**Inhibition and Compressive-Strength Performance of
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Inhibition and Compressive-Strength Performance of $\text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ in Steel-Reinforced Concrete in Corrosive Environments

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Abstract

This paper studied corrosion-inhibition and compressive-strength performances of $\text{Na}_2\text{Cr}_2\text{O}_7$ (sodium dichromate) and $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ (ethylenediaminetetraacetic disodium salt: EDTA- Na_2) admixtures in steel-reinforced concrete immersed in NaCl and in H_2SO_4 corrosive environments. Electrochemical methods were used for studying corrosion responses of different concentrations of the individual admixtures and their synergies, in the model that partially replace the toxic $\text{Na}_2\text{Cr}_2\text{O}_7$ by the environmentally-friendly $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$, in steel-reinforced concretes. After the electrochemical experiment, the steel-reinforced concrete samples were subjected to the compressive-strength testing and analyses of ASTM C39/C39M-03 and ASTM C267-01. Results showed that the use of environmentally-friendly EDTA- Na_2 for partially replacing toxic $\text{Na}_2\text{Cr}_2\text{O}_7$ chemical exhibited better corrosion-inhibition and compressive-strength improvement in the NaCl-immersed concretes, than in the H_2SO_4 -immersed concretes. The 2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 admixture (representing partial replacement model of 6g $\text{Na}_2\text{Cr}_2\text{O}_7$ by 6g EDTA- Na_2) exhibited optimal corrosion inhibition efficiency, $\eta = 99.0\%$, and very good compressive-strength improvement advantage in the NaCl-immersed concretes. In contrast, comparatively low compressive-strength reduction trade-off with the good inhibition effectiveness of $\eta = 79.9\%$ support use of 6g EDTA- Na_2 admixture only (i.e. without $\text{Na}_2\text{Cr}_2\text{O}_7$ addition) for inhibiting reinforcing-steel corrosion in the H_2SO_4 -immersed concretes.

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Keywords: Inhibitor of concrete steel-reinforcement corrosion; total/partial replacement of toxic $\text{Na}_2\text{Cr}_2\text{O}_7$ by environmentally-friendly $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ admixture; statistical distribution analyses; compressive-strength modelling of concrete with admixtures; saline/marine simulating environment; microbial/industrial simulating-environment

1.0 Introduction

Corrosion of steel-reinforcement (steel-rebar) in concrete is the major source of deterioration and service failure of steel-reinforced concrete, a widely used construction material in building structures and infrastructures (Srubar III 2015; Bouteiller et al. 2012; Zafeiropoulou et al. 2011). Usually, steel-rebar is protected within the concrete pore structure due to the stable thin film layer from the hydration products of cement paste. However, corrosion attack of steel-reinforcement in concrete is initiated by natural and artificial agents in the service environment of the concrete which could include carbonation, chloride ingress and acidic sulphate attack. While carbonation attack in steel-reinforced concrete could be linked to the atmosphere of the concrete service-environment, chloride ingress could be due to natural marine in the coastal region or artificial de-icing salt in the temperate region (Mohammed et al. 2013; Shi et al. 2012; Zafeiropoulou et al. 2011). Acidic sulphate attack could result from microbial activities in sewage or other groundwater or acid rain from industrial environment (Gerengi et al. 2014; Li et al. 2014; Tang et al. 2012). By-products from the attack of these environmental agents are expansive within concrete, culminating in stresses that lead to physical degradation features in the form of cracks, spalling, delamination and reduced load bearing integrity of concrete structures (Mohammed et al. 2013; Tang et al. 2012; Charles et al. 2011; Zafeiropoulou et al. 2011). These lead to costly budget, globally, for maintenance, rehabilitation and repairs for prolonging service life of concrete structures and ensuring safety of life and properties (Mohammed et al. 2013; Li et al. 2014; Shi et al. 2012).

