% risk of corrosion)
21	0.16M $K_2Cr_2O_7$	NaCl	380.792	High (>90% risk of corrosion)
22	0.03M $K_2Cr_2O_7$, 0.27M $NaNO_2$	NaCl	386.792	High (>90% risk of corrosion)
23	0.14M $NaNO_2$	NaCl	394.890	High (>90% risk of corrosion)
24	0.03M $K_2Cr_2O_7$, 0.27M $NaNO_2$	H_2SO_4	397.180	High (>90% risk of corrosion)
25	0.27M $NaNO_2$	NaCl	398.083	High (>90% risk of corrosion)
26	0.13M $K_2Cr_2O_7$	NaCl	398.616	High (>90% risk of corrosion)
27	0.10M $K_2Cr_2O_7$, 0.05M K_2CrO_4, 0.14M $NaNO_2$	NaCl	401.786	High (>90% risk of corrosion)
28	0.10M $K_2Cr_2O_7$	NaCl	406.577	High (>90% risk of corrosion)
29	0.05M K_2CrO_4	NaCl	416.931	High (>90% risk of corrosion)
30	0.06M $K_2Cr_2O_7$	NaCl	418.971	High (>90% risk of corrosion)
31	0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4	H_2SO_4	422.611	High (>90% risk of corrosion)
32	0.05M K_2CrO_4	H_2SO_4	437.718	High (>90% risk of corrosion)
33	Control	NaCl	449.621	High (>90% risk of corrosion)
34	0.03M $K_2Cr_2O_7$, 0.14M $NaNO_2$	H_2SO_4	462.667	High (>90% risk of corrosion)

Table 4 continue…

| S/N	Admixture	Medium	ν	Predicted Corrosion condition
35	0.05M K_2CrO_4, 0.27M $NaNO_2$	NaCl	463.494	High (>90% risk of corrosion)
36	0.10M $K_2Cr_2O_7$, 0.05M K_2CrO_4, 0.14M $NaNO_2$	H_2SO_4	485.944	High (>90% risk of corrosion)
37	0.03M $K_2Cr_2O_7$	NaCl	496.135	High (>90% risk of corrosion)
38	0.05M K_2CrO_4, 0.27M $NaNO_2$	H_2SO_4	499.171	High (>90% risk of corrosion)
39	0.24M K_2CrO_4	H_2SO_4	517.198	Severe corrosion
40	0.10M K_2CrO_4	H_2SO_4	520.091	Severe corrosion
41	Control	H_2SO_4	546.846	Severe corrosion
42	0.06M $K_2Cr_2O_7$, 0.05M K_2CrO_4	H_2SO_4	563.233	Severe corrosion
43	0.13M $K_2Cr_2O_7$	H_2SO_4	583.803	Severe corrosion
44	0.19M K_2CrO_4	H_2SO_4	589.469	Severe corrosion
45	0.03M $K_2Cr_2O_7$	H_2SO_4	605.050	Severe corrosion
46	0.06M $K_2Cr_2O_7$	H_2SO_4	618.112	Severe corrosion
47	0.19M $K_2Cr_2O_7$	H_2SO_4	620.583	Severe corrosion
48	0.54M $NaNO_2$	H_2SO_4	659.043	Severe corrosion
49	0.10M K_2CrO_4, 0.14M $NaNO_2$	H_2SO_4	664.410	Severe corrosion
50	0.14M $NaNO_2$	H_2SO_4	666.323	Severe corrosion
51	0.27M $NaNO_2$	H_2SO_4	679.979	Severe corrosion
52	0.16M $K_2Cr_2O_7$	H_2SO_4	716.289	Severe corrosion
53	0.10M $K_2Cr_2O_7$	H_2SO_4	728.907	Severe corrosion
54	0.68M $NaNO_2$	H_2SO_4	729.378	Severe corrosion
55	0.41M $NaNO_2$	H_2SO_4	757.543	Severe corrosion
56	0.82M $NaNO_2$	H_2SO_4	937.469	Severe corrosion
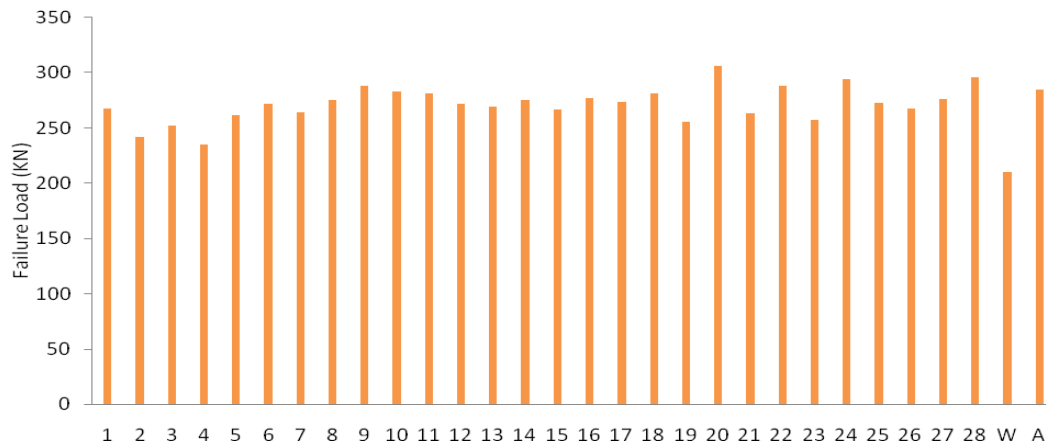
Fig. 7. Histogram of the compressive failure load for the reinforced concrete specimens immersed in sulfuric acid. W=concrete specimen cured in water, A= concrete specimen cured in air. Numbers 1 to 7 represents the list of concrete specimen described previously in table 2.

