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Assessing the Performance of Potassium Dichromate and Aniline on Concrete Steel Rebar Deterioration in Marine and Microbial Media

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Abstract: The study used the two-parameter Weibull distribution function to analyze data obtained from electrochemical potential monitoring experiments. Two sets of fifteen steel-rebar test samples admixed with varying concentration of aniline, potassium dichromate and their synergistic combination with fixed amount of sodium chloride salt partially immersed in NaCl and H_2SO_4 solution at ambient temperature had their potential readings taken in accordance with ASTM C 876. Performance 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 study also investigated the effect of the inhibitors on the compressive strengths of the reinforced concrete samples. Test sample admixed with 0.34 and 0.41 M aniline was predicted as exhibiting the best inhibiting quality in NaCl medium while in the H_2SO_4 medium the synergistic combination of 0.03 M $K_2Cr_2O_7$ and 0.30 M aniline exhibited the best performance. The compressive strength values of test sample admixed with 0.41 M aniline was the highest in both the microbial (303 KN) and marine (315 KN) medium while the control test sample in the NaCl medium showed the highest overall increase (330 KN) in compressive strength.

Key words: Potential, steel rebar, potassium dichromate, aniline, compressive strength, Weibull distribution, kolmogorov-smirnov statistics, marine/microbial medi

INTRODUCTION

Concrete infrastructure is a fundamental part of the development of an economy and provides basic services that people need in their daily life. Well-developed infrastructure in the form of bridges, sewage systems, drinking water systems, highways, weir and other municipal works, provides key economic services efficiently, improves competitiveness, extends vital support to productive sectors, generates high productivity and supports economic growth. Even though, substantial effort and resources have been expended on development and maintenance infrastructure over the past years, results of such efforts have largely remained fruitless since the incidences of collapsed structures have pervaded the tabloids. Collapsed building inventories (1978-2007) released Lagos state Physical Planning Development Authority in Nigeria show that Lagos island has the highest incidence (about 30%) of collapsed building. Lagos is along the coast therefore the reason for this high incidence is the presence of tons of chloride ions in the soils of Lagos island.

These chloride ions in conjunction with oxygen, carbon dioxide, atmospheric moisture and sulphate ions from microbial environment of sewage systems find their way into concrete structures and destroy the normally alkaline region existing between the steel rebar and concrete (NEA/CSNI, 2002; Gaal, 2004; Parande et al., 2006; Song and Saraswathy, 2007; Hewayde et al., 2007). Once the passive film is destroyed corrosion is initiated and the volume of corrosion products on the steel rebar increases by almost halve of the initial volume. The continuous expansion and contraction of the resulting corrosion products induce tensile stresses in the concrete that eventually leads to cracks, spalling and catastrophic collapse. Therefore, to maintain concrete infrastructure in Nigeria and to remove infrastructure decay in the country, research into more ways of combating concrete steel rebar degradation should be initiated and aggressively undertaken. Hence, the use of corrosion inhibitors is an option that needs to be explored, though other means exist but when inhibitors are utilized during the construction process they prevent corrosion before it is even initiated.

There is however, dearth of articles employing a statistical approach of an extreme value distribution to evaluate the effectiveness of potassium dichromate and aniline as inhibitors in reinforced concrete. Several studies have examined the effect of varying inhibitor concentration on concrete steel rebar corrosion in microbial, marine and other media (Loto, 1992; Smith and

Virmani, 2000; Schiegg et al., 2000; Parande et al., 2006; Hewayde et al., 2007; Song and Saraswathya, 2007; Afolabi, 2007; Burubai and Dagogo, 2007) without any investigation yet on the synergistic combination of potassium dichromate and aniline in marine and microbial medium, two-parameter Weibull based analysis of the potential readings emanating from the experiments and subsequent classification using the Weibull results according to the ASTM C 876 standard.