Many methods had been proposed for protecting steel-rebar from corrosion degradation in aggressive media. These include coating of the steel-rebar or concrete, electrochemical realkalisation, installation of cathodic protection, use of waterproofing membrane or admixtures and the use of corrosion inhibitor admixtures in concretes (Fei et al. 2014; Ribeiro et al. 2013; Geetha and Perumal 2012; Tang et al. 2012). From these, the use of corrosion inhibitor admixture had been identified as a simple, economical and effective method for protecting concrete steel-rebar from corrosion degradation in aggressive environments (Fei et al. 2014; Tang et al. 2012). Known chemical admixtures for inhibiting rebar corrosion include chromates and nitrites based inhibitors (Okeniyi et al. 2014a), but usage of these are being restricted in many countries due to their toxicity and hazardousness to the environmental eco-systems (Zhou et al. 2012; Cicek and Al-Numan 2011). These have necessitated needs for research studies on the search for total or partial replacement of the toxic chemicals by non-toxic and environmentally-friendly inhibitors, so that the use of the toxic chemicals as inhibitors of metallic corrosion could be reduced (Zhou et al. 2012; Feng et al. 2011).

$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (ethylenediaminetetraacetic disodium salt; EDTA- Na_2), Fig. 1, is an environmentally-benign, organic poly-carboxylate compound. The effectiveness of ethylenediaminetetraacetic acid as corrosion inhibitor in NaCl-immersed steel-reinforced concrete was investigated by Ormellese et al. (2011), along with other organic compounds with positive corrosion-inhibition results. Also the effectiveness of ethylenediaminetetraacetic disodium as inhibitor of carbon steel corrosion in hydrochloric acid was studied by Zohdy (2015) also with very high inhibition efficiencies at the various temperatures studied in the work. However, no research work had investigated EDTA- Na_2 as a possible substitute of sodium dichromate ($Na_2Cr_2O_7$) inhibitor for reinforcing-steel in concrete slab immersed in saline/marine and in microbial/industrial simulating media. Also,

while the compressive-strength of the organic inhibitor admixed concretes were tested before electrochemical experiment in Ormellese et al. (2011), the post experimental effect of the inhibitor on the compressive strength of concrete was not investigated in that study. This paper, therefore, investigates the corrosion-inhibition and the compressive-strength performance of $\text{Na}_2\text{Cr}_2\text{O}_7$ and $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ (EDTA- Na_2) in steel-reinforced concrete in NaCl and in H_2SO_4 media. The study involves the use of these substances as individual admixtures and as synergies, in which the toxic $\text{Na}_2\text{Cr}_2\text{O}_7$ was partially replaced by $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ admixture in steel-reinforced concrete samples immersed in the corrosive environments.

2.0 Materials and Methods

2.1.1 Steel-reinforced concrete specimens

The diameter 12mm steel-rebar used in this work with the composition: 0.27% C, 0.40% Si, 0.78% Mn, 0.04% P, 0.04% S, 0.14% Cr, 0.11% Ni, 0.02% Mo, 0.24% Cu, 0.01% Co, 0.01% Nb, 0.01% Sn and the balance Fe, was cut into 190mm rods of specimen. Each of these was subjected to the same surface treatment as detailed in Singh et al. (2012) and in ASTM G109-99a.

Forty-eight steel-reinforced concrete blocks, used for the electrochemical monitoring experiment, each of 100 mm $\times$ 100 mm $\times$ 200 mm, were produced as detailed in Okeniyi et al. (2014b) following the prescription of ASTM C192/192M-02). Embedded in each of these blocks were 150 mm of the rod of steel-rebar which were placed symmetrically across the width of each of the blocks and with the remaining length protruding for electrochemical connections. The protrusion from the embedded concrete rebar was painted with glossy paint.

2.1.2 Admixture concentrations in concrete samples

The different concentrations of $\text{Na}_2\text{Cr}_2\text{O}_7$ (sodium dichromate) and $\text{C}_{10}\text{H}_{14}\text{N}_2\text{Na}_2\text{O}_8 \cdot 2\text{H}_2\text{O}$ (ethylenediaminetetraacetic disodium salt: EDTA- Na_2) in each of the forty-eight steel-reinforced concrete samples, studied in this work, are as shown in Table 1. For each batch of concrete mix, the admixtures were weighed and then thoroughly mixed with some water before being made up to the volume of water required for the concrete batch, as per ASTM C192/192M-02. Admixture concentrations were varied, in replicate samples totalling thirty-six steel-reinforced concrete blocks, from 0 g (for the control/blank specimens) in increments of 2 g up to 8 g of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 . The remaining twelve blocks were admixed with combinations, also in replicates, of 2 g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6 g EDTA- Na_2 , 4 g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4 g EDTA- Na_2 and 6 g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2 g EDTA- Na_2 for studying partial replacement model of $\text{Na}_2\text{Cr}_2\text{O}_7$ as inhibitor of rebar corrosion. These concentrations, in Table 1, which are conveniently referred to hereafter in the paper by their admixture masses, were computed in mol/dm^3 (Molarity) from the inhibitor masses in relation to the concrete mixing water.