In addition, the mean values obtained from the Weibull assessment are suitable for appraising the level of corrosion according to ASTM C 876 standard of classification with reference to CSE as presented in table 4.

The performance ranking based on the prediction by the Weibull mean of inhibiting quality of admixed inhibitor in the reinforced concrete samples is presented in figure 6.

From figure 6, specimen number 1 as shown in table 4 with 0.15M K_2CrO_4 admixture partially immersed in the H_2SO_4 medium has a maximum Weibull mean evaluation of -282.882 mV (CSE). The dependability of this predicted mean value stands at a probability of 69.1%. Directly at the rear of specimen 1 are specimens admixed with 0.68M $NaNO_2$ and the synergetic admixtures of 0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4, 0.27M $NaNO_2$ and 0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4 all partially immersed in
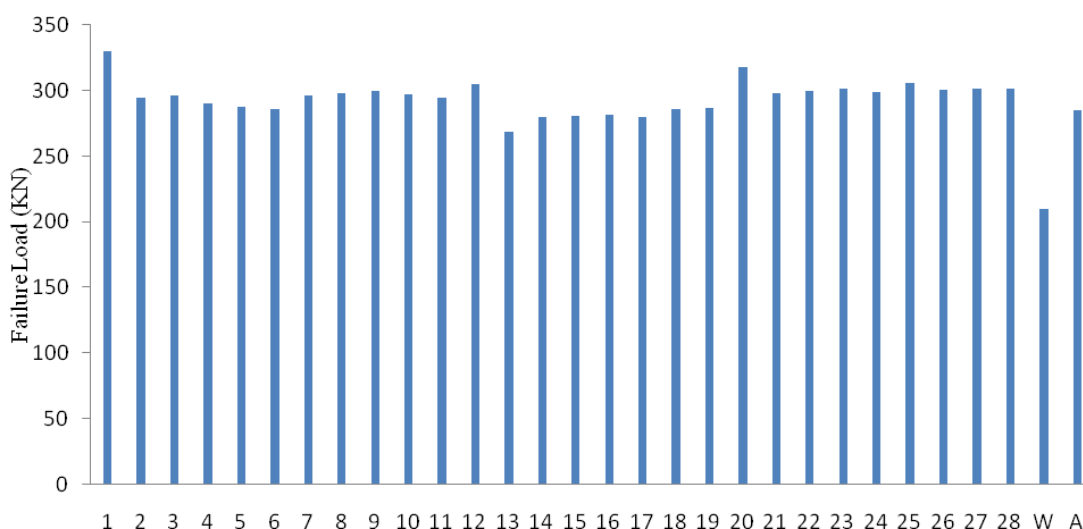
Fig. 8. Histogram of the compressive failure load for the reinforced concrete specimens immersed in sodium chloride medium. W=concrete specimen cured in water, A= concrete specimen cured in air. Numbers 1 to 28 represents the list of concrete specimen described previously in table 2.