The target of this study therefore is to investigate the individual and synergistic effect of potassium dichromate and aniline on concrete steel rebar degradation in saline and sewage environments by using a two-parameter Weibull probability distribution function to analyze the fluctuating potential readings in order to be able to interpret data appropriately and to identify the most effective inhibitor concentration. All concrete samples used for the experiments were also subjected to compressive strength tests.

MATERIALS AND METHODS

Concrete mix ratio was prepared according to method adopted in literature (Omotosho *et al.*, 2010). Portland cement, sand and gravel in a mix ratio of 1:2:4 mixed with water were used for the concrete blocks employed for the experiment. The formulation used for the reinforced concrete specimens in kg m⁻³ was cement 320, water 140, sand -700 and gravel -1150. The water/cement (w/c) ratio was 0.44.

The first assemblage of the two assemblages of block made consisted of thirty sets of block (fifteen sets of blocks partially immersed in the NaCl and suphuric acid medium, respectively) comprising several specimens, cast with varying inhibitor concentration and admixed with fixed amount of sodium chloride. The percentages quoted below for each of the admixed inhibitors and the sodium chloride was estimated based on every 10 kg weight of the sample from which the blocks were made. All the chemicals used were AnalaR grade. Table 1 shows concrete block samples with inhibitor concentration and Set 1 in the table represents the control sample. Table 2 shows the chemical compostion of the steel employed in the study.

The rebar was cut into several pieces each with a length of 160 and 10 mm diameter. Mill scale and rust stains on the steel specimens was removed by an abrasive grinder before insertion in each concrete block. The remaining 20 mm protruded at one end of the block and was painted to prevent atmospheric corrosion (Omotosho *et al.*, 2010). This part was also employed for completing the electrical connection. The test media used

Table 1: List of inhibitor admixtures with fixed amount of NaCl in concrete Inhibitor concentration Concrete sample Solution without inhibitor None (control sample) Concrete admixed with 0.1 M NaCl 0.03 M K2Cr2O2 Concrete admixed with 0.1 M NaCl 0.06 M K2Cr2O7 Concrete admixed with 0.1 M NaCl 0.10 M K2Cr2O2 Concrete admixed with 0.1 M NaCl $0.13 \text{ M K}_2\text{Cr}_2\text{O}_7$ Concrete admixed with 0.1 M NaCl 0.16 M K2Cr2O2 Concrete admixed with 0.1 M NaCl 019 M K2Cr2O2 Concrete admixed with 0.1 M NaCl 0.07 M aniline 0.14 M aniline Concrete admixed with 0.1 M NaCl Concrete admixed with 0.1 M NaCl 0.21 M aniline Concrete admixed with 0.1 M NaCl 0.30 M aniline Concrete admixed with 0.1 M NaCl 0.34 M aniline Concrete admixed with 0.1 M NaCl 0.41 M aniline Concrete admixed with 0.1 M NaCl 0.03 M K₂Cr₂O₇, 0.30 M aniline 0.10 M K2Cr2O7, 0.07 M aniline Concrete admixed with 0.1 M NaCl

| Table 2: Steel rebar chemical composition | | | | | | | | | |
|---|-----|------|-----|------|------|------|-----|------|-------|
| Composition | С | Si | Mn | P | S | Cu | Cr | Ni | Fe |
| Content (%) | 0.3 | 0.25 | 1.5 | 0.04 | 0.64 | 0.25 | 0.1 | 0.11 | 96.81 |

for the investigation were 3.5% NaCl solution and 0.5 M dilute sulphuric acid. The sodium chloride and sulphuric acid is to simulate marine/saline and microbial/sewerage environment, respectively. The second assemblage consisted of two concrete blocks without any premixed inhibitor which were made expressly for determining strength under different curing conditions. One of the concrete blocks in the second assemblage was cured in air for 2 weeks and the other was cured in water for the same period (Loto, 1992; Omotosho *et al.*, 2010). The sketch of the steel/concrete block assembly can be found in literature (Loto, 1992; Omotosho *et al.*, 2010).

The concrete block samples were partly immersed in their respective test medium such that the liquid level was just below the bare part of the reinforcing steel to avoid direct contact. Open Circuit Potential (OCP) readings were then obtained by placing a Copper/copper Sulphate Electrode (CSE) firmly on the concrete block (Loto, 1992; Omotosho et al., 2010). 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 bare part of the embedded steel rebar. The readings were taken at three different points on each concrete block directly over the embedded steel rebar (Loto, 1992; Omotosho et al., 2010). The mean of the three readings was calculated as the potential reading for the embedded rebar in 2 days intervals for a period of 32 days. All the experiments were performed under free corrosion potential and at ambient temperature.

The analysis of data obtained during the experiments was performed using the approach adopted in literature (Omotosho *et al.*, 2010). This involved the use of a two-parameter Weibull distribution function given by Eq. 1.

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

where, d and c 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):

$$\eta = c\Gamma \left(1 + \frac{1}{d}\right) \tag{2}$$

where, Γ () is the gamma function of (). 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 (Omotosho *et al.*, 2010). The K-S test measures the difference between the empirical F^* and the theoretical distribution function F(x) (Omotosho *et al.*, 2010)

$$g = g\left(x_{1},...,x_{n}\right) = \sqrt{n} \sup_{-\infty < x < \infty} \left|F^{*}(x) - F(x)\right| \tag{3}$$

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 hypothesis test:

$$I_o: P \ge \alpha$$
 $I_A: P \ge \alpha$
(4)

where, I_{o} is the null hypothesis such that the OCP data followed the two-parameter Weibull distribution and I_{A} is the alternative hypothesis such that the OCP data does not follow the two-parameter Weibull distribution.

Furthermore, 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 device. 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 7 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 (Loto, 1992).

RESULTS AND DISCUSSION

The potential versus time curves for steel reinforced concrete premixed with varying amounts of potassium dichromate partially immersed in H₂SO₄ and NaCl media are shown in the Fig. 1 and 2. Comparing the two curves for the different media it is obvious that the inhibitor was

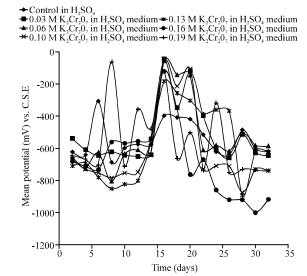


Fig. 1: Relationship of corrosion potential with time for test sample admixed with varying concentration of K₂Cr₂O₇ and 0.1 M NaCl in H₂SO₄ medium

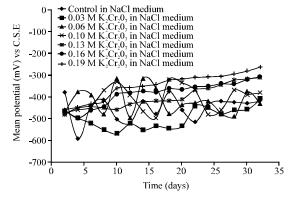


Fig. 2: Relationship of corrosion potential with time for test sample admixed with varying concentration of K₂Cr₂O₇ and 0.1 M NaCl in NaCl medium

more effective in the NaCl media. A reduction in the negative potential of steel was demonstrated by the NaCl media throughout the experimental period. It is also seen that higher amount of the inhibitor produced better inhibition for both media but it could not be sustained in the H_2SO_4 medium. The repassivation (formation of surface film coating) and depassivation phenomenon was fluctuating throughout the experimental period in both medium but was milder in the H_2SO_4 medium. Furthermore, it is observed that the inhibitor did not totally stop corrosion but only reduced or delayed the onset in a corrosive environment. The inhibition effectiveness in the NaCl medium at high amount is as a result of anions becoming inhibitive or acting in such a way as to plug holes in a passive film.

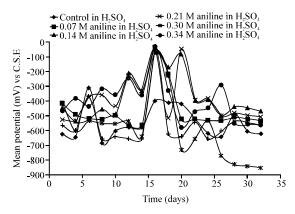


Fig. 3: Relationship of corrosion potential with time for steel-reinforced concrete admixed with varying aniline concentration and 0.1 M NaCl in H₂SO₄ medium

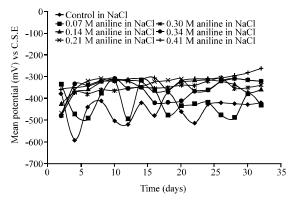


Fig. 4: Relationship of corrosion potential with time for steel-reinforced concrete admixed with varying aniline concentration and 0.1 M NaCl in NaCl medium

The sulphate ions in the H₂SO₄ media did not permit the anions to become effective rather it suppressed their activity which resulted in the fluctuating depassivation and repassivation phenomenon that researchers saw throughout experimental period.

In Fig. 3 and 4 potential versus time curves for steel reinforced concrete premixed with varying amounts of aniline partially immersed in $\rm H_2SO_4$ and NaCl media are presented. Comparing the performance of the aniline in $\rm H_2SO_4$ and NaCl media, it is seen that potential readings showed more persistent fluctuations in the $\rm H_2SO_4$ medium than in the NaCl medium.

This may be an indication of the better performance in the NaCl medium. However, fluctuations of the potential readings of steel in the NaCl medium were also observed but they were fewer and milder; this did not show clearly the inhibitor concentration with the best performance.

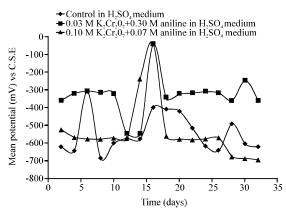


Fig. 5: Relationship of corrosion potential with time for steel-reinforced concrete admixed with synergetic combination of K₂Cr₂O₇, aniline and 0.1 M NaCl in H₂SO₄ medium

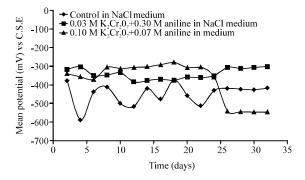


Fig. 6: Relationship of corrosion potential with time for steel-reinforced concrete admixed with synergetic combination of K₂Cr₂O₇, aniline and 0.1 M NaCl in NaCl medium

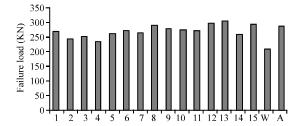


Fig. 7: Histogram of the compressive fracture load for the reinforced concrete specimens immersed in sulphuric acid. W = concrete specimen cured in water, A = concrete specimen cured in air. Numbers 1-15 is shown in Table 1

The curves of the synergistic combination of the inhibitors are shown in Fig. 5 and 6. The trend observed is not particularly different from what was shown when the inhibitors were used individually, though looking analytically at Fig. 7 there is seen a slight improvement in terms of the behavior of the potential readings; a fairly

stable reading fewer persistent and erratic fluctuations. After the observations made in Fig. 1-6 for each of the inhibitor concentration the conclusion is that potential readings displayed same pattern. This curves essentially drifted from a region of passivity to active corrosion, this was occasioned by the destruction of the passive film on the steel rebar. The return of the steel rebar to the passive region is as a result of the formation of passive film (repassivation).

This passivation and depassivation phenomenon could be credited to the incessant contest between the alkaline medium existing between steel rebar and concrete test sample and the aggressive ions present in the medium. A complex reaction resulting from the interaction between steel, alkaline pore solution, medium and inhibitor could also be a reason for this behavior.

However, this fluctuating behavior has made data interpretation difficult and the identification of the most efficient inhibitor concentration impossible. Therefore, deploying a tool with resultant analytical ability became essential. A two-parameter Weibull distribution function was employed to analyze the data from the experiments. The benefit of employing a statistical analysis for investigating the quality and reliability of inhibitions in the respective test medium is a proper understanding in spite of the fluctuations of the inhibiting effectiveness of the admixed inhibitors in the medium. Weibull distribution fittings to the OCP measurements for the admixed inhibitors were also 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 3. For all the admixed inhibitor examination in Table 3, the values of d shows that the record spread exhibits good uniformity with relative scatter. Also, most of the samples with inhibitor admixtures satisfy the null hypothesis confirming that the OCP data came from a two-parameter Weibull distribution based on the p-value of the K-S test (p≥0.05). However, the null hypothesis was not satisfied for specimens No. 2, 4, 8, 13 and 15. Corrosion potential in the range of -100 to -43 mV (CSE) attained on or about the 20th day of partial immersion coupled with the sharp change in potential of -100 to -500 mV (CSE) after the 20th day could have initiated pitting corrosion because sulphate ions in sufficient quantity hit the rebar surface. This might have accounted for the disparities which may not be unconnected to instances of outliers within their corresponding populations measurements, common to these five specimens (Omotosho et al., 2010).

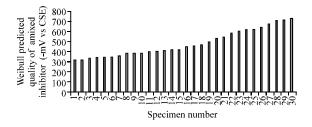
Table 3: Weibull distribution fitting results of inhibitor admixtures in reinforced concrete samples

| | | | | | Prob | p-value |
|--|--------------------------------|--------|---------|---------|-------|------------|
| Admixture | Medium | d | С | μ | (μ) | (K-S) test |
| Control | H_2SO_4 | 4.985 | 595.688 | 546.846 | 0.479 | 0.572 |
| 0.03 M K ₂ Cr ₂ O ₇ | H_2SO_4 | 1.378 | 662.188 | 605.050 | 0.586 | 0.027 |
| 0.06 M K ₂ Cr ₂ O ₇ | H_2SO_4 | 1.311 | 670.344 | 618.112 | 0.593 | 0.087 |
| 0.10 M K ₂ Cr ₂ O ₇ | H_2SO_4 | 0.365 | 515.080 | 728.901 | 0.820 | 0.049 |
| $0.13~\mathrm{M~K_2Cr_2O_7}$ | H_2SO_4 | 2.338 | 658.847 | 583.803 | 0.529 | 0.925 |
| 0.16 M K ₂ Cr ₂ O ₇ | H_2SO_4 | 2.056 | 808.576 | 716.289 | 0.541 | 0.360 |
| $0.19 \text{ M K}_2\text{Cr}_2\text{O}_7$ | H_2SO_4 | 1.475 | 686.007 | 620.583 | 0.578 | 0.076 |
| 0.07 M aniline | H_2SO_4 | 1.724 | 593.035 | 528.646 | 0.560 | 0.014 |
| 0.14 M aniline | H_2SO_4 | 1.576 | 448.404 | 402.602 | 0.570 | 0.208 |
| 0.21 M aniline | H_2SO_4 | 1.262 | 489.814 | 455.208 | 0.598 | 0.056 |
| 0.27 M aniline | H_2SO_4 | 1.680 | 716.183 | 639.542 | 0.563 | 0.192 |
| 0.34 M aniline | H_2SO_4 | 1.410 | 512.115 | 466.223 | 0.584 | 0.105 |
| 0.41 M aniline | H_2SO_4 | 1.244 | 763.819 | 712.189 | 0.600 | 0.005 |
| 0.03 M K2Cr2O7+ | H ₂ SO ₄ | 1.578 | 423.446 | 380.139 | 0.570 | 0.056 |
| 0.30 M aniline | | | | | | |
| 0.10 M K ₂ Cr ₂ O ₇ + | H ₂ SO ₄ | 1.259 | 727.006 | 676.033 | 0.598 | 0.016 |
| 0.07 M aniline | | | | | | |
| Control | NaCl | 8.723 | 475.482 | 449.621 | 0.459 | 0.356 |
| 0.03 M K ₂ Cr ₂ O ₇ | NaCl | 11.628 | 518.347 | 496.135 | 0.452 | 0.936 |
| 0.06 M K ₂ Cr ₂ O ₇ | NaCl | 7.593 | 446.035 | 418.971 | 0.463 | 0.896 |
| $0.10 \text{ M K}_2\text{Cr}_2\text{O}_7$ | NaCl | 7.643 | 432.697 | 406.577 | 0.463 | 0.552 |
| $0.13 \text{ M K}_2\text{Cr}_2\text{O}_7$ | NaCl | 7.821 | 423.742 | 398.616 | 0.462 | 0.787 |
| $0.16 \text{ M K}_2\text{Cr}_2\text{O}_7$ | NaCl | 7.688 | 405.138 | 380.792 | 0.463 | 0.263 |
| $0.19 \text{ M K}_2\text{Cr}_2\text{O}_7$ | NaCl | 6.415 | 372.313 | 346.669 | 0.469 | 0.495 |
| 0.07 M aniline | NaCl | 7.049 | 445.544 | 416.931 | 0.465 | 0.852 |
| 0.14 M aniline | NaCl | 11.290 | 357.148 | 341.455 | 0.452 | 0.277 |
| 0.21 M aniline | NaCl | 7.969 | 357.002 | 336.141 | 0.461 | 0.059 |
| 0.27 M aniline | NaCl | 9.841 | 374.249 | 355.799 | 0.456 | 0.164 |
| 0.34 M aniline | NaCl | 13.049 | 327.350 | 314.648 | 0.449 | 0.521 |
| 0.41 M aniline | NaCl | 13.049 | 327.350 | 314.648 | 0.449 | 0.521 |
| 0.03 M K ₂ Cr ₂ O ₇ , | | | | | | |
| 0.30 M aniline | NaCl | 12.705 | 356.693 | 342.528 | 0.450 | 0.807 |
| 0.10 M K ₂ Cr ₂ O ₇ , | | | | | | |
| 0.07 M aniline | NaCl | 3.825 | 421.763 | 381.325 | 0.493 | 0.148 |

Furthermore, it has been established by Omotosho that mean values resulting from Weibull analysis is suitable for predicting the level of corrosion according to ASTM C 876 standard of classification with reference to CSE. The picture is shown in Table 4.

Performance ranking of the inhibiting quality of the test samples with admixed inhibitors is shown in Fig. 8. This is based on the prediction of their measure of quality predicted by the Weibull mean as showed in Table 3. Figure 8 shows that specimen No. 1 and 2 is predicted as exhibiting optimum inhibiting quality. This is the test sample admixed with 0.34 and 0.41 M aniline both partially immersed in NaCl medium. The reliability of the Weibull mean evaluation of -314.648 mV (CSE) stands at approximately 50% for both test sample. Closely following after this are those of specimen No. 3, 4 and 5 admixed with 0.21, 0.14 M aniline and the synergetic combination of 0.03 M K₂Cr₂O₇ and 0.30 M aniline with Weibull mean values of 336.141, 341.455 and 342.528 mV (CSE). The reliability of these samples stands at 46.1, 45.2 and 45%, respectively. A trend seemed to have emerged; non-establishment of neither direct nor indirect relationship between aniline concentration performance, though it is clear that aniline performed better in the NaCl medium.

| Table 4: Predicted corrosion condition (arranged in ascending order) | | | | | |
|--|-----------|---------|----------------------------------|--|--|
| Admixture | Medium | μ | Predicted corrosion condition | | |
| 0.34 M aniline | NaCl | 314.648 | Intermediate corrosion condition | | |
| 0.41 M aniline | NaCl | 314.648 | Intermediate corrosion condition | | |
| 0.21 M aniline | NaCl | 336.141 | Intermediate corrosion condition | | |
| 0.14 M aniline | NaCl | 341.455 | Intermediate corrosion condition | | |
| 0.03 M K ₂ Cr ₂ O ₇ + | NaCl | 342.528 | Intermediate corrosion condition | | |
| 0.30 M aniline | | | | | |
| 0.19 M K ₂ Cr ₂ O ₇ | NaCl | 346.669 | Intermediate corrosion condition | | |
| 0.27 M aniline | NaCl | 355.799 | Intermediate corrosion condition | | |
| 0.03 M K ₂ Cr ₂ O ₇ + | H_2SO_4 | 380.139 | High (90% risk of corrosion) | | |
| 0.30 M aniline | | | | | |
| 0.16 M K ₂ Cr ₂ O ₇ | NaCl | 380.792 | High (90% risk of corrosion) | | |
| 0.10 M K ₂ Cr ₂ O ₇ + | · NaCl | 381.325 | High (90% risk of corrosion) | | |
| 0.07 M aniline | | | | | |
| 0.13 M K ₂ Cr ₂ O ₇ | NaCl | 398.616 | High (90% risk of corrosion) | | |
| 0.14 M aniline | H_2SO_4 | 402.602 | High (90% risk of corrosion) | | |
| $0.10 \text{ M K}_2\text{Cr}_2\text{O}_7$ | NaCl | 406.577 | High (90% risk of corrosion) | | |
| 0.07 M aniline | NaCl | 416.931 | High (90% risk of corrosion) | | |
| 0.06 M K ₂ Cr ₂ O ₇ | NaCl | 418.971 | High (90% risk of corrosion) | | |
| Control | NaCl | 449.621 | High (90% risk of corrosion) | | |
| 0.21 M aniline | H_2SO_4 | 455.208 | High (90% risk of corrosion) | | |
| 0.34 M aniline | H_2SO_4 | 466.223 | High (90% risk of corrosion) | | |
| 0.03 M K ₂ Cr ₂ O ₇ | NaCl | 496.135 | High (90% risk of corrosion) | | |
| 0.07 M aniline | H_2SO_4 | 528.646 | Severe corrosion | | |
| Control | H_2SO_4 | 546.846 | Severe corrosion | | |
| 0.13 M K ₂ Cr ₂ O ₇ | H_2SO_4 | 583.803 | Severe corrosion | | |
| 0.03 M K2Cr ₂ O ₇ | H_2SO_4 | 605.050 | Severe corrosion | | |
| 0.06 M K ₂ Cr ₂ O ₇ | H_2SO_4 | 618.112 | Severe corrosion | | |
| $0.19 \text{ M K}_2\text{Cr}_2\text{O}_7$ | H_2SO_4 | 620.583 | Severe corrosion | | |
| 0.27 M aniline | H_2SO_4 | 639.542 | Severe corrosion | | |
| 0.10 M K ₂ Cr ₂ O ₇ + | H_2SO_4 | 676.033 | Severe corrosion | | |



712.189

716.289

728.901

Severe corrosion

Severe corrosion

Severe corrosion

0.07 M aniline

0.41 M aniline

0.16 M K₂Cr₂O₇

0.10 M K2Cr2O7

H₂SO₄

H2SO4

H2SO4

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

While the admixed inhibitors deemed as exhibiting optimal qualities in this study are in the intermediate corrosion risk range according to ASTM C 876, they still show better inhibition efficiency in contrast to the control specimens as shown by their predicted values of Weibull mean in Fig. 8.

Weibull mean values of the control specimen in the H₂SO₄ and NaCl medium is given as approximately -547 and -450 mV (CSE), respectively. All the test specimens partially immersed in the NaCl medium except specimen No. 19 is predicted as possessing some degree

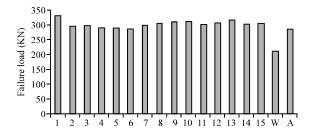


Fig. 9: Histogram of the compressive fracture load for the reinforced concrete specimens immersed in NaCl medium. W = concrete specimen cured in water, A = concrete specimen cured in air. Numbers 1-15 is shown in Table 1

of positive inhibiting quality in the NaCl medium as shown in Table 4. Specimen 19 which is the test sample corresponding to sample admixed with 0.03 M K₂Cr₂O₇ could be regarded as the only sample in the NaCl medium predicted in this investigation to show negative inhibiting quality when compared to its control. On the other hand, specimen No. 8, 12, 17, 18 and 20 in the H₂SO₄ medium corresponding to test sample admixed with 0.03 M $K_2Cr_2O_7$ and 0.3 M aniline, 0.14, 0.21 and 0.07 M aniline is also predicted as showing positive inhibiting qualities. The samples with negative inhibiting quality in the H₂SO₄ medium include sample No. 22-30 since their Weibull mean values fall below that of the control in H₂SO₄ medium. Clearly therefore, all the inhibitors used performed better in the NaCl medium essentially because of the aggressive sulphate ions present in the H₂SO₄ medium simulating microbial environment.

The examination of compressive fracture load data for steel rebar concrete samples partially immersed in NaCl and H₂SO₄ media are shown in Fig. 7 and 9. The strengths of all the test samples partially immersed in NaCl and H₂SO₄ media employed in the study were higher than those of the specimen cured in water for 2 weeks. This shows that the admixed inhibitors had no deleterious 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 relative chemical reactions hardening effect of the inhibitor with the concrete. In addition the specimens used for the monitoring experiments were partially immersed in H₂SO₄ and NaCl media while the other halves were exposed to the air throughout the experimental period. This twofold hardening method might also 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 H₂SO₄ 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, 3, 4, 5, 6, 7, 9, 10, 11 and 14 in the H₂SO₄ medium and none of the test samples in the NaCl medium (Table 1) gave a loss in compressive strength when compared with specimens cured in air. However, specimens 8, 12, 13 and 15 in the H₂SO₄ medium and all the specimens in the NaCl medium (Table 1) gave increases in the compressive strength. This therefore, suggests that the use of inhibitor admixtures that led to increased strength would be appropriate for making concrete. Control sample in the H₂SO₄ medium showed a reduction in compressive strength while it displayed increased strength in the NaCl medium showing that sulphuric acid had an adverse effect on the strength of concrete. All of the test samples partially immersed in the NaCl medium showed increases in compressive strength indicating that potassium dichromate, aniline and the synergistic combination of the two inhibitors was more effective in the NaCl medium than in the H2SO4 medium.

CONCLUSION

The study examined the effect of aniline, $K_2Cr_2O_7$ and their synergistic combination on concrete steel rebar damage in marine and microbial media. The potential readings obtained from the potential monitoring experiments were subjected to a two-parameter Weibull analysis. Compressive strength tests were also carried out for all test samples used in the study. However, results revealed that Weibull distribution modeled statistically the performance of aniline, $K_2Cr_2O_7$ and their synergistic combination on concrete steel rebar damage.

Twenty five of the thirty samples were well fitted based on the K-S goodness of fit test while five had outliers.

Test sample admixed with 0.34 and 0.41 M aniline both with Weibull mean value of -314.648 mV (CSE) at a probability of approximately 50% is predicted as exhibiting the best inhibiting quality in NaCl medium while in the $\rm H_2SO_4$ medium the synergistic combination of 0.03 M $\rm K_2Cr_2O_7$ and 0.30 M aniline with Weibull mean of -380.139 mV (CSE) and probability of 57% exhibited the best performance. This synergetic combination was also the best amongst all the synergetic combination employed in the study.

The compressive strength values of test sample admixed with 0.41 M aniline was the highest in both the microbial (303 KN) and marine (315 KN) medium while the control test sample in the NaCl medium showed the highest overall increase (330 KN) in compressive strength. Hence from the results aniline with concentration of 0.41 M aniline is recommended as an inhibitor for concrete

structures in saline environment, since it showed the highest resistance to corrosion and highest improvement in compressive strength.

Weibull mean values of corrosion potential obtained from the experiments has made the interpretation of data using ASTM C 876 standard possible erasing any form of inconsistency.

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