2.2 Experimental Procedures

2.2.1 Setup of corrosion test-specimens

The two sets of steel-reinforced concrete samples, used in this study, were partially and longitudinally immersed in two sets of plastic bowls containing corrosive test-environments. The first set of bowls contained 3.5% NaCl for simulating marine/saline environment (Zhou et al. 2012) while the second set contained 0.5 M H_2SO_4 for simulating microbial/industrial environment (Gerengi et al. 2014). The mode of sample immersion employed and the maintenance of corrosive environment in each bowls were as described in Okeniyi et al. (2014b). All the chemicals used in the study were of analytical grade.

2.2.2 *Electrochemical test-measuring methods*

The electrochemical monitoring techniques were employed for taking corrosion test-measurements were as described in Okeniyi et al. (2014b). The electrochemical measurements were taken from each sample in five days interval for the first forty days and thereafter in seven days interval for the following eight weeks. These translate to ninety-six days experimental setup. The electrochemical techniques used in the study include:

- i Half-cell potential (HCP) measurements: of the reinforcing-steel were measured versus Cu/CuSO₄ electrode (CSE) from Tinker & Rasor®, using a high impedance digital multimeter as detailed in literature (Okeniyi et al. 2014a; Bouteiller et al. 2012; Omotosho et al. 2011; ASTM C876-91 R99).
- ii Electrochemical cell current (ECC) measurements: in the concrete test-environment system were measured versus CSE, using zero resistance ammeter (ZRA), Model ZM3P from Corrosion Service® (Okeniyi et al. 2014b).
- iii Corrosion rate (CR) measurements: were obtained through direct instrument conversion to mpy (Okeniyi et al. 2014b; Abosrra et al. 2011) using the three-electrode LPR Data Logger, Model MS1500L from Metal Samples®. This equipment, that operates as detailed in Okeniyi et al. (2014b), have its electrodes connected to Ag/AgCl SCE reference electrode (EDT direct-ION), brass plate auxiliary and the steel-rebar working electrode (Bouteiller et al. 2012).

2.2.3 *Compressive-strength measuring technique*

After the ninety-six days electrochemical monitoring period, compressive-strengths of the steel-reinforced concrete samples were measured using hydraulically powered compression testing machine, Model YES 2000 by Eccles Technical Engineering Ltd, England. These were used for evaluating change in compressive-strength by averaging the crushing strength in each replicates of admixture concentration and comparing this with the averaged

compression strength of three additionally cast blank steel-reinforced concrete samples. These compression strength control samples were identical to the experimental specimens, but were cured in water for 28 days (Ormellese et al. 2011). From these, the compressive-strength analyses employed were as prescribed by ASTM C39/C39M-03 and ASTM C267-01.

2.3 Data Analyses

2.3.1 Statistical fitting functions and goodness-of-fit modelling

Measurements of electrochemical test-variables from the corrosion test-setup were subjected to statistical analyses of the Normal and the Weibull distribution fitting functions (Okeniyi et al. 2014b, 2013). Compatibility of the electrochemical test-data to the Normal and the Weibull distributions were ascertained by subjecting datasets of each test-variable to the goodness-of-fit (GoF) modelling of the Kolmogorov–Smirnov (K-S) test-statistics at $\alpha = 0.05$ significant level (Okeniyi and Okeniyi 2012; Omotosho et al. 2011).

2.3.2 Inhibition efficiency and synergistic parameter analyses

The probability distribution function describing the scatter of the corrosion rate test-data have its mean model, $\mu_{dist,CR}$, averaged over each concentration of admixture replicates, used for estimating inhibition efficiency, η . This was computed for each admixture concentration relative to the mean model of the blank or control sample, by the formula (Zohdy 2015; Zhou et al. 2012):

$$\eta = \frac{\mu_{dist,ctrl} - \mu_{dist,inh}}{\mu_{dist,ctrl}} \times 100 \quad (1)$$

The mean models of the statistical-distribution describing the data were further used for studying synergistic effects of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 on steel-rebar corrosion inhibition.

By this, synergistic parameter, S , for each combination of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixture concentrations was estimated from:

$$S = \frac{\mu_{\text{Na}_2\text{Cr}_2\text{O}_7, \text{conc}} \times \mu_{\text{EDTA-Na}_2, \text{conc}}}{\mu_{(\text{Na}_2\text{Cr}_2\text{O}_7, \text{conc} + \text{EDTA-Na}_2, \text{conc})}} \quad (2)$$

2.3.3 Compressive-strength performance of admixtures in concrete

The post-experimental compressive-strength performance of admixture in concrete was studied according to ASTM C267-01 by evaluating the compressive-strength change factor, $\text{CSCF}_{(\%)}$, from:

$$\text{CSCF}_{(\%)} = \frac{f'_{c_{w,28}} - f'_{c_{\text{after corrosion}}}}{f'_{c_{w,28}}} \times 100 \quad (3)$$

Where $f'_{c_{w,28}}$ is the compressive-strength of the control sample cured in water for 28 days and $f'_{c_{\text{after corrosion}}}$ is the compressive-strength of the immersed concrete test-sample after ninety-six days electrochemical experiment (Okeniyi et al. 2014c).

3.0 Results and discussions

3.1 Statistical modelling of electrochemical test-variables

The Normal and the Weibull mean models of the data of electrochemical test-variables are presented as plots in Fig. 2, for the half-cell potential, the cell current and the corrosion rate.

The plots of mean test-data, Fig. 2, showed that many of the replicates of concrete samples exhibited good agreements in the modelled mean of their electrochemical test-data, by the statistical modelling tools employed. Also, both modelling functions portrayed predominance of corrosion activities in many of the NaCl-immersed replicates of steel-reinforced concrete samples in comparisons with the H_2SO_4 -immersed samples. These imply the higher potential models in the NaCl-immersed samples, Fig. 2(a), indicated higher probability of rebar

corrosion risks, as per ASTM C876-91 while the higher current models, Fig. 2(b), portend higher rebar dissolution activity than that occurring in the H_2SO_4 -immersed samples. It could also be noted in Fig. 2(c) that the corrosion rate models, which depicted mitigations in the samples with admixtures relative to the control samples, had modelled mean from the samples in NaCl that were slightly higher than the modelled mean from the samples in H_2SO_4 .

However, it could be observed from the modelled electrochemical test-variables in Fig. 2 that some model estimations by the Weibull overshoot that of the Normal fitting function which could lead to discrepancies in the interpretation of the modelled results. Recommendations of ASTM G16-95 R04 for tackling this include that of ascertaining the statistical fitting function that described the prevailing condition in the corrosion test-systems. Thus, the results of the application of the Kolmogorov-Smirnov goodness-of-fit test for ascertaining this descriptive statistics are shown, for each test-variable, in Fig. 3.

At 0.05 significant level, five samples in NaCl, two in H_2SO_4 , have their modelled half-cell potential (HCP) data not following the Normal distribution, according to the K-S GoF criteria, Fig. 3(a), while HCP of eight samples in NaCl and one in H_2SO_4 did not follow the Weibull. Seven samples, all in the H_2SO_4 medium, have modelled cell current data that did not follow the Normal while the cell current data of all concrete samples in this study come from the Weibull distribution, Fig. 3(b). Also, the corrosion rate of twenty-five concrete samples, twelve in NaCl and thirteen in H_2SO_4 medium did not scatter like the Normal probability distribution function according to the K-S GoF test-criteria, Fig. 3(c).

However, from the plots in Fig. 3(c), it could be observed that the corrosion rate of all samples in the study scattered like the Weibull distribution function, according to the K-S GoF test, at $\alpha = 0.05$ significance. As per ASTM G16-95 R04, the scatter of the corrosion rate test-data, from the samples in this study, like the Weibull distribution supports preference of

this distribution model as the descriptive statistics for representing the prevalent conditions of corrosive activities in the concrete samples.

3.2 Inhibition efficiency performance and synergistic parameter models

From the applications of the Weibull mean model of corrosion rate test-data to Eq. (1), the inhibition efficiency, averaged over the replicated samples of concrete admixtures, relative to that of their replicated control samples, were computed for each test-media. These are presented in Fig. 4, according to the performance ranking of inhibition effectiveness on the corrosion of concrete steel-rebar in each test-media, by the $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures.

Fig. 4 showed that all the concentrations of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures studied, both individually and in synergistic combinations positively inhibited corrosion in the steel-reinforced concrete samples immersed in the NaCl medium and in the H_2SO_4 media. With inhibition efficiency, η , ranging from 96.6% (by 8g $\text{Na}_2\text{Cr}_2\text{O}_7$) to 84.6% (by 2g $\text{Na}_2\text{Cr}_2\text{O}_7$) in the NaCl medium and from 80.0% (by 8g $\text{Na}_2\text{Cr}_2\text{O}_7$) to 65.8% (by 6g $\text{Na}_2\text{Cr}_2\text{O}_7$) in the H_2SO_4 medium, these results re-affirmed $\text{Na}_2\text{Cr}_2\text{O}_7$ as an effective inhibitor in both media. However, the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ in the NaCl medium was surpassed in efficiency by the 8g EDTA- Na_2 , $\eta = 98.9\%$, the synergistic/partial $\text{Na}_2\text{Cr}_2\text{O}_7$ replacement models of 4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2 , $\eta = 96.7\%$, and of 2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 , $\eta = 99.0\%$. This later 2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 was modelled with the optimal inhibition efficiency in the saline/marine simulating medium. In the H_2SO_4 medium, the inhibition effectiveness performance by 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ was also surpassed by that of the 8g EDTA- Na_2 , $\eta = 87.0\%$. This 8g EDTA- Na_2 exhibited the optimal inhibition efficiency performance on steel-reinforcement corrosion in the concretes immersed in the acidic medium.

These results bare implications on the suitability of EDTA- Na_2 admixtures for the total/partial replacement model of 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ and 6g $\text{Na}_2\text{Cr}_2\text{O}_7$ and the partial replacement model of 4g $\text{Na}_2\text{Cr}_2\text{O}_7$ as inhibitor of steel-rebar corrosion in the NaCl-immersed concrete. However, the result only support the total replacement of 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ and of 6g $\text{Na}_2\text{Cr}_2\text{O}_7$ as inhibitor in reinforced concrete immersed in the H_2SO_4 medium but did not support use of the synergistic/partial $\text{Na}_2\text{Cr}_2\text{O}_7$ replacement models in the acidic sulphate medium. The synergistic/partial $\text{Na}_2\text{Cr}_2\text{O}_7$ replacement models exhibited comparatively low inhibition performances in steel-reinforced concrete immersed in the H_2SO_4 medium.

Results of the synergistic parameter modelling of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures in the steel-reinforced concrete samples are presented in Table 2. It could be observed from the table that only the synergistic combination of 2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 in NaCl medium was modelled with synergistic parameter that was greater than unity, i.e. $S = 7.58$. Subjecting this to the interpretations from Eduok et al (2012) showed that synergistic interaction between the 2g $\text{Na}_2\text{Cr}_2\text{O}_7$ and the 6g EDTA- Na_2 admixtures prevailed with cooperative effects on the inhibition of steel-rebar corrosion in NaCl-immersed concretes. Also, $S = 0.85$ (close to unity) for the 4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2 while $S = 0.13$ for the 6g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2g EDTA- Na_2 , which suggest lack of interaction between the former and antagonistic interaction between the later admixtures. From Table 2, modelled synergistic parameter, S , is much less than unity (i.e. $S < 1$) for the combinations of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures, employed for the H_2SO_4 -immersed concrete samples in the study. These results indicate prevalence of antagonistic interaction and imply competitive adsorption, between the combined admixtures in the acidic medium.

3.3 Compressive-strength performance of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures in concretes

The post-experimental compressive-strength performance of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures in the steel-reinforced concrete samples in their corrosive test-environments were

used for modelling the compressive-strength change factor, $CSCF_{(%)}$, according to Eq. (3). Results of these, in ranking order of compressive-strength improvement in the studied concrete samples, are presented in Fig. 5. By this, negative $CSCF$ indicates improvement in the concrete's compressive-strength while positive $CSCF$ indicate reduction in the concrete's compressive-strength relative to the compressive-strength of the control specimen cured in water for 28 days (Ctrl W_28).

Ranking in the NaCl medium showed that the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ and the 4g $\text{Na}_2\text{Cr}_2\text{O}_7$, with high corrosion inhibition in Fig. 4(a), exhibited good compressive-strength improvements, with $CSCF = -40.5\%$ and $CSCF = -30.3\%$ respectively, in their admixed concretes, Fig. 5(a). By taken consideration of admixtures with higher inhibition efficiency than that of the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ (the optimally effective dichromate admixture), only the 2g $\text{Na}_2\text{Cr}_2\text{O}_7 + 6\text{g EDTA-Na}_2$ synergy also exhibited better compressive-strength improvement, $CSCF = -51.9\%$. This indicates that the optimal inhibition efficiency performance by the 2g $\text{Na}_2\text{Cr}_2\text{O}_7 + 6\text{g EDTA-Na}_2$ admixture in the NaCl medium, Fig. 4(a), is attended by the added advantage of higher compressive-strength improvement in the concretes of its admixture. Another EDTA- Na_2 admixture exhibiting advantage close to this in the medium include the 6g EDTA- Na_2 which was modelled with inhibition efficiency $\eta = 95.2\%$ and compressive-strength improvement $CSCF = -33.9\%$. These inhibition efficiency and compressive-strength improvement performances by the 6g EDTA- Na_2 compare well with those of the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ to which they were just next in performances both from the rankings in Fig. 4(a) and Fig. 5(a).

The other admixtures with higher inhibition efficiencies than the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$, in the saline medium, the 8g EDTA- Na_2 and the 4g $\text{Na}_2\text{Cr}_2\text{O}_7 + 4\text{g EDTA-Na}_2$ had respective $CSCF = 4.4\%$ and $CSCF = 39.4\%$ implying compressive-strength reductions in their admixed concretes. This limits the applicability of these, later two admixtures, for inhibiting corrosion

in steel-reinforced concrete to low strength bearing applications such as steel-reinforced pavements.

Ranking in the H_2SO_4 medium showed that many of the admixtures in the medium were modelled with compressive-strength reductions in the concretes in which they were admixed, Fig. 5(b). The exceptions to this, in the acidic medium, are the 6g $\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{g EDTA-Na}_2$ with optimal compressive-strength improvement, $\text{CSCF} = -4.9\%$, followed, in compressive-strength improvement performance, by the 2g EDTA- Na_2 with $\text{CSCF} = -0.1\%$. However, both of these admixtures suffered the setback that they exhibited comparatively low inhibition efficiencies in the medium, Fig. 4(b). Fig. 5(b) also showed that the 8g EDTA- Na_2 , modelled with optimal inhibition efficiency in the H_2SO_4 medium exhibited the disadvantage that its use in concrete would culminate in the highest compressive-strength reduction among the concrete samples studied in this work. All these considerations bare supports for the 6g EDTA- Na_2 admixture, modelled with inhibition efficiency $\eta = 79.9\%$, that is just slightly lower than the $\eta = 80.0\%$ by the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$, for effecting corrosion inhibition in steel-reinforced concrete without jeopardising concrete strength. This is potent at being a suitable trade-of for the better compressive-strength change factor exhibited by the 6g EDTA- Na_2 admixture, at the slightly low strength reduction factor of $\text{CSCF} = 1.5\%$, than that from the lower load bearing strength by the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ having $\text{CSCF} = 8.8\%$.

4.0 Conclusion

The results from this study confirmed that the $\text{Na}_2\text{Cr}_2\text{O}_7$ is a very good inhibitor of steel-reinforcement corrosion in the NaCl and H_2SO_4 media, with compressive-strength improvement advantage in the concrete samples of it admixtures in both media. The study established that the 8g $\text{Na}_2\text{Cr}_2\text{O}_7$ exhibited inhibition efficiencies of $\eta = 96.6\%$ and $\eta = 80.0\%$, respectively, in the NaCl and the H_2SO_4 media. This performance by the dichromate admixture was combined with higher compressive-strength improvements, $\text{CSCF} = -40.5\%$

(in NaCl) or 8.8% (in H₂SO₄) than the control sample of steel-reinforced concrete, $CSCF = 17.1\%$ (in NaCl) or 47.4% (in H₂SO₄) in both media.

This highly effective performance was only surpassed by the synergy of 2g Na₂Cr₂O₇ + 6g EDTA-Na₂ admixture in the NaCl that exhibited inhibition efficiencies $\eta = 99.0\%$ combined with better compressive-strength improvement in concrete, $CSCF = -51.9\%$. Results in the study suggested that the effective performance by this combined admixtures was due to cooperative synergistic interactions between the 2g Na₂Cr₂O₇ and 6g EDTA-Na₂, for which synergistic parameter is greater than unity, $S = 7.58$. Among the other admixture concentrations studied, only the 6g EDTA-Na₂ also exhibited inhibition efficiency, $\eta = 95.2\%$, and compressive-strength improvement, $CSCF = -33.9\%$, performance that find comparison with the performance from the highly effective 8g Na₂Cr₂O₇ in the NaCl medium.

In the H₂SO₄ medium, the 6g EDTA-Na₂ exhibited a trade-off of slightly lower inhibition efficiency, $\eta = 79.9\%$, for higher compressive-strength improvement, $CSCF = 1.5\%$, that finds comparison with the performance of the also effective 8g Na₂Cr₂O₇ in the medium. Performance in H₂SO₄ medium exhibited contrast with that from NaCl medium, more especially, from the consideration that the synergistic admixtures exhibited low corrosion inhibition effect in the H₂SO₄ whereas they exhibited good performance in the NaCl medium.

From these results, it could be concluded that C₁₀H₁₄N₂Na₂O₈.2H₂O (EDTA-Na₂) is a suitable inhibitor for partially replacing Na₂Cr₂O₇ in NaCl, simulating saline/marine, and for totally replacing the toxic chemical in H₂SO₄, simulating microbial/industrial environments. These replacement models exhibit the advantage of reducing environmental effects from the use of toxic Na₂Cr₂O₇ chemical as inhibitor of steel-reinforcement corrosion and also potent with improving the load bearing (compressive) strength of the steel-reinforced concrete.

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Table 1. $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures insteel reinforced concrete samples

S/No	Admixture mass(concentration) in medium	S/No	Admixture mass(concentration) in medium
1.	0gadmixture (Control/Blank in NaCl)	2.	0gadmixture (Control/Blank in H_2SO_4)
3.	0gadmixture (Control/Blank in NaCl_Rep)	4.	0gadmixture (Control/Blank in H_2SO_4 _Rep)
5.	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl	6.	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
7.	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep	8.	2 g (0.0064M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
9.	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl	10.	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
11.	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep	12.	4 g (0.0127M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
13.	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl	14.	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
15.	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep	16.	6 g (0.0191M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
17.	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl	18.	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4
19.	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in NaCl_Rep	20.	8 g (0.0254M) $\text{Na}_2\text{Cr}_2\text{O}_7$ in H_2SO_4 _Rep
21.	2 g (0.0045M) EDTA- Na_2 in NaCl	22.	2 g (0.0045M) EDTA- Na_2 in H_2SO_4
23.	2 g (0.0045M) EDTA- Na_2 in NaCl_Rep	24.	2 g (0.0045M) EDTA- Na_2 in H_2SO_4 _Rep
25.	4 g (0.0090M) EDTA- Na_2 in NaCl	26.	4 g (0.0090M) EDTA- Na_2 in H_2SO_4
27.	4 g (0.0090M) EDTA- Na_2 in NaCl_Rep	28.	4 g (0.0090M) EDTA- Na_2 in H_2SO_4 _Rep
29.	6 g (0.0134M) EDTA- Na_2 in NaCl	30.	6 g (0.0134M) EDTA- Na_2 in H_2SO_4
31.	6 g (0.0134M) EDTA- Na_2 in NaCl_Rep	32.	6 g (0.0134M) EDTA- Na_2 in H_2SO_4 _Rep
33.	8 g (0.0179M) EDTA- Na_2 in NaCl	34.	8 g (0.0179M) EDTA- Na_2 in H_2SO_4
35.	8 g (0.0179M) EDTA- Na_2 in NaCl_Rep	36.	8 g (0.0179M) EDTA- Na_2 in H_2SO_4 _Rep
37.	2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 in NaCl	38.	2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 in H_2SO_4
39.	2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 in NaCl_Rep	40.	2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2 in H_2SO_4 _Rep
41.	4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2 in NaCl	42.	4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2 in H_2SO_4
43.	4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2 in NaCl_Rep	44.	4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2 in H_2SO_4 _Rep
45.	6g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2g EDTA- Na_2 in NaCl	46.	6g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2g EDTA- Na_2 in H_2SO_4
47.	6g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2g EDTA- Na_2 in NaCl_Rep	48.	6g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2g EDTA- Na_2 in H_2SO_4 _Rep

Table 2. Synergistic parameter model of $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures in steel-reinforced concretes

Admixture	Synergistic Parameter, <i>S</i>	
	NaCl Medium	H_2SO_4 Medium
2g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 6g EDTA- Na_2	7.58	0.03
4g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 4g EDTA- Na_2	0.85	0.07
6g $\text{Na}_2\text{Cr}_2\text{O}_7$ + 2g EDTA- Na_2	0.13	0.06

Draft

Figure Captions

Fig. 1. $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (ethylenediaminetetraacetic disodium salt: EDTA- Na_2) in optimised ball-and-stick model

Fig. 2 Statistical modelling of electrochemical test variables (a) half-cell potential; (b) cell current; (c) corrosion rate

Fig. 3 K-S goodness-fit-tests of electrochemical test variables (a) potential (b) cell current (c) corrosion rate

Fig. 4 Performance ranking of the corrosion inhibition effectiveness of $Na_2Cr_2O_7$ and EDTA- Na_2 admixtures in steel reinforced concretes immersed in (a) NaCl medium (b) H_2SO_4 medium

Fig. 5 Ranking model of compressive strength performance by $Na_2Cr_2O_7$ and EDTA- Na_2 admixtures in steel-reinforced concrete immersed in (a) NaCl medium (b) H_2SO_4 medium

Fig. 1. $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (ethylenediaminetetraacetic disodium salt: EDTA- Na_2) in optimised ball-and-stick model

Fig. 1. $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (ethylenediaminetetraacetic disodium salt: EDTA- Na_2) in optimised ball-and-stick model
126x95mm (114 x 113 DPI)

(a)

(b)

(c)

Fig. 2 Statistical modelling of electrochemical test variables (a) half-cell potential; (b) cell current; (c) corrosion rate

Fig. 2 Statistical modelling of electrochemical test variables (a) half-cell potential; (b) cell current; (c) corrosion rate

129x283mm (200 x 200 DPI)

Fig. 3 K-S goodness-fit-tests of electrochemical test variables (a) potential (b) cell current (c) corrosion rate

Fig. 3 K-S goodness-fit-tests of electrochemical test variables (a) potential (b) cell current (c) corrosion rate
127x284mm (200 x 200 DPI)

Fig. 4 Performance ranking of the corrosion inhibition effectiveness of Na₂Cr₂O₇ and EDTA-Na₂ admixtures in steel reinforced concretes immersed in (a) NaCl medium (b) H₂SO₄ medium

Fig. 4 Performance ranking of the corrosion inhibition effectiveness of Na₂Cr₂O₇ and EDTA-Na₂ admixtures in steel reinforced concretes immersed in (a) NaCl medium (b) H₂SO₄ medium 255x159mm (200 x 200 DPI)

Fig. 5 Ranking model of compressive strength performance by $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures in steel-reinforced concrete immersed in (a) NaCl medium (b) H_2SO_4 medium

Fig. 5 Ranking model of compressive strength performance by $\text{Na}_2\text{Cr}_2\text{O}_7$ and EDTA- Na_2 admixtures in steel-reinforced concrete immersed in (a) NaCl medium (b) H_2SO_4 medium
252x155mm (200 x 200 DPI)