NaCl medium having Weibull mean values of 307.296, 308.648 and 316.090 mV (CSE). The reliability of this predicted mean value stands at a probability of 59.4, 68.3 and 25.3% respectively. Though the synergetic admixtures did not show optimal performance, it clearly indicated that using the inhibitors in synergy in this particular case improved the inhibiting performance. Despite the fact that the first fifteen samples that exhibited optimal inhibiting qualities in table 4 are in the intermediate corrosion risk range according to ASTM C 876, yet their inhibiting performances was still better than that of the control samples in the NaCl and sulphuric acid medium.

Moreover, by examining table 4 and figure 6, the predicted Weibull mean values can be used to clearly identify specimens 1 to 32 and 34 to 40 as exhibiting positive and negative inhibiting qualities respectively when compared to the control sample in the NaCl medium (specimen 33). However, samples 34 to 40 and 42 to 56 exhibited positive and negative inhibiting qualities respectively when compared to the control in sulphuric acid medium.

Compressive strengths of concrete test sample
Compressive fracture load data evaluation for concrete steel rebar samples immersed in NaCl and H_2SO_4 medium are presented in figures 7 and 8 respectively. The strengths of all reinforced concrete specimens used in the experiments and partially immersed in H_2SO_4 and NaCl media were higher than those of the specimen cured in water for two weeks. This indicates that the admixed inhibitor had no adverse effect on the concrete samples used. The reason for the higher compressive strength in

the admixed samples than in the sample cured in water could probably be due to the consolidation effect of the inhibitors on the concrete because of the chemical reactions. The exposure of the concrete samples partially to the air and the media might also have led to the dual hardening mechanism linked to the samples.

After examining the compressive strength values obtained for the samples immersed in the H_2SO_4 and NaCl media it was discovered that no precise trend was established. Increasing inhibitor concentration did not lead to increase in compressive strength values and vice-versa when compared to the concrete specimens cured in air. However, in the H_2SO_4 medium specimens 1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 21, 23, 25, 26 and 27 (as depicted in Table 2) gave a loss in compressive strength while specimen 9, 20, 22, 24 and 28 gave an increase when compared to the specimen cured in air. On the other hand, in the NaCl medium specimens 13, 14, 15, 16 and 17 (as depicted in Table 2) showed losses in compressive strength, whereas specimens 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27 and 28 was observed to show increases in compressive strength when compared to the sample cured in air. The result of the compressive strength test also indicated that more samples showed losses in compressive strength in the H_2SO_4 medium than the NaCl medium indicating that the sulphate ions in the sulphuric acid medium had a deleterious effect on the concrete sample. Therefore, the inhibitor admixtures that resulted in an increase in the compressive strength of the concrete samples could become useful formulations in concrete block making for construction in the various media.

CONCLUSION

The effect of three inhibitors, namely potassium dichromate, potassium chromate and sodium nitrite on concrete steel rebar corrosion, individually and synergistically in saline and sulphate media using the OCP technique was investigated in this study. The subsequent fluctuating corrosion potential readings were statistically evaluated using the Weibull probability distribution. The study also determined the compressive strength of concrete test samples in order to ascertain the effect of the inhibitor on the compressive strength of the samples. The experimental results showed potassium chromate (0.15M) as having the best overall and individual performance in its inhibiting ability in the H_2SO_4 medium. Furthermore, Weibull distribution has modeled statistical-based performance evaluation of three inhibitors (individually and synergistically) on concrete steel rebar corrosion. Forty six of the samples were well fitted based on K–S goodness of fit test, while ten had outliers. Rebar concrete samples admixed with 0.15M potassium chromate inhibitor with Weibull $\nu = -282.882$ mV (CSE) at a probability of 69.1% is predicted as exhibiting optimum inhibiting quality in H_2SO_4 medium, while 0.68M sodium nitrite admixture with Weibull $\nu = -307.296$ mV (CSE) and probability of 59.4% was pr`edicted as showing the lowest probability of corrosion risk in NaCl medium. Also, the best synergistic performance was shown by sample admixed with 0.06M $K_2Cr_2O_7$, 0.15M K_2CrO_4 and 0.27M $NaNO_2$ partially immersed in the NaCl medium with Weibull $\nu = -308.648$ mV (CSE) and probability of 68.3%. Thus, Weibull mean values of corrosion potential obtained for all samples made the interpretation of the data using ASTM C 876 achievable despite the fluctuations. The compressive strength of concrete sample admixed with 0.03M $K_2Cr_2O_7$ and 0.10M K_2CrO_4 (specimen 20 in Table 2) was the highest amongst samples admixed with inhibitor in both the sulfuric acid (306KN) and NaCl media (318KN). However, the control sample had the highest overall compressive strength value of 330KN when it was partially immersed in the NaCl medium. Therefore, from the results potassium chromate with concentration of 0.15 M is suggested as an inhibitor for concrete structures in sulphate environment, while 0.68 M sodium nitrite is recommended for concrete structures in NaCl medium, since they both showed highest resistance to corrosion in their respective medium. The performance of concrete sample admixed with the synergistic combination of 0.03M $K_2Cr_2O_7$, 0.10M K_2CrO_4 in NaCl medium is also quite impressive because apart from ranking number four on table 4 it ranked number one in compressive strength value amongst samples admixed with inhibitors. Consequently, it is also suggested as a construction formulation for concrete infrastructure.

REFERENCES

Bertolini, L., Elsener, B., Pedeferri, P. and Polder, RP. 2004. Corrosion of Steel in Concrete: Prevention, Diagnosis, Repair. WILEY-VCH Verlag GmbH & Co, Weinheim.

Hewayde, E., Nehdi, ML., Allouche, E. and Nakhla, G. 2007. Using concrete admixtures for sulphuric acid resistance. Proceedings of the Institution of Civil Engineers, Construction Materials. 160:25-35.

Liu, Y. 1996. Modeling the Time to Corrosion Cracking of the Cover Concrete in Chloride Contaminated Reinforced Concrete Structures. Ph.D thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia, USA.

Loto, CA., Omotosho, OA. and Popoola, API. 2011. Inhibition effect of potassium dichromate on the corrosion protection of mild steel reinforcement in concrete. Int. Journal of Physical Sciences. 6 (9):2275-2284.

Nuclear Energy Agency/Committee on the Safety of Nuclear Installations (NEA/CSNI). 2002. Electrochemical techniques to detect corrosion in concrete structures in nuclear installations. Organisation for Economic Co-operation and Development (OECD). [Technical note].

Omotosho, OA. 2011. Assessing the Performance of Potassium Dichromate and Aniline on Concrete Steel Rebar Deterioration in Marine and Microbial Media. Research Journal of Applied Science. 6(3):143-149.

Omotosho, OA., Loto, CA., Ajayi, OO. and Okeniyi, JO. 2011. Aniline effect on concrete steel rebar degradation in saline and sulfate media. Agricultural Engineering International: The CIGR E journal. 13(2): Inpress

Omotosho, OA., Okeniyi, JO. and Ajayi, OO. 2010. Performance evaluation of potassium dichromate and potassium chromate inhibitors on concrete steel rebar corrosion. J Fail. Anal. and Preven.10 (5):408-415.

Parande, AK., Ramsamy, PL., Ethirajan, S., Rao, CRK. and Palanisamy, N. 2006. Deterioration of reinforced concrete in sewer environments. Proceedings of the Institution of Civil Engineers, Municipal Engineer. (159):11-20.

Richard, RL. 2002. Leading the Way in Concrete Repair and Protection Technology. Concrete Repair Association, Costa Rica. 1.

Schiegg, Y., Hunkeler F. and Ungricht, H. 2000. The Effectiveness of Corrosion Inhibitors - a Field Study. 16th Congress of IABSE Paper 234, Lucerne.

Smith, JL. and Virmani, YP. 2000. Materials and Methods for Corrosion Control of Reinforced and Prestressed Concrete Structures in New Construction. US Department of Transportation – Federal Highway Administration. Publication No. 00- 081.

Vollertsen, J., Nielsen, AH., Jensen, HS., Wium-Andersen, T. and Hvitved- Jacobsen, T. 2008. Corrosion of concrete sewers – The kinetics of hydrogen sulfide oxidation. Science of the Total Environment. (394):162-170.