Research Article

Effect of NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ Synergistic Admixtures on Steel-Rebar Corrosion in Concrete Immersed in Aggressive Environments

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This paper studies effect of different combinations of NaNO_2 (sodium nitrite) and $\text{C}_6\text{H}_{15}\text{NO}_3$ (triethanolamine (TEA)), as synergistic admixtures in concrete immersed in NaCl and in H_2SO_4 test environments, on the corrosion of the concrete reinforcing steel (rebar). Although statistically analysed electrochemical test results confirmed NaNO_2 effectiveness, synergistic combinations of 4 g NaNO_2 + 4 g $\text{C}_6\text{H}_{15}\text{NO}_3$ in NaCl medium and of 2 g NaNO_2 + 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ in H_2SO_4 medium were also highly effective at inhibiting rebar corrosion. Synergistic parameter analyses showed that the effective synergistic admixtures that inhibited concrete steel-rebar corrosion in their respective medium were the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ combinations that exhibited synergistic interactions of cooperative adsorption on steel-rebar. These support the suitability of requisite concentration of triethanolamine as additive admixture with sodium nitrite for steel-rebar corrosion mitigation, which is potent with reduced environmental effects, in concrete immersed in NaCl and in H_2SO_4 corrosive media.

1. Introduction

Concrete is the most widely used cement-based construction materials for buildings structures and infrastructures [1–3]. However, corrosion degradation of the reinforcing steel (steel-rebar) in concrete is affecting sustainability and service performance of concrete building and infrastructures and generating safety and economic concerns among construction stakeholders, globally [3–6]. Normally, steel embedded in concrete is protected from corrosion attack by a passive layer of thin oxide film from the highly alkaline, pH of about 12.5–13, cement hydration products [3, 7, 8]. Steel-rebar corrodes in concrete due to breakdown of the protective oxide film by aggressive agents of the environments, in the form of chloride ingress, from natural marine or artificial saline (deicing salts) [8, 9], or sulphate attack, from microbial

or industrial environments [7, 10–12]. Corroded products from these are expansive within concrete leading to cracks, spalling, delamination, and loss of structural integrity of the reinforced concrete [8, 9, 13].

Among many methods [1], the use of corrosion inhibitors had been identified as an easy, effective, and economical approach for mitigating steel-rebar corrosion and for improving durability of steel-reinforced concrete structures in aggressive environments [2, 5, 14, 15]. However, important criteria for achieving acceptable mitigation of corrosion rate in a corrosive environment include responsible application of the inhibiting substance at a suitable concentration in the corrosive system [2, 16]. That the presence of an inhibiting substance at an unsuitable concentration in the corrosive system could aggravate, instead of inhibiting, corrosion [16, 17] necessitates studies of suitable concentrations of admixture

FIGURE 1: Triethanolamine ($C_6H_{15}NO_3$; TEA): (a) molecular structure and (b) optimized ball and stick model.

for mitigating steel-rebar corrosion in their corrosive service environments.

Nitrites are well-known corrosion inhibiting substance [2, 5, 15, 18] although they suffer the setback that their use is being restricted in many countries due to their toxicity and hazardousness to the environmental ecosystems [1, 19, 20]. This is fostering research deliberations on the search for more environmentally friendly substances for totally or partially replacing the traditional but toxic inhibitor. However, such search had been difficult due to the high effectiveness of nitrites at inhibiting steel-rebar corrosion. Triethanolamine ($C_6H_{15}NO_3$; TEA) is an organic chemical with the molecular structure shown in Figure 1 that is nontoxic to the environment and which had been employed for mitigating chloride-induced carbon steel corrosion in simulated alkaline pore solution [21]. Yet, there is paucity of studies on the suitability of triethanolamine as an environmentally benign alternative for synergistic partial replacement of the highly effective, but toxic, nitrite admixture as inhibitor of steel-rebar corrosion in concrete slab immersed in aggressive media. Specific motivation for this paper was especially drawn from [22] that showed that inhibition effectiveness of nitrites could be improved by requisite addition of another chemical. This is because such additional model channeled using nontoxic chemical is potent with reduction in environmental effects from the consequently lower usage of the toxic $NaNO_2$ inhibitor quantity required for adequate corrosion inhibition. This paper, therefore, investigates the effect of synergistic combinations of different sodium nitrite ($NaNO_2$) and triethanolamine ($C_6H_{15}NO_3$; TEA) concentrations as synergistic admixtures on the corrosion of steel-rebar in concrete immersed in $NaCl$ and in H_2SO_4 media.

2. Materials and Methods

2.1. Reinforcing Steel and Reinforced Concrete Block Specimens. Steel reinforcement used in the study was obtained from the Federated Steel Rolling Mills, Ota, Ogun State, Nigeria. The $\varnothing 12$ mm deformed rebar has composition in % of 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. The steel-rebar was cut into specimen rods each of which was 190 mm long.

Surface preparation was then maintained uniformly for each of these rods. Each rod of rebar was ground with coarse and fine abrasive papers, pickled for 10 minutes in 10% H_2SO_4 [23], rinsed and cleaned in ultrasonic cleaner, degreased with acetone, dried with warm air stream, and kept in desiccator prior to being used for the experiment [24, 25].

Forty steel-reinforced concrete samples used for the experiment were produced as replicated blocks [26], four blocks per batch, and each of size 100 mm $\times$ 100 mm $\times$ 200 mm, such as volume of each concrete block = 2×10^3 m³. In each of these blocks 150 mm length of the $\varnothing 12$ mm steel-rebar was embedded, which was symmetrically placed across the width of each of the blocks implying 44 mm concrete cover thickness, with the remaining length of the rebar protruding for electrochemical connections. This protruded rebar from the concrete was painted with glossy paint. Drinkable water was used for mixing the concrete blocks. Each block was formulated using ordinary Portland cement, clean natural sand, and granite stones. The formulation used for the mixing of each steel-reinforced concrete specimen includes cement = 300.0 kg/m³, sand = 890.6 kg/m³, granite stones = 1106.3 kg/m³, and mixing water of 149.7 kg/m³, thus making the water/cement (w/c) ratio = 0.499 [14, 23].

2.2. Inhibitor Admixture. The admixture concentrations of $NaNO_2$ and $C_6H_{15}NO_3$ by mass, in synergistic combinations and individual admixtures, in each 100 mm $\times$ 100 mm $\times$ 200 mm concrete specimen, and in each of the corrosive media of specimen immersion were as presented in Table 1. These, in duplicate samples (tagged as “_Dup”), include blank concretes, without admixture followed by concretes admixed with different combinations of $NaNO_2$ and $C_6H_{15}NO_3$ concentrations, and then concretes with individual concentrations of the $NaNO_2$ and of the $C_6H_{15}NO_3$. This was designed for facilitating synergistic parameter modelling [27, 28]. Addition of the admixtures to the cast concrete samples was as prescribed by ASTM C192/192M-02 [29]. For admixing in concrete sample, the admixture was weighed on analytical weighing balance, mixed thoroughly with concrete mixing water that was made up to the required water volume for the water-cement ratio of the concrete sample for the casting of the concrete sample.

TABLE 1: Inhibitor admixtures by mass in the steel reinforced concrete samples.

Serial/number	Inhibitor admixture by mass	Serial/number	Inhibitor admixture by mass
1	0 g admixture (blank or control in NaCl)	2	0 g admixture (blank or control in H ₂ SO ₄)
3	0 g admixture (blank or control in NaCl-Dup)	4	0 g admixture (blank or control in H ₂ SO ₄ -Dup)
5	6 g NaNO ₂ + 2 g C ₆ H ₁₅ NO ₃ in NaCl	6	6 g NaNO ₂ + 2 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄
7	6 g NaNO ₂ + 2 g C ₆ H ₁₅ NO ₃ in NaCl-Dup	8	6 g NaNO ₂ + 2 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄ -Dup
9	4 g NaNO ₂ + 4 g C ₆ H ₁₅ NO ₃ in NaCl	10	4 g NaNO ₂ + 4 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄
11	4 g NaNO ₂ + 4 g C ₆ H ₁₅ NO ₃ in NaCl-Dup	12	4 g NaNO ₂ + 4 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄ -Dup
13	2 g NaNO ₂ + 6 g C ₆ H ₁₅ NO ₃ in NaCl	14	2 g NaNO ₂ + 6 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄
15	2 g NaNO ₂ + 6 g C ₆ H ₁₅ NO ₃ in NaCl-Dup	16	2 g NaNO ₂ + 6 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄ -Dup
17	6 g NaNO ₂ in NaCl	18	6 g NaNO ₂ in H ₂ SO ₄
19	6 g NaNO ₂ in NaCl-Dup	20	6 g NaNO ₂ in H ₂ SO ₄ -Dup
21	4 g NaNO ₂ in NaCl	22	4 g NaNO ₂ in H ₂ SO ₄
23	4 g NaNO ₂ in NaCl-Dup	24	4 g NaNO ₂ in H ₂ SO ₄ -Dup
25	2 g NaNO ₂ in NaCl	26	2 g NaNO ₂ in H ₂ SO ₄
27	2 g NaNO ₂ in NaCl-Dup	28	2 g NaNO ₂ in H ₂ SO ₄ -Dup
29	2 g C ₆ H ₁₅ NO ₃ in NaCl	30	2 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄
31	2 g C ₆ H ₁₅ NO ₃ in NaCl-Dup	32	2 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄ -Dup
33	4 g C ₆ H ₁₅ NO ₃ in NaCl	34	4 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄
35	4 g C ₆ H ₁₅ NO ₃ in NaCl-Dup	36	4 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄ -Dup
37	6 g C ₆ H ₁₅ NO ₃ in NaCl	38	6 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄
39	6 g C ₆ H ₁₅ NO ₃ in NaCl-Dup	40	6 g C ₆ H ₁₅ NO ₃ in H ₂ SO ₄ -Dup

2.3. Experimental Procedures

2.3.1. Corrosion Test Setup. Steel reinforced concrete specimens were divided into two sets. Each of the specimens in each set was partially immersed, longitudinally, in plastic bowl containing corrosive test environment. A duplicated set of twenty samples was partially immersed in 3.5% NaCl solution [30, 31], for simulating saline/marine environment, while the second duplicated set was partially immersed in 0.5 M H₂SO₄ solution [2, 10, 32, 33], for simulating microbial/industrial environment. In each bowl, the test medium was made up to just below the concrete steel-rebar but was not touching it. Also, according to the practice described in [24], the test medium in each bowl was replenished every three weeks to prevent dryness and induce continuous system of corrosive environment through the ninety-six-day immersion of the steel-reinforced concrete samples. All chemicals used for both chemical admixtures and corrosive test environments are analytical grade.

2.3.2. Electrochemical Measurements. Nondestructive electrochemical measurements [14, 32–35] were taken, from the experimental setup, first, in five-day interval for forty days and thereafter in seven-day interval for the following eight weeks. This totalled 17 measurements within the experimental period of ninety-six days for the study. The nondestructive electrochemical test methods used for evaluating corrosion inhibition performance of the NaNO₂ and C₆H₁₅NO₃ admixtures in concrete include the following.

- (i) Half-cell potential (HCP) measurements: these were taken through the experimental period versus Cu/CuSO₄ electrode (CSE), Model 8-A (Tinker &

Rasor), using high impedance digital multimeter, Model DT-9205A, according to ASTM C876-91 R99 [36].

- (ii) Electrochemical cell current (ECC) measurements: these were taken versus the CSE, using zero resistance ammeter (ZRA), Model ZM3P (corrosion service) [14, 37, 38]. This was done for the measurement model of the reinforcing steel dissolution activity [14, 39] in the aggressive test solution systems sharing porous partitioning with the Cu/CuSO₄.
- (iii) Corrosion rate (CR) measurements: these were obtained through direct instrument conversion to mpy [14] using the three-electrode LPR Data Logger, Model MSI500L (metal samples) [40].

2.4. Data Analyses

2.4.1. Statistical Distributions and Goodness-of-Fit Analyses. As prescribed in [41, 42], measurements of electrochemical test data from the corrosion test setup were subjected to the statistical analysis of the Weibull probability distribution function [2, 14, 32, 33, 42]. This statistical modelling tool has probability distribution function given by

$$f(x)_w = \left(\frac{k}{c}\right) \left(\frac{x}{c}\right)^{k-1} \exp \left[-\left(\frac{x}{c}\right)^k \right], \quad (1)$$

where x is corrosion test data from the requisite corrosion variable, which could be the half-cell potential, the cell current, or the corrosion rate. Also, k is the Weibull shape parameter and c is the Weibull scale parameter, both of which are estimated from the $n = 17$ test data of corrosion test

variable from each sample from the solution of simultaneous maximum likelihood equations [43, 44]:

$$\begin{aligned} \frac{n}{\hat{k}} - n \log(\hat{c}) + \sum_{i=1}^n \log x_i - \sum_{i=1}^n \left(\frac{x_i}{\hat{c}} \right)^{\hat{k}} \log \left(\frac{x_i}{\hat{c}} \right) &= 0, \\ \hat{c} - \left\{ \frac{1}{n} \sum_{i=1}^n x_i^{\hat{k}} \right\}^{1/\hat{k}} &= 0. \end{aligned} \quad (2)$$

The unbiased estimates of c and k from these equations find usefulness for computing Weibull mean, μ_W , through

$$\mu_W = c \Gamma \left(1 + \frac{1}{k} \right). \quad (3)$$

Compatibility of the electrochemical test data to each of the Weibull distributions was ascertained by subjecting each variable of measured data to the Kolmogorov-Smirnov (K-S) goodness-of-fit (GoF) test criteria [42, 43, 45, 46]. This, K-S GoF, measures the absolute difference between empirical distribution function $F^*(x)$ and theoretical distribution function $F(x)$ [45, 47, 48] through the statistics:

$$D_n = D(x_1, \dots, x_n) = \sup_{-\infty < x < \infty} |F^*(x) - F(x)|, \quad (4)$$

where $n = 17$ data points obtained from the days of measurements for each electrochemical test variable. The D value evaluation from (4) was used for direct computation of the K-S P value using the procedures from [45]. By this, criteria were set such that, for $\alpha = 0.05$ significant level, K-S P value $< \alpha$ for a probability distribution of corrosion test data indicates that such data did not follow that distribution while K-S P value $\geq \alpha$ showed that the test data followed the distribution.

2.4.2. Inhibition Efficiency and Synergistic Parameter Analyses. The mean corrosion rate performance, μ , obtained from the Weibull analysis of corrosion rate data finds usefulness for evaluating inhibition efficiency, η , for each admixture concentration employed, relative to that of the blank sample, from the formula [14, 27, 30, 37]:

$$\eta = \frac{\mu_{\text{blank}} - \mu_{\text{inh}}}{\mu_{\text{blank}}} \times 100. \quad (5)$$

Also, these mean performances were employed for investigating synergistic effect of the partial NaNO_2 replacement by $\text{C}_6\text{H}_{15}\text{NO}_3$ admixtures on the inhibition of concrete steel-rebar. This entails evaluating synergistic parameter, S , for each combination of the $\text{NaNO}_2 + \text{C}_6\text{H}_{15}\text{NO}_3$ admixture concentrations using the formula [27, 28]:

$$S = \frac{\mu_{\text{NaNO}_2, \text{conc}} \times \mu_{\text{C}_6\text{H}_{15}\text{NO}_3, \text{conc}}}{\mu_{(\text{NaNO}_2, \text{conc} + \text{C}_6\text{H}_{15}\text{NO}_3, \text{conc})}}. \quad (6)$$

3. Results and Discussions

3.1. Statistical Modelling of Corrosion Test Data Measurements. Plots of the Weibull mean of variables of corrosion test data

measurements, the half-cell potential, cell current, and corrosion rate are shown in Figure 2, for NaNO_2 and TEA admixed steel reinforced concretes samples. Figure 2(a) showed additional horizontal parallel lines, as specified in ASTM C876-91 R99 [36], delineating probability of corrosion risks for direct interpretation of the Weibull mean performance of half-cell potential in each of the reinforced concrete samples. In the plots, the electrochemical monitoring methods employed showed good agreements among many of the duplicated samples. Also, the test methods revealed higher prevalence of corrosive activities in the samples immersed in the chloride test environments compared to those in the sulphate test environments. For instance (see Figure 2(a)) the Weibull mean performance of corrosion potential obtained from the reinforced concrete samples immersed in the saline simulating medium highly overshoot the corrosion potential performance of samples immersed in the acidic medium. This, according to interpretations from ASTM C876-91 R99 [36] which are shown by the horizontal lines in Figure 2(a), implies existence of higher probability of corrosion risk in the concrete samples in NaCl medium compared to the samples in H_2SO_4 medium. In Figure 2(b) also, the trends of corrosion cell currents in the samples in chloride medium overshoot the trends of cell currents of samples immersed in the sulphuric acid medium, thus suggesting higher dissolution activity in the NaCl -immersed concrete samples.

The corrosion rate performance in Figure 2(c) tends to follow these trends of the other corrosion test variables. By this, the mitigated corrosion rates of the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA) admixed samples, relative to the overshoot of corrosion rates obtained from the duplicates of control samples, in NaCl were still generally higher, compared to the corrosion rates samples immersed in the H_2SO_4 medium.

Common to all these plots are the identifiable mitigations and, in some other cases, peaks denoting aggravations, of corrosion activities by the concentrations of NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA) admixtures in the steel reinforced concrete samples immersed in aggressive media. According to interpretation of ASTM C876-91 R99 [36], Figure 2(a) reaffirmed that the HCP of the blank samples in the saline media was more negative than the “severe corrosion” condition range of the ASTM standard. Also, the HCP of the blank samples in the acidic media is classified to the “high (>90%) corrosion risk” region. These suggest the inference that the media of concrete immersions employed in the study were aggressive to the embedded steel-rebar in the reinforced concretes not containing admixtures. It is based on these that mitigations of corrosion rate relative to the blank concrete samples by the synergistic partial NaNO_2 replacement by $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA) admixtures in the reinforced concrete samples, especially in the severe saline media (see Figure 2(c)), could be noted.

The plots of the K-S P values, from the application of the K-S GoF test statistics to the measurements of corrosion test variables from the steel-reinforced concrete samples in aggressive media, are presented in Figure 3. Each of these plots includes the delineating line plot of the significant level $\alpha = 0.05$ for directly ascertaining, from the figure, dataset of test variable that followed or did not follow the Weibull probability distribution function. From this, it could

FIGURE 2: Weibull mean models of the electrochemical test data of steel-reinforced concrete samples immersed in aggressive media for ninety-six days of experimental period: (a) half-cell potential (with corrosion risk levels as per ASTM C876-91 R99 [36]), (b) cell current, and (c) corrosion rate.

be deduced that all datasets of the half-cell potential from the duplicated concrete samples studied scattered like the Weibull probability distribution function; see Figure 3(a). However, the cell current datasets of the 4g TEA, the 2g TEA, and the synergistic 2g NaNO₂ + 6g TEA admixed steel-reinforced concrete samples, in the H₂SO₄ medium, were not distributed like the Weibull fitting function; see Figure 3(b).

All the other datasets of measured test variables from the reinforced concrete samples follow the Weibull probability

distribution function. By this, the entire corrosion rate datasets measured from the duplicated samples of steel-reinforced concretes considered in the study also followed the Weibull probability distribution function according to the K-S GoF test criteria (see Figure 3(c)). These, in line with ASTM G16-95 R04 [41], support the use of the Weibull analyses of the mean of the corrosion rate test data from the steel reinforced concrete samples for representing the prevailing corrosion conditions in each of the corrosive test systems.

FIGURE 3: K-S goodness of fit test of measured corrosion test variables from concrete samples: (a) half-cell potential, (b) cell current, and (c) corrosion rate.

The choice of corrosion rate for detailing corrosion condition in the samples, instead of corrosion potential that the test data also followed the Weibull model, was due to the identification from [49] that the corrosion potential gives poor indication of absolute corrosion activity.

3.2. Admixture Performance and Inhibition Efficiency Estimations. The Weibull mean corrosion rate was employed for interpreting levels of corrosion degree as per [16, 35, 50] and estimating averaged inhibition efficiency of the duplicated samples of admixed reinforced concrete relative to the duplicated blank samples in each test medium. The results of admixture performance from these are presented in

Figure 4, in ranking order of effectiveness of the admixtures at inhibiting concrete steel-rebar corrosion in each of the aggressive test environments. The use of delineating lines of requisite levels of corrosion degree interpretations from [16, 35, 50] was employed in the parts of the plots in Figure 4 involving rankings of the corrosion rate performance of the studied admixture concentrations. The results of admixture performance ranking in Figure 4(a) showed that the blank samples without admixture in the NaCl medium exhibited corrosion rate that was higher than the upper bound of “very high” degree of corrosion rate, $0.1 \leq CR \text{ (mm/y)} < 1$, as per [16, 35, 50]. This supports the inference that the degree of corrosion rate in these blank samples in NaCl medium was

FIGURE 4: Performance effectiveness ranking of admixtures at inhibiting concrete steel-rebar corrosion in concrete immersed in aggressive media for ninety-six days of experimental period: (a) corrosion rate ranking in NaCl medium, (b) inhibition efficiency ranking in NaCl medium, (c) corrosion rate ranking in H₂SO₄ medium, and (d) inhibition efficiency ranking in H₂SO₄ medium.

in the very severe level, which is an important requirement prescribed by [42], even as this finds agreements with the HCP interpretation as per ASTM C876-91 R99 [36] for these blank samples in Figure 2(a). Also, the admixture performance rankings in Figure 4(a) and Figure 4(b) reaffirmed high effectiveness of the NaNO_2 admixtures at inhibiting steel-rebar corrosion in concrete immersed in the aggressive saline/marine simulating environments. However, in this highly corrosive NaCl medium, the effective 6 g NaNO_2 admixture with inhibition efficiency, $\eta = 94.6\%$, was followed closely in ranking order by the equal-mass synergistic combination of the 4 g $\text{NaNO}_2 + 4$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture. This synergistic admixture has inhibition efficiency, $\eta = 92.2\%$, which compares well with that obtained from the 6 g NaNO_2 admixture and which surpasses other NaNO_2 admixtures studied in effectiveness. By corrosion rate interpretations from [16, 35, 50] in Figure 4(a), both the 6 g NaNO_2 and the 4 g $\text{NaNO}_2 + 4$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixtures mitigated steel-rebar corrosion from the very severe corrosion in the blank samples to well below the upper bound of “very high” corrosion. Also, consideration of the half-cell potential trends in Figure 2(a) showed that duplicate concrete samples with 4 g $\text{NaNO}_2 + 4$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture exhibited lower probability of corrosion risks than the duplicate concrete samples with 6 g NaNO_2 admixtures. Also, the cell current trends, in Figure 2(b), showed that the concrete samples with 4 g $\text{NaNO}_2 + 4$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture find better agreements in lowered trends of reinforcing steel dissolution activities than those obtained from concrete samples with 6 g NaNO_2 admixture. These agreements from electrochemical test results by different instruments strongly suggest suitability of this synergistic combination of NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ for reducing environmental effects due to lower usage of NaNO_2 as inhibitor of steel-rebar corrosion in NaCl medium.

From the consideration of the admixture performance in this study, it could also be inferred that multiplicative NaNO_2 -mass amount would be required for suitable $\text{C}_6\text{H}_{15}\text{NO}_3$ -mass that would synergistically combine with NaNO_2 admixture in order to attain inhibition performance that compares with that of the individual NaNO_2 that was initially reduced for the synergistic combination model. A specific example from this study includes the 4 g NaNO_2 (a 2 g $\text{NaNO}_2 + 2$ g NaNO_2 amount) which was modelled with the same inhibition efficiency, $\eta = 89.4\%$, as that of the synergistic 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ in the NaCl medium; see Figure 4(a). This constitutes triplication of the 2 g NaNO_2 part as the 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ part for attaining the same inhibition effectiveness as the individual NaNO_2 that was initially reduced for the synergy, in the NaCl test medium.

The admixture performance ranking in Figure 4(c) showed that the blank samples without admixture in the H_2SO_4 medium exhibited corrosion rate that was higher than the upper bound of “high” degree of corrosion rate, $0.01 \leq \text{CR (mm/y)} < 0.1$, according to [16, 35, 50]. This corrosion rate classification also finds agreements with the HCP interpretation for the blank samples in H_2SO_4 medium that was also in the “high (>90%) corrosion risk” region as per ASTM C876-91 R99 [36], in Figure 2(a). In furtherance of

this, the admixture performance rankings in Figure 4(c) and Figure 4(d) also identified many of the NaNO_2 admixtures with good effectiveness at mitigating steel-rebar corrosion in the H_2SO_4 medium. However, the NaNO_2 admixtures were all surpassed in effectiveness at inhibiting concrete steel-rebar corrosion by the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixture. In this medium, it is only the corrosion rate of the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixture that was classified as below the upper bound of the “high” degree of corrosion rate as per [16, 35, 50] in Figure 4(c). This evaluated to the inhibition efficiency of $\eta = 64.7\%$ by the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixture, which indicated that the 2 g NaNO_2 and the 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ combined to improve effectiveness of one another at inhibiting rebar corrosion in H_2SO_4 . Also, other trends of electrochemical test variables identified the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixed concrete with lower probability of corrosion risk, in Figure 2(a), and lesser steel-rebar dissolution activity, in Figure 2(b), than those of the blank samples in the acidic medium. The admixture of proximate effectiveness to the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixture at inhibiting steel-rebar corrosion includes the 4 g $\text{C}_6\text{H}_{15}\text{NO}_3$ ($\eta = 32.2\%$) followed by the 4 g NaNO_2 ($\eta = 30.8\%$). But these individual admixtures exhibited much higher corrosion rates which translated to much lower corrosion inhibition effectiveness than the $\eta = 64.7\%$ inhibition effectiveness performance by the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixture. These considerations support the suitability of the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture as optimal admixture and synergistic combination of NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ for inhibiting steel-rebar corrosion in acidic microbial/industrial simulating environment studied. And by this, also, the synergistic 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture exhibits potency of higher reduction of NaNO_2 admixture usage in concretes immersed in H_2SO_4 medium. However, the other synergistic admixtures exhibited aggravations of concrete steel-rebar corrosion in the acidic medium, instead of corrosion inhibition. This fosters interests on the mode of synergistic interactions between the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ combinations constituting these synergistic partial NaNO_2 replacement admixtures.

3.3. Synergistic Parameter Modelling. Results of synergistic parameter modelling of the combinations of NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA) admixtures in the steel reinforced concretes studied are plotted in Figure 5. This figure identified the 4 g $\text{NaNO}_2 + 4$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ and the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixtures with optimal performance of synergistic parameter in their respective NaCl and H_2SO_4 media. It could also be noted from the figure that the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ also exhibited high synergistic parameter performance in the NaCl medium. Interpretations from [27, 28] showed that the 4 g $\text{NaNO}_2 + 4$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ with synergistic parameter $S = 3.97$ and the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ with $S = 2.42$ exhibited prevalent synergistic interaction, $S > 1$, between NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ admixtures in the NaCl medium. Also, application of similar interpretation showed that the 2 g $\text{NaNO}_2 + 6$ g $\text{C}_6\text{H}_{15}\text{NO}_3$ with $S = 1.19$ exhibited prevalent synergistic interaction in the H_2SO_4 medium. According to [27, 28], these prevalent synergistic

FIGURE 5: Synergistic interaction modelling NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA) admixtures on steel-rebar corrosion.

interactions indicate cooperative adsorption of the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ on the steel-rebar, especially according to the schematic representation presented in [27]. That schematic synergistic mechanism in [27] suggested the adsorption of the highly effective NaNO_2 on the steel-rebar surface, while the $\text{C}_6\text{H}_{15}\text{NO}_3$ adsorbed on the layer of the NaNO_2 adsorption at the same sites of the embedded steel-rebar in concrete. It is especially worth noting that the synergistic admixtures that exhibited the mechanism of cooperative adsorption as their prevalent synergistic interaction in this study were the admixtures that were found suitable for reducing NaNO_2 usage as inhibitor in their test media. The improved inhibition efficiency from the 4 g NaNO_2 + 4 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture in the NaCl medium and the 2 g NaNO_2 + 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture in the NaCl and H_2SO_4 media relative to their individual admixtures were due to the synergistic interactions between these admixtures.

The other remaining synergistic admixtures in both media exhibited the synergistic mechanism of antagonistic interactions, by their synergistic parameter $S < 1$, between the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ admixtures in their respective environments. According to [27, 28], these synergistic mechanisms of antagonistic interactions are due to competitive adsorption of the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ on the steel-rebar. This synergistic interaction of competitive adsorption indicates that the NaNO_2 and the $\text{C}_6\text{H}_{15}\text{NO}_3$ admixtures adsorb at different sites on the steel-rebar surface. It is also worth noting that the admixture combinations exhibiting this kind of antagonistic interaction, in this study, were not also found suitable for inhibiting steel-rebar corrosion in their admixed concretes immersed in their respective test media. The comparatively low inhibition efficiency from the 4 g NaNO_2 + 4 g $\text{C}_6\text{H}_{15}\text{NO}_3$ in the H_2SO_4 and the 6 g NaNO_2 + 2 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture in the NaCl and

the H_2SO_4 relative to their individual admixtures were due to the antagonistic interaction between the admixtures.

4. Conclusions

The effect of NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixtures in concrete slab immersed in the aggressive NaCl and H_2SO_4 environments on the corrosion of the embedded concrete steel-rebar had been studied in this work. Conclusions that could be drawn from these include the following.

- (i) The statistical analyses of electrochemical test results identified, in agreements, the prevalence of corrosive activities in the sodium chloride medium above that occurring in the sulphuric acid test medium, across all the concentrations of admixtures studied; these electrochemical test results also showed that both of the NaCl and H_2SO_4 test media employed constitute aggressive environments, especially, to concrete steel-rebar in blank concrete samples not having inhibitor admixture.
- (ii) Although many of the NaNO_2 admixtures exhibited good effectiveness at inhibiting steel-rebar corrosion in both media, inhibition efficiency (η) modelling supports the combined usage of 4 g NaNO_2 + 4 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture, with $\eta = 92.2\%$, as effective synergistic inhibitor of steel-rebar corrosion in steel-reinforced concrete immersed in the NaCl medium while the combination of 2 g NaNO_2 + 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture with inhibition efficiency $\eta = 64.7\%$ was found suitable as effective synergistic inhibitor of steel-rebar corrosion in steel-reinforced concrete immersed in H_2SO_4 medium.
- (iii) Synergistic parameter modelling identified the 4 g NaNO_2 + 4 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture, $S = 3.97$, and the 2 g NaNO_2 + 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture, $S = 2.42$, with prevalent synergistic interaction of cooperative adsorption on steel-rebar between the NaNO_2 and $\text{C}_6\text{H}_{15}\text{NO}_3$ synergistic admixtures in the NaCl medium while the 2 g NaNO_2 + 6 g $\text{C}_6\text{H}_{15}\text{NO}_3$ admixture exhibited this kind of prevalent synergistic interaction of cooperative adsorption on steel-rebar, $S = 1.19$, in the H_2SO_4 medium.
- (iv) All the synergistic admixtures exhibiting prevalent synergistic interaction of cooperative adsorption on steel-rebar in the study were also highly effective at inhibiting concrete steel-rebar corrosion in their corrosive media of test immersions. These strongly support suitability of requisite concentration of $\text{C}_6\text{H}_{15}\text{NO}_3$ as additive admixture with sodium nitrite for inhibiting steel-rebar corrosion in concrete immersed in NaCl and H_2SO_4 corrosive media. This is potent with the additional advantage of reduced environmental effects due to lower NaNO_2 usage as corrosion inhibitor admixture in concrete designed for the aggressive service environments studied.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

- [1] F.-L. Fei, J. Hu, J.-X. Wei, Q.-J. Yu, and Z.-S. Chen, "Corrosion performance of steel reinforcement in simulated concrete pore solutions in the presence of imidazoline quaternary ammonium salt corrosion inhibitor," *Construction and Building Materials*, vol. 70, pp. 43–53, 2014.
- [2] J. O. Okeniyi, O. A. Omotosho, O. O. Ajayi, and C. A. Loto, "Effect of potassium-chromate and sodium-nitrite on concrete steel-rebar degradation in sulphate and saline media," *Construction and Building Materials*, vol. 50, pp. 448–456, 2014.
- [3] S. L. Rodríguez Reyna, J. M. Miranda Vidales, C. Gaona Tiburcio, L. Narváez Hernández, and L. S. Hernández, "State of corrosion of rebars embedded in mortar specimens after an electrochemical chloride removal," *Portugaliae Electrochimica Acta*, vol. 28, no. 3, pp. 153–164, 2010.
- [4] L. Sadowski, "Methodology for assessing the probability of corrosion in concrete structures on the basis of half-cell potential and concrete resistivity measurements," *The Scientific World Journal*, vol. 2013, Article ID 714501, 8 pages, 2013.
- [5] A. Królikowski and J. Kuziak, "Impedance study on calcium nitrite as a penetrating corrosion inhibitor for steel in concrete," *Electrochimica Acta*, vol. 56, no. 23, pp. 7845–7853, 2011.
- [6] L. Bertolini, "Steel corrosion and service life of reinforced concrete structures," *Structure and Infrastructure Engineering*, vol. 4, no. 2, pp. 123–137, 2008.
- [7] Z. Cao, M. Hibino, and H. Goda, "Effect of nitrite ions on steel corrosion induced by chloride or sulfate ions," *International Journal of Corrosion*, vol. 2013, Article ID 853730, 16 pages, 2013.
- [8] L. Adelaide, B. Richard, F. Ragueneau, and C. Cremona, "A simplified numerical approach of global behaviour of RC beams degraded by corrosion," *European Journal of Environmental and Civil Engineering*, vol. 16, no. 3–4, pp. 414–439, 2012.
- [9] N. Ukrainczyk, I. B. Pecur, and N. Bolf, "Evaluating rebar corrosion damage in RC structures exposed to marine environment using neural network," *Civil Engineering and Environmental Systems*, vol. 24, no. 1, pp. 15–32, 2007.
- [10] H. Gerengi, Y. Kocak, A. Jazdzewska, M. Kurtay, and H. Durgun, "Electrochemical investigations on the corrosion behaviour of reinforcing steel in diatomite- and zeolite-containing concrete exposed to sulphuric acid," *Construction and Building Materials*, vol. 49, pp. 471–477, 2013.
- [11] M. A. G. Tommaselli, N. A. Mariano, and S. E. Kuri, "Effectiveness of corrosion inhibitors in saturated calcium hydroxide solutions acidified by acid rain components," *Construction and Building Materials*, vol. 23, no. 1, pp. 328–333, 2009.
- [12] E. Hewayde, M. L. Nehdi, E. Allouche, and G. Nakhla, "Using concrete admixtures for sulphuric acid resistance," *Proceedings of the Institution of Civil Engineers—Construction Materials*, vol. 160, no. 1, pp. 25–35, 2007.
- [13] B. Richard, M. Quiertant, V. Bouteiller, L. Adelaide, J.-L. Tailhan, and C. Cremona, "Influence of accelerated corrosion on the reinforced cover concrete cracking behavior: experimental and numerical study," *European Journal of Environmental and Civil Engineering*, vol. 16, no. 3–4, pp. 450–459, 2012.
- [14] J. O. Okeniyi, I. O. Oladele, I. J. Ambrose et al., "Analysis of inhibition of concrete steel-rebar corrosion by $\text{Na}_2\text{Cr}_2\text{O}_7$ concentrations: implications for conflicting reports on inhibitor effectiveness," *Journal of Central South University*, vol. 20, no. 12, pp. 3697–3714, 2013.
- [15] M. B. Valcarce and M. Vázquez, "Carbon steel passivity examined in alkaline solutions: the effect of chloride and nitrite ions," *Electrochimica Acta*, vol. 53, no. 15, pp. 5007–5015, 2008.
- [16] T. A. Söylev and M. G. Richardson, "Corrosion inhibitors for steel in concrete: state-of-the-art report," *Construction and Building Materials*, vol. 22, no. 4, pp. 609–622, 2008.
- [17] A. M. Vaysburd and P. H. Emmons, "Corrosion inhibitors and other protective systems in concrete repair: concepts or misconceptions," *Cement and Concrete Composites*, vol. 26, no. 3, pp. 255–263, 2004.
- [18] M. Aoyama, S. Miyazato, and M. Kawamura, "Protection of steel corrosion in concrete members by the combination of galvanic anode and nitrite penetration," *International Journal of Corrosion*, vol. 2014, Article ID 618280, 11 pages, 2014.
- [19] J. O. Okeniyi, C. A. Loto, and A. P. I. Popoola, "*Rhizophora mangle* L. effects on steel-reinforced concrete in 0.5 M H_2SO_4 : implications for corrosion-degradation of wind-energy structures in industrial environments," *Energy Procedia*, vol. 50, pp. 429–436, 2014.
- [20] L. Feng, H. Yang, and F. Wang, "Experimental and theoretical studies for corrosion inhibition of carbon steel by imidazoline derivative in 5% NaCl saturated $\text{Ca}(\text{OH})_2$ solution," *Electrochimica Acta*, vol. 58, no. 1, pp. 427–436, 2011.
- [21] M. Ormellese, L. Lazzari, S. Goidanich, G. Fumagalli, and A. Brenna, "A study of organic substances as inhibitors for chloride-induced corrosion in concrete," *Corrosion Science*, vol. 51, no. 12, pp. 2959–2968, 2009.
- [22] I. Carrillo, B. Valdez, R. Zlatev, M. Stoycheva, M. Schorr, and M. Carrillo, "Corrosion inhibition of the galvanic couple copper-carbon steel in reverse osmosis water," *International Journal of Corrosion*, vol. 2011, Article ID 856415, 7 pages, 2011.
- [23] ASTM G109-99a, *Standard Test Method for Determining the Effects of Chemical Admixtures on the Corrosion of Embedded Steel Reinforcement in Concrete Exposed to Chloride Environments*, ASTM International, West Conshohocken, Pa, USA, 2004.
- [24] S. Muralidharan, V. Saraswathy, S. P. M. Nima, and N. Palaniswamy, "Evaluation of a composite corrosion inhibiting admixtures and its performance in Portland pozzolana cement," *Materials Chemistry and Physics*, vol. 86, no. 2–3, pp. 298–306, 2004.
- [25] A. K. Singh, S. K. Shukla, M. A. Quraishi, and E. E. Ebenso, "Investigation of adsorption characteristics of $\text{N,N}'$ -(methylimino)dimethylidene]di-2,4-xylylidine as corrosion inhibitor at mild steel/sulphuric acid interface," *Journal of the Taiwan Institute of Chemical Engineers*, vol. 43, no. 3, pp. 463–472, 2012.
- [26] F. H. Haynie, "Statistical treatment of data, data interpretation, and reliability," in *Corrosion Tests and Standards: Application and Interpretation*, R. Baboian, Ed., pp. 83–88, ASTM International, West Conshohocken, Pa, USA, 2nd edition, 2005.
- [27] A. S. Fouda, M. Abdallah, and A. A. Attia, "Inhibition of carbon steel corrosion by some cyanoacetohydrazide derivatives in HCL solution," *Chemical Engineering Communications*, vol. 197, no. 8, pp. 1091–1108, 2010.
- [28] Q. Qu, S. Jiang, W. Bai, and L. Li, "Effect of ethylenediamine tetraacetic acid disodium on the corrosion of cold rolled steel in the presence of benzotriazