

## Investigating Potassium Chromate and Aniline Effect on Concrete Steel Rebar Degradation in Saline and Sulphate Media

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Potential monitoring experiments were performed on steel rebars embedded in concrete admixed with potassium chromate, aniline and their synergetic combinations with fixed amount of sodium chloride salt partially immersed in sulphuric acid and sodium chloride solution. Two-sets of fifteen steel-rebar concrete specimens were employed for the study and potential readings were taken in accordance with ASTM C 876. Quality and consistency of the inhibitor was then estimated by the Weibull probability density distribution as an extreme value statistical modeling approach to study the efficacy and predict the most efficient inhibitor concentration in each media. The effect of the inhibitors on the compressive strengths of the test samples was also conducted. Results revealed that test sample admixed with 0.15M potassium chromate partially immersed in sulphuric acid medium exhibited the best overall performance while 0.34M aniline admixture was identified as exhibiting the best performance in the sodium chloride medium. The results also show that the admixture combination of 0.15M potassium chromate and 0.07M aniline in the sodium chloride medium produced the best result amongst the synergistic combination used. Control sample in the saline medium gave the highest increase in compressive strength (330KN) amongst all the samples considered. Also, in the NaCl medium the 0.14M aniline admixture gave the highest increase in compressive strength amongst the inhibited samples. However, the 0.41M aniline admixture gave the highest increase in compressive strength amongst all the samples considered in the H<sub>2</sub>SO<sub>4</sub> medium.

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**Keywords:** Open circuit potential, steel rebar, aniline, potassium chromate, compressive strength, Weibull distribution, Kolmogorov–Smirnov statistics, and marine/sewage media.

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### 1. INTRODUCTION

Lately concerns over the phenomenon of deteriorating reinforced concrete infrastructure have become issues of discussion worldwide instigating various guidelines, arguments and pronouncements

to reference only some. Specifically in the U.S, senate unanimously passed the “National Infrastructure Improvement Act of 2007” to address the deteriorating condition of bridges, drinking water systems, roads, dams and other public works. Though, most of the discussions have preferred building new structures to the repair and improvement of aging infrastructure to revitalize weakening infrastructure, fact still remains that the protection of existing infrastructure and inclusion of corrosion prevention or retarding techniques during the construction process is of paramount importance.

These protection techniques have been found to include lower whole-life costs achieved by choosing effective protection systems in the form of rebar coatings, corrosion inhibitors, use of admixtures, methods for decreasing permeability, increased concrete cover, cathodic protection and lifetime monitoring of corrosion processes [1, 2, 3]. Coatings for steel like epoxy, vinyl, inorganic zinc, furan, urethane, coal-tar epoxy and chlorinated rubber on one hand and that for concrete like cement, polyurethane, poly urea and elastomeric compounds on the other hand protect the materials only where they come in contact with the substrate [1]. However, the presence of corrosion causing agents like oxygen, carbon dioxide, atmospheric moisture [4], with aggressive ions in the form of chloride and sulphate ions existing in saline [5,6] and sewerage environments [7, 5, 6] have been known to be responsible for some of these failures. These ions destroy the alkaline environment existing between steel and concrete by eroding the passive film on the steel rebar [8-15]. The steel subsequently undergoes corrosion, with deposits of the corrosion products increasing the volume of the rebar by about 40%. The expansion and contraction of the resulting corrosion products induce tensile stresses in the concrete that eventually leads to cracks, spalling and catastrophic collapse.

The consequences of infrastructural failure due to uncertainty in predicting degradation could be disastrous to the populace and catastrophic to the nation’s economy. A study initiated by National Association of Corrosion Engineers (NACE) and released by the Federal Highway Administration (FHWA) puts the direct costs associated with highway bridges at 8 billion USD [1, 10]. In view of this, research into new ways of dealing with the challenges associated with reinforced concrete degradation has been encouraged. Several authors have investigated the effect of varying concentration of different inhibitors on concrete steel rebar corrosion in salt, sulphate and numerous environments [10-20], but none has investigated the synergistic combination of aniline and potassium chromate in saline and sewerage medium. Also, none of such works have analyzed the experimental data using a statistical tool in the form of Weibull probability distribution to interpret data and perform a classification according to the ASTM C 876 standard.

Traditionally, potential readings are interpreted straightway without recourse to the use of any statistical tool. However, such interpretations are always very difficult to carry out and sometimes impossible because of the fluctuations and variability in potential readings. To make interpretation possible and easy, an extreme value statistical modelling technique can be employed. This can be achieved with the aid of a Weibull statistical distribution. Moreover, it has also been proven in previous studies that Weibull probability distribution function has the ability to analyze life data having high degree of variability [21-23]. It is also reported that the Weibull probability distribution function is capable and reliable in describing prevailing conditions inherent in a highly variable test data. Thus this study employed the Weibull statistical distribution function for data analysis and result predictions. In addition, the study focused on investigating the effect of potassium chromate and

aniline as well as their synergistic combination on concrete steel rebar degradation in saline and sewage environments using a two-parameter Weibull probability distribution function. Further to this, the statistical distribution was deployed to analyze the fluctuating potential readings in order to be able to interpret data appropriately and to identify the most effective inhibitor concentration. Compressive strength tests were also conducted for all the concrete test samples used.

## 2. EXPERIMENTAL PROCEDURE

### 2.1 Preparation of concrete block samples

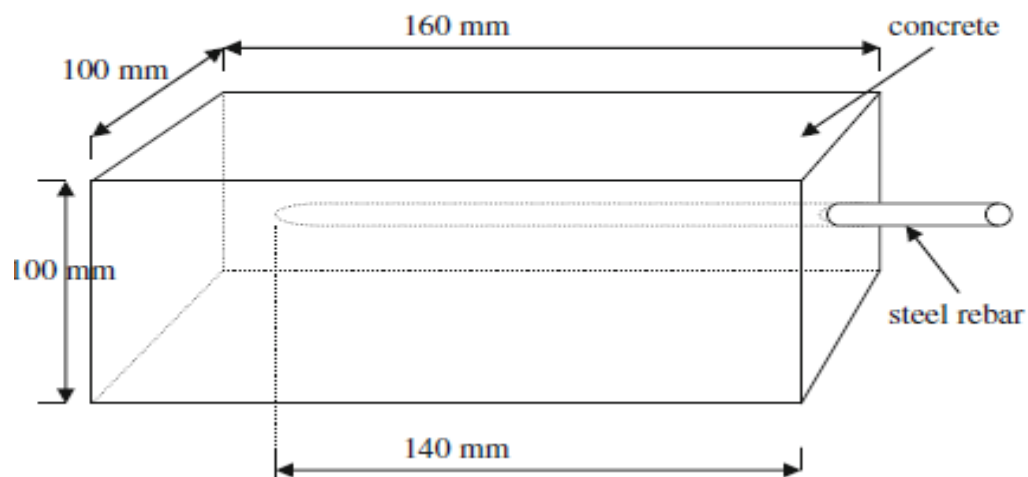
A mix ratio of 1:2:4 consisting of portland cement, sand and gravel were used for the concrete blocks employed for the experiment. The formulation used for the reinforced concrete specimens in  $\text{kg/m}^3$ , was cement-320, water-140, sand-700, and gravel-1150. The water/cement (w/c) ratio was 0.44 [9-15].

**Table 1.** List of Inhibitor Admixtures with fixed amount of NaCl in concrete.

| S/N | Concrete sample                             | Inhibitor concentration                        |
|-----|---|--|
| 1   | Solution without inhibitor (control sample) | None   |
| 2   | Concrete admixed with 0.1M NaCl.            | 0.05M $\text{K}_2\text{CrO}_4$                 |
| 3   | Concrete admixed with 0.1M NaCl.            | 0.10M $\text{K}_2\text{CrO}_4$                 |
| 4   | Concrete admixed with 0.1M NaCl.            | 0.15M $\text{K}_2\text{CrO}_4$                 |
| 5   | Concrete admixed with 0.1M NaCl.            | 0.19M $\text{K}_2\text{CrO}_4$                 |
| 6   | Concrete admixed with 0.1M NaCl.            | 0.24M $\text{K}_2\text{CrO}_4$                 |
| 7   | Concrete admixed with 0.1M NaCl.            | 0.29M $\text{K}_2\text{CrO}_4$                 |
| 8   | Concrete admixed with 0.1M NaCl.            | 0.07M aniline                                  |
| 9   | Concrete admixed with 0.1M NaCl.            | 0.14M aniline                                  |
| 10  | Concrete admixed with 0.1M NaCl.            | 0.21M aniline                                  |
| 11  | Concrete admixed with 0.1M NaCl.            | 0.27M aniline                                  |
| 12  | Concrete admixed with 0.1M NaCl.            | 0.34M aniline                                  |
| 13  | Concrete admixed with 0.1M NaCl.            | 0.41M aniline                                  |
| 14  | Concrete admixed with 0.1M NaCl.            | 0.05M $\text{K}_2\text{CrO}_4$ + 0.27M aniline |
| 15  | Concrete admixed with 0.1M NaCl.            | 0.10M $\text{K}_2\text{CrO}_4$ + 0.07M aniline |

Two groups of blocks were made. The first group consisted of thirty sets of block (first fifteen sets of blocks was partially immersed in the NaCl, while the other fifteen sets was partially immersed in sulphuric acid medium) comprising several specimens, which were cast with varying inhibitor concentration, admixed with fixed amount of sodium chloride (0.1M). The percentages quoted below for each of the admixed inhibitors and the sodium chloride was computed based on every 10 kg weight of the concrete from which the blocks were made. All the chemicals used were AnalaR grade. The sets were prepared as presented in Table 1 and Set 1 in the table was the control sample. The steel rebar used for the reinforcement has the chemical composition of: 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 rest Fe. The rebar was cut into several pieces each with a length of 160mm and 10mm diameter. Mill scale and rust stains on the steel specimens was removed

by an abrasive grinder before insertion in each concrete block. The remaining 20mm protruded at one end of the block, and was painted to prevent atmospheric corrosion [9-15]. This part was also used for electrical connection. The test media used for the investigation were; 3.5% NaCl solution and 0.5M dilute sulphuric acid.



**Figure 1.** Sample of concrete block (drawing is not to scale).

The second group consisted of two concrete blocks without any admixed inhibitor, which were made purposely for determining strength under different 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 [16].

## 2.2 Corrosion potential measurement

The concrete block samples were partially immersed in their respective test medium such that the liquid level was just below the exposed part of the reinforcing steel to avoid direct contact. Corrosion potential or open circuit potential (OCP) readings were obtained by placing a copper/copper sulphate electrode (CSE) firmly on the concrete block [9-15]. A complete electrical circuit was made by connecting one of the two lead terminals of a digital multimeter to a copper sulphate electrode while the other was connected to the exposed part of the embedded steel rebar. The readings were taken at three different points on each concrete block directly over the embedded steel rebar [9-15]. The average of the three readings was estimated as the potential reading for the embedded rebar in 2-day intervals for a period of 32 days. All the experiments were performed under free corrosion potential and at ambient temperature.

### 2.3 Data Assessment

The analysis of data obtained during the experiments was performed using a two-parameter Weibull distribution function given by Equation 1.

$$F(x) = 1 - \exp\left(-\left(\frac{x}{a}\right)^b\right) \quad (\text{Eq 1})$$

Where  $b$  and  $a$  are the shape and scale parameters respectively.

The quality of the data was also measured by a Weibull prediction of the mean  $\eta$  [9, 12-15].

$$\eta = a\Gamma\left(1 + \frac{1}{b}\right) \quad (\text{Eq 2})$$

Where  $\Gamma(\cdot)$  is the gamma function of  $(\cdot)$

A goodness of fit test was also employed to determine the consistency of the OCP data to Weibull distribution, through the Kolmogorov-Smirnov (K-S) test [9]. The K-S test measures the difference between the empirical  $F^*$  and the theoretical distribution function  $F(x)$  [9,10, 12-15].

$$g = g(x_1, \dots, x_n) = \sqrt{n} \sup_{-\infty < x < \infty} |F^*(x) - F(x)| \quad (\text{Eq 3})$$

Where  $n$  is the number of the examined data points.

Consequently, at a significant level of  $\alpha=0.05$ , the P-value of the K-S test is subjected to the test of hypothesis:

$$\begin{aligned} J_o: P &\geq \alpha \\ J_A: P &\geq \alpha \end{aligned} \quad (4)$$

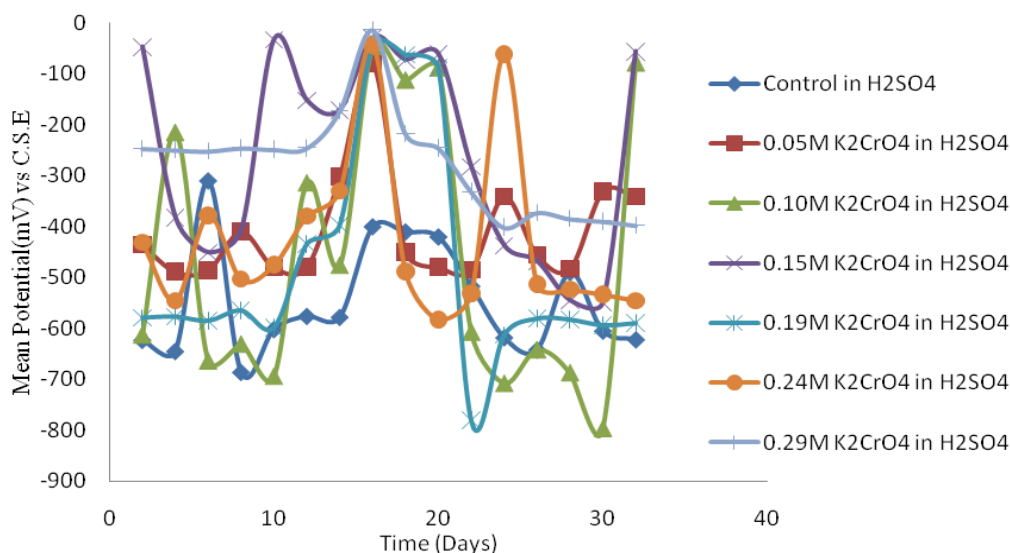
Where  $J_o$  and  $J_A$  is the null and alternative hypothesis that the OCP data does and does not follow the two-parameter Weibull distribution respectively.

### 2.4 Determination of the compressive strength of the test specimens

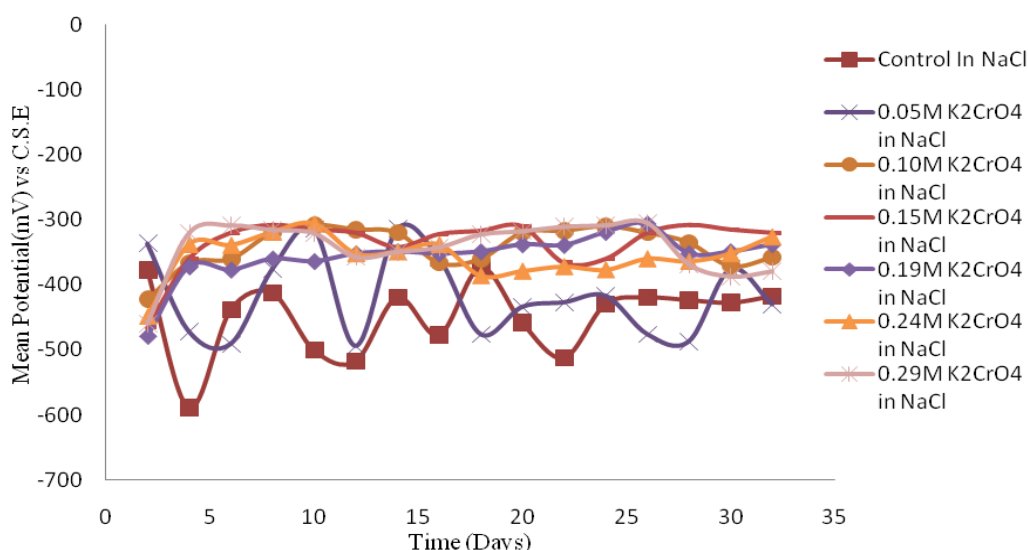
The effect of potassium chromate, aniline and their synergistic combination on the compressive strength of the concrete test samples was determined using the compressive fracture machine. After the potential monitoring period, the original steel-reinforced concrete test specimen were removed from their respective test media and allowed to air harden for seven days. Then each of the concrete blocks was carefully weighed, placed on a compressive fracture machine lengthwise and carefully loaded until the concrete block gently crumbled [16].

### 3. RESULTS AND DISCUSSION

The OCP readings obtained for all concrete test samples partially immersed in sulphuric acid and sodium chloride are presented in Figs. 2 to 7. Observing the Figures, it is obvious that the potential readings fluctuated from the beginning of the experiment to the end in the two test media, though this persistent spikes and fluctuations of the readings were less in the NaCl medium pointing to the existence of a relationship between OCP readings and the NaCl medium. It was also observed that fluctuations also reduced when the inhibitors were synergistically combined and in fact reduced more in the NaCl medium.

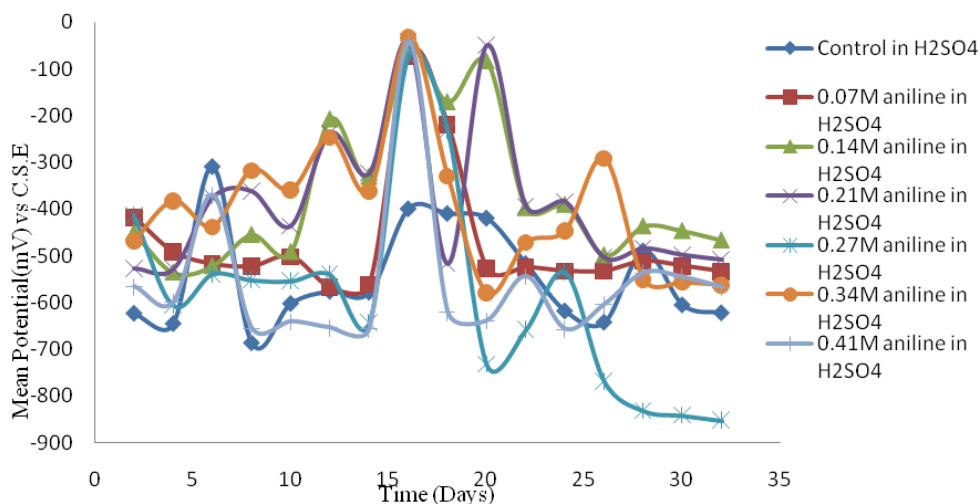


**Figure 2.** Variation of corrosion potential with time for steel-reinforced concrete admixed with varying concentration of K<sub>2</sub>CrO<sub>4</sub> and 0.1M NaCl in H<sub>2</sub>SO<sub>4</sub> medium.

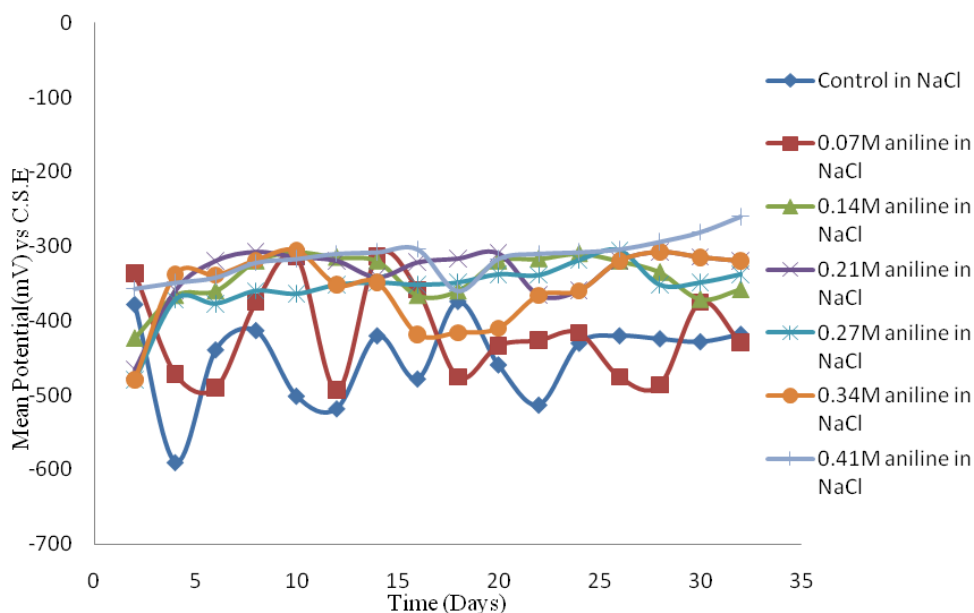


**Figure 3.** Variation of corrosion potential with time for steel-reinforced concrete admixed with varying concentration of K<sub>2</sub>CrO<sub>4</sub> and 0.1M NaCl in NaCl medium.

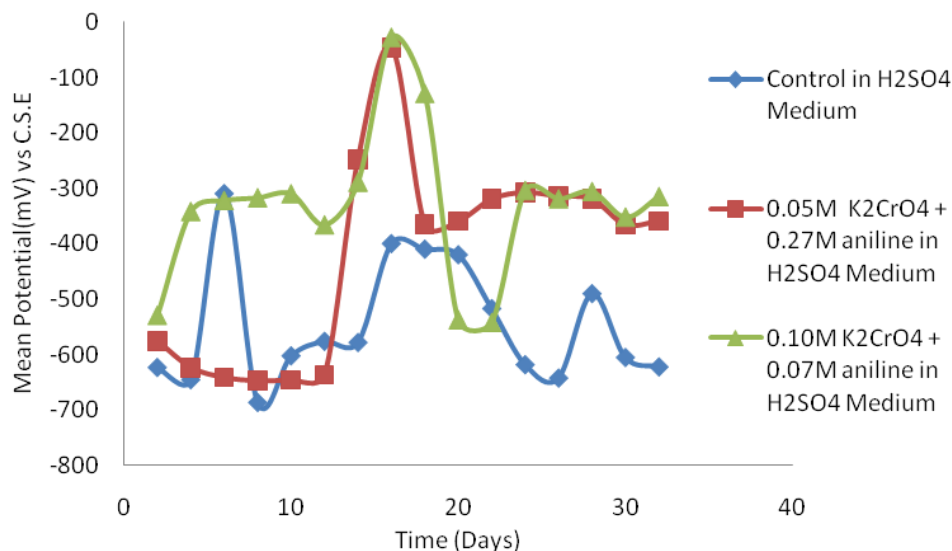
Essentially the drift of steel rebar potential readings towards the passive region indicates that the inhibitors were able to protect steel rebar from corrosion through the formation of a thin passive film on the surface of the metal while the drift into the active region shows that the aggressive film present in the medium succeeded in destroying the passive film on the steel rebar. In some cases, as was observed in the curves in Figs. 2 to 7 the destruction of the film was momentary, while in other instances it was prolonged. This phenomenon of repeated destruction and repair of the passive film on the steel rebar led to the persistent and frequent fluctuations.



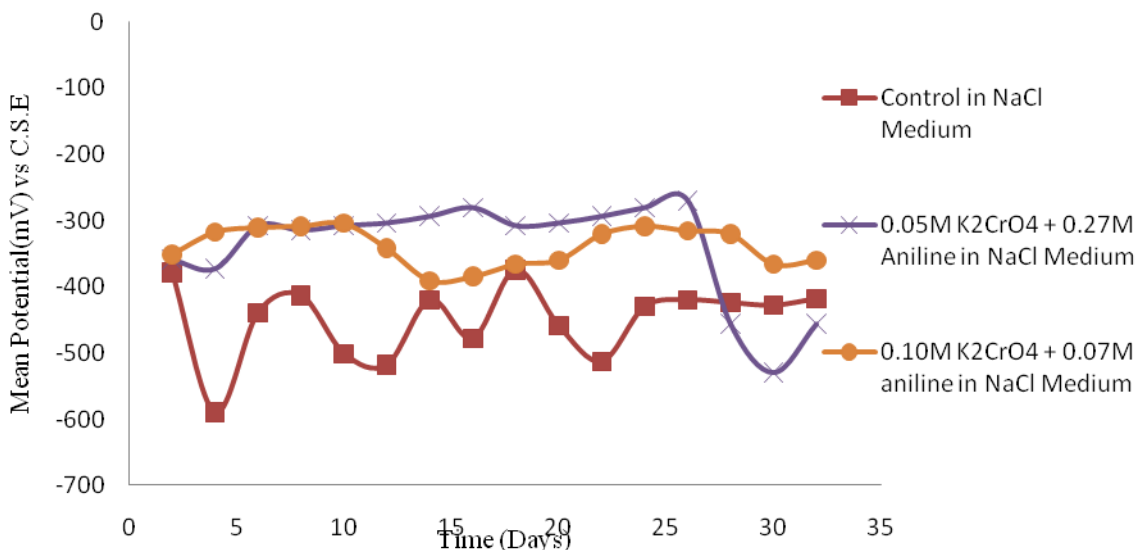
**Figure 4.** Variation of corrosion potential with time for steel-reinforced concrete admixed with varying aniline concentration and 0.1M NaCl in H<sub>2</sub>SO<sub>4</sub> medium.



**Figure 5.** Variation of corrosion potential with time for steel-reinforced concrete admixed with varying aniline concentration and 0.1M NaCl in NaCl medium.



**Figure 6.** Variation of corrosion potential with time for steel-reinforced concrete admixed with synergetic combination of  $K_2CrO_4$ , aniline and 0.1M NaCl in  $H_2SO_4$  medium.



**Figure 7.** Variation of corrosion potential with time for steel-reinforced concrete admixed with synergetic combination of  $K_2CrO_4$ , aniline and 0.1M NaCl in NaCl medium.

These fluctuations may have been a result of the persistent contest between the alkaline environments around steel rebar in the concrete test samples and the acidic environment of the sulphuric acid or the chloride ions in the NaCl medium. It may also have resulted from the complex reaction between the steel, concrete, inhibitor and media. Therefore since the  $H_2SO_4$  medium was more aggressive because of the presence of sulphate ions, the fluctuations became more frequent, persistent, erratic and evident. The samples in the NaCl medium and those in which the inhibitors were synergistically combined showed fewer fluctuations when compared to the  $H_2SO_4$  medium. The results of previous studies by Burubai and Dagogo [20] and Izquierdo et al. [24] also show persistent



fluctuations. While Izquierdo et al. [24] used the log-normal distribution function to analyze data and K-S goodness of fit test, Burubai and Dagogo [20] did not employ any statistical tool. However, in this study Weibull probability function was employed in conjunction with the K-S goodness of fit test since its ability to analyze and adequately predict data has been demonstrated in some other studies [21-23]. Further to this, the Weibull probability density function is known to produce a better goodness-of-fit than the log-normal when dealing with system of high variable data.

The inference that could be drawn from Figs. 2 to 7 is that data became difficult to understand and almost impossible to identify the most efficient inhibitor concentration. Consequently, it became clear that a tool having the capacity to analyze data sufficiently would be needed to interpret and establish the most effective inhibitor concentration. A two-parameter Weibull distribution function was therefore deployed to undertake the task. Employing a statistical tool to determine the quality and the reliability of inhibitions in the respective medium, subsequently gave a clear interpretation of the inhibitions in the test media, regardless of the fluctuations displayed by the admixed inhibitors. Weibull distribution fittings to the OCP measurements for the admixed inhibitor were made. The suitability and reliability of the fittings were then investigated using the K-S goodness of fit test in a bid to determine the consistencies of the OCP measurements for each admixed inhibitor with the Weibull distribution fittings. The results obtained are shown in Table 2.

**Table 2.** Weibull distribution fitting results of inhibitor admixtures in reinforced concrete samples

| S/<br>N | Admixture   | Medium                         | b      | a       | $\eta$  | Prob<br>( $\eta$ ) | P-value (K-<br>S) Test |
|---------|---|--------------------------------|--------|---------|---------|--------------------|------------------------|
| 1       | Control   | H <sub>2</sub> SO <sub>4</sub> | 4.985  | 595.688 | 546.846 | 0.479              | 0.572                  |
| 2       | 0.05 M K <sub>2</sub> CrO <sub>4</sub>                | H <sub>2</sub> SO <sub>4</sub> | 2.115  | 494.230 | 437.718 | 0.539              | 0.076                  |
| 3       | 0.10M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 1.142  | 545.374 | 520.091 | 0.612              | 0.022                  |
| 4       | 0.15M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 1.009  | 283.942 | 282.882 | 0.631              | 0.316                  |
| 5       | 0.19M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 1.104  | 611.594 | 589.469 | 0.617              | 0.691                  |
| 6       | 0.24M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 1.254  | 555.679 | 517.198 | 0.599              | 0.103                  |
| 7       | 0.29M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 1.171  | 373.278 | 353.410 | 0.609              | 0.044                  |
| 8       | 0.07M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 1.724  | 593.035 | 528.646 | 0.560              | 0.004                  |
| 9       | 0.14M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 1.576  | 448.404 | 402.602 | 0.570              | 0.014                  |
| 10      | 0.21M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 1.262  | 489.814 | 455.208 | 0.598              | 0.208                  |
| 11      | 0.27M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 1.680  | 716.183 | 639.542 | 0.563              | 0.056                  |
| 12      | 0.34M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 1.410  | 512.115 | 466.223 | 0.584              | 0.192                  |
| 13      | 0.41M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 1.244  | 763.819 | 712.189 | 0.600              | 0.105                  |
| 14      | 0.05M K <sub>2</sub> CrO <sub>4</sub> + 0.27M Aniline | H <sub>2</sub> SO <sub>4</sub> | 1.593  | 518.284 | 464.884 | 0.569              | 0.016                  |
| 15      | 0.15M K <sub>2</sub> CrO <sub>4</sub> + 0.07M Aniline | H <sub>2</sub> SO <sub>4</sub> | 1.407  | 420.495 | 382.933 | 0.584              | 0.317                  |
| 16      | Control   | NaCl                           | 8.723  | 475.482 | 449.621 | 0.459              | 0.356                  |
| 17      | 0.05M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 7.049  | 445.544 | 416.931 | 0.465              | 0.263                  |
| 18      | 0.10M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 11.290 | 357.148 | 341.455 | 0.452              | 0.495                  |
| 19      | 0.15M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 7.969  | 357.002 | 336.141 | 0.461              | 0.852                  |
| 20      | 0.19M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 9.841  | 374.249 | 355.799 | 0.456              | 0.277                  |
| 21      | 0.24M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 11.893 | 371.702 | 356.077 | 0.451              | 0.059                  |
| 22      | 0.29M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 8.574  | 361.505 | 341.570 | 0.459              | 0.164                  |
| 23      | 0.07M Aniline   | NaCl                           | 7.049  | 445.544 | 416.931 | 0.465              | 0.594                  |
| 24      | 0.14M Aniline   | NaCl                           | 11.290 | 357.148 | 341.455 | 0.452              | 0.914                  |

|    |   |      |        |         |         |       |       |
|----|---|------|--------|---------|---------|-------|-------|
| 25 | 0.21M Aniline   | NaCl | 7.969  | 357.002 | 336.141 | 0.461 | 0.852 |
| 26 | 0.27M Aniline   | NaCl | 9.841  | 374.249 | 355.799 | 0.456 | 0.277 |
| 27 | 0.34M Aniline   | NaCl | 13.049 | 327.350 | 314.648 | 0.449 | 0.059 |
| 28 | 0.41M Aniline   | NaCl | 13.049 | 327.350 | 314.648 | 0.449 | 0.164 |
| 29 | 0.05M K <sub>2</sub> CrO <sub>4</sub> + 0.27M Aniline | NaCl | 4.775  | 372.991 | 341.555 | 0.481 | 0.807 |
| 30 | 0.15M K <sub>2</sub> CrO <sub>4</sub> + 0.07M Aniline | NaCl | 12.230 | 352.957 | 338.472 | 0.451 | 0.148 |

**Table 3.** Predicted corrosion condition (arranged in ascending order)

| S/N | Admixture   | Medium                         | $\eta$  | Predicted corrosion condition |
|-----|---|--------------------------------|---------|-------------------------------|
| 1   | 0.15M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 282.882 | Intermediate corrosion risk   |
| 2   | 0.34M Aniline   | NaCl                           | 314.648 | Intermediate corrosion risk   |
| 3   | 0.41M Aniline   | NaCl                           | 314.648 | Intermediate corrosion risk   |
| 4   | 0.15M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 336.141 | Intermediate corrosion risk   |
| 5   | 0.21M Aniline   | NaCl                           | 336.141 | Intermediate corrosion risk   |
| 6   | 0.15M K <sub>2</sub> CrO <sub>4</sub> + 0.07M Aniline | NaCl                           | 338.472 | Intermediate corrosion risk   |
| 7   | 0.10M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 341.455 | Intermediate corrosion risk   |
| 8   | 0.14M Aniline   | NaCl                           | 341.455 | Intermediate corrosion risk   |
| 9   | 0.05M K <sub>2</sub> CrO <sub>4</sub> + 0.27M Aniline | NaCl                           | 341.555 | Intermediate corrosion risk   |
| 10  | 0.29M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 341.570 | Intermediate corrosion risk   |
| 11  | 0.29M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 353.410 | Intermediate corrosion risk   |
| 12  | 0.19M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 355.799 | Intermediate corrosion risk   |
| 13  | 0.27M Aniline   | NaCl                           | 355.799 | Intermediate corrosion risk   |
| 14  | 0.24M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 356.077 | Intermediate corrosion risk   |
| 15  | 0.15M K <sub>2</sub> CrO <sub>4</sub> + 0.07M Aniline | H <sub>2</sub> SO <sub>4</sub> | 382.933 | High(90% risk of corrosion)   |
| 16  | 0.14M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 402.602 | High(90% risk of corrosion)   |
| 17  | 0.05M K <sub>2</sub> CrO <sub>4</sub>                 | NaCl                           | 416.931 | High(90% risk of corrosion)   |
| 18  | 0.07M Aniline   | NaCl                           | 416.931 | High(90% risk of corrosion)   |
| 19  | 0.05M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 437.718 | High(90% risk of corrosion)   |
| 20  | Control   | NaCl                           | 449.621 | High(90% risk of corrosion)   |
| 21  | 0.21M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 455.208 | High(90% risk of corrosion)   |
| 22  | 0.05M K <sub>2</sub> CrO <sub>4</sub> + 0.27M Aniline | H <sub>2</sub> SO <sub>4</sub> | 464.884 | High(90% risk of corrosion)   |
| 23  | 0.34M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 466.223 | High(90% risk of corrosion)   |
| 24  | 0.24M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 517.198 | Severe corrosion              |
| 25  | 0.10M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 520.091 | Severe corrosion              |
| 26  | 0.07M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 528.646 | Severe corrosion              |
| 27  | Control   | H <sub>2</sub> SO <sub>4</sub> | 546.846 | Severe corrosion              |
| 28  | 0.19M K <sub>2</sub> CrO <sub>4</sub>                 | H <sub>2</sub> SO <sub>4</sub> | 589.469 | Severe corrosion              |
| 29  | 0.27M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 639.542 | Severe corrosion              |
| 30  | 0.41M Aniline   | H <sub>2</sub> SO <sub>4</sub> | 712.189 | Severe corrosion              |

For all admixed inhibitor analysis, the values of  $b$  in Table 2 indicated that the data spread demonstrated good uniformity with relatively small scatter. Most of the samples with inhibitor admixture satisfy the null hypothesis confirming that the OCP came from a two-parameter Weibull distribution based on the P-value of the K-S test ( $P \geq 0.05$ ). On other hand, the null hypothesis was not satisfied for specimens No. 3,7,8,9 and 14 (Table 2). The reason for the null hypothesis could be that a complex reaction between steel rebar, inhibitor, concrete pore solution and test medium resulted in potential readings averaging between -120 to -43mV (CSE) on or about the 20<sup>th</sup> day of partial immersion. Corrosion pits could therefore, have been initiated after the 20<sup>th</sup> day marked by a sudden shift in potential of -120 to -623mV (CSE) which happened when sulphate ions in sample concentration hit the steel rebar surface [9]. This could be the reason for the differences which may not be unconnected to the instances of outliers within their respective populations of OCP measurements, common to these five samples of concrete admixture.

Moreover, the mean value resulting from the Weibull analysis is suitable in predicting the level of corrosion according to ASTM C 876 standard of classification with reference to CSE as shown in Table 3.

The performance ranking of inhibiting quality of the reinforced concrete samples with admixed inhibitor is presented in Fig. 8 and it is based on the prediction by the Weibull mean. Table 3 and Fig. 8 show specimen number 1 which is the sample admixed with 0.15M  $K_2CrO_4$  inhibitor in the sulphuric acid medium has having the maximum Weibull mean evaluation of approximately -283 mV (CSE). This is closely followed by the sample admixed with 0.34M aniline in the NaCl medium. The reliability of these predicted mean values stands at a probability of 63.1 and 44.9% respectively. The other specimens following after this are those of 0.41M aniline, 0.15M  $K_2CrO_4$ , 0.21M aniline and the synergetic combination of 0.15M  $K_2CrO_4$  and 0.7M aniline all partially immersed in NaCl with probabilities of 44.9, 46.1, 46.1 and 45.1% respectively. These sets of admixed inhibitors points to the existence of some kind of relationship(s) between the concentration of inhibitors and its inhibiting qualities.

In Table 3, samples number 1 to 14 believed to have exhibited optimal qualities in this study are still in the intermediate corrosion risk range according to ASTM C 876, they still show better inhibition effectiveness compared to the control specimens (No. 20 and 27).

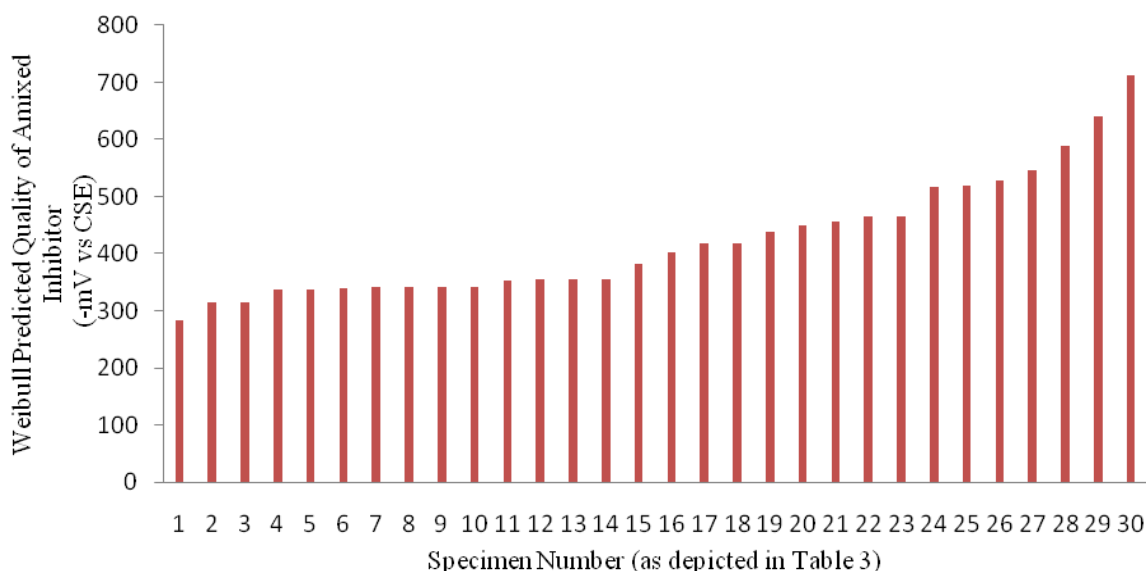
For the control specimen in NaCl medium the predicted mean ( $\eta$ ) is more than that predicted for the control specimen in  $H_2SO_4$  medium confirming that the sulphate ions drove the reaction further into the active corrosion range. This explains why most of the potential readings for the concrete specimen partially immersed in  $H_2SO_4$  medium were in the active corrosion range despite the fact that they were admixed with inhibitors.

In Table 3, apart from specimen number 1 and 11 that fell in the intermediate corrosion risk range according to ASTM C 876 classification all other samples partially immersed in  $H_2SO_4$  medium were in the high and severe corrosion risk range corroborating the fact that the sulphate ions in the sulphuric acid medium were aggressive enough to destroy the passive film formed by the inhibitors.

Specimens 1 to 14 depicted in Fig. 8 on the abscissa is predicted according to ASTM C 876 classification to be in the intermediate corrosion risk range while specimens 15 to 23 and 24 to 30 is in the high and severe corrosion risk range respectively.

Amongst all concrete samples partially immersed in NaCl medium none exhibited negative inhibiting effect as predicted by the Weibull mean because according to Fig. 8 and Table 3, their values were higher than the control, while samples 28, 29 and 30 exhibited negative inhibiting qualities since its predicted Weibull mean were lower than the control sample in H<sub>2</sub>SO<sub>4</sub> medium.

Furthermore, all test samples partially immersed in the NaCl medium exhibited positive inhibiting qualities since the predicted Weibull mean values were higher than that of the control in the NaCl medium, while on the other hand specimens 1,11,15,16,19,21,22,23,24,25 and 26 in Fig. 8 and Table 3 is predicted as showing positive inhibiting qualities as Weibull mean values were higher than the control in H<sub>2</sub>SO<sub>4</sub> medium.



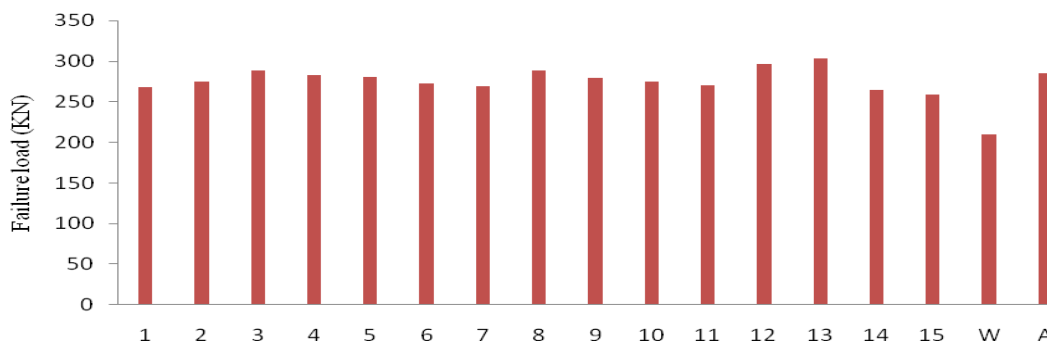
**Figure 8.** Performance ranking of inhibiting quality of admixed inhibitor based on prediction by the Weibull distribution.

### 3.1 Compressive strengths of concrete test sample

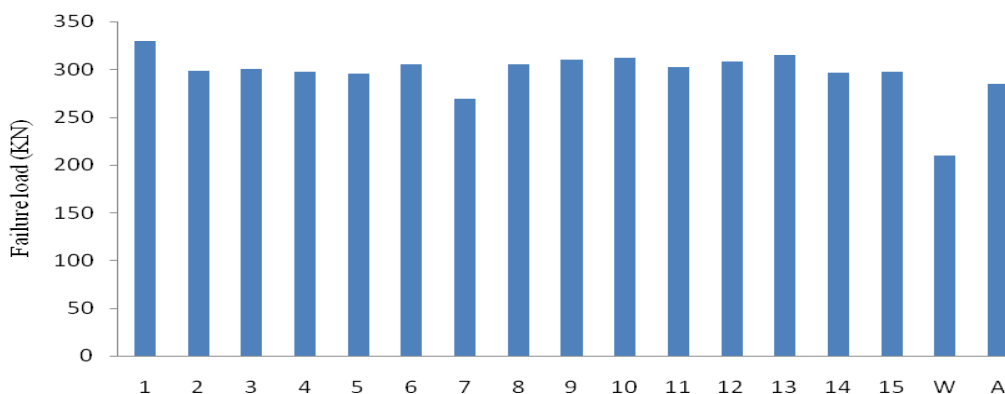
The examination of compressive fracture load data for steel-reinforced concrete samples partially immersed in NaCl and H<sub>2</sub>SO<sub>4</sub> medium are presented in Figs. 9 and 10 respectively. The strengths of all reinforced concrete specimens used in the experiments and partially immersed in H<sub>2</sub>SO<sub>4</sub> and NaCl media were higher than those of the specimen cured in water for two weeks, indicating that the admixed inhibitor had no adverse effect on the concrete samples. The higher compressive strength observed in the concrete samples with inhibitor could probably be due to the relative chemical reactions hardening effect of the inhibitor with the concrete. Moreover, since the specimens used for the monitoring experiments were partially immersed in H<sub>2</sub>SO<sub>4</sub> and NaCl media such that the other halves were exposed to air throughout the experimental period, it resulted in a dual hardening method which might have accounted for the higher strength associated with the partially immersed specimens.

Compressive strength values obtained for all the specimens used for the monitoring experiments and partially immersed in H<sub>2</sub>SO<sub>4</sub> and NaCl media did not follow a particular trend, the order of increasing concentration of inhibitor did not translate to increased compressive strength. Specimens 1, 2, 4, 5, 6, 7, 9, 10, 11, 14 and 15 in the H<sub>2</sub>SO<sub>4</sub> medium and specimen 7 in the NaCl medium (as depicted in Table 1) gave a loss in compressive strength when compared with specimens cured in air. However, specimens 3, 8, 12 and 13 in the H<sub>2</sub>SO<sub>4</sub> medium and specimens 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14 and 15 in the NaCl medium (as depicted in Table 1) gave increases in the compressive strength. Therefore this infers that the inhibitor admixtures that led to increased strength would be appropriate for making concrete while the use of admixtures that resulted in reduced strength should be discouraged since it will cause a loss in compressive strength of the blocks.

The control sample in the NaCl medium showed an increase in compressive strength while it displayed reduced strength in the H<sub>2</sub>SO<sub>4</sub> medium showing that sulphuric acid had a deleterious effect on the strength of concrete. All of the concrete samples partially immersed in the NaCl medium except specimen 7 showed increases in compressive strength, indicating that potassium chromate, aniline and the synergistic combination of the two inhibitors was more effective in the NaCl medium than in the H<sub>2</sub>SO<sub>4</sub> medium.



**Figure 9.** Histogram of the compressive fracture load for the reinforced concrete specimens immersed in sulphuric acid. W=concrete specimen cured in water, A= concrete specimen cured in air. Numbers 1 to 15 is as depicted in Table 1.



**Figure 10.** Histogram of the compressive fracture load for the reinforced concrete specimens immersed in NaCl medium. W=concrete specimen cured in water, A= concrete specimen cured in air. Numbers 1 to 15 is as depicted in Table 1.

#### 4. CONCLUSION

Electrochemical potential monitoring experiments was carried out to study the effect of  $K_2CrO_4$ , aniline and their synergistic combination on concrete steel rebar partially immersed in  $H_2SO_4$  and NaCl medium. A Weibull distribution function was employed to analyze the data from the study due to the fluctuating nature of the readings which made data interpretation difficult and identification of the most effective inhibitor concentration impossible. Furthermore, compressive strengths were determined to find out if the inhibitors had any effect on the strength of the test samples used in the experiment. For each inhibitor used ( $K_2CrO_4$ , aniline and their synergistic combination), the Weibull results revealed that concrete steel rebar admixed with 0.15M  $K_2CrO_4$  and partially immersed in  $H_2SO_4$  medium exhibited the best overall performance while the 0.34M aniline admixture is identified as exhibiting the best performance in the NaCl medium. The results also show that the admixture combination of 0.15M  $K_2CrO_4$  and 0.07M aniline in the NaCl medium produced the best result amongst the synergistic combination used. The inhibitors ( $K_2CrO_4$  and aniline) according to the Weibull results also performed better in the NaCl medium as most of the Weibull mean values were ranked in the intermediate corrosion risk range using the ASTM C 876 standard. According to the Weibull results twenty five of the samples were well fitted based on K-S goodness of fit test, while five samples had outliers.

More specimens gave a loss in compressive strength in the  $H_2SO_4$  medium, while more specimens gave an increase in compressive strength in the NaCl medium. Conversely fewer specimens gave a loss in compressive strength in the NaCl medium, while fewer specimens gave an increase in compressive strength in the  $H_2SO_4$  medium. Specifically in the NaCl medium the control sample gave the highest increase in compressive strength (330KN) amongst all the samples considered. Also, in the NaCl medium the 0.14M aniline admixture gave the highest increase in compressive strength amongst the inhibited samples. However, the 0.41M aniline admixture gave the highest increase in compressive strength amongst all samples considered in the  $H_2SO_4$  medium.

Weibull mean values of corrosion potential obtained for all concrete samples made the interpretation of the data using ASTM C 876 possible. It also eliminated any possible systematic errors of interpretation.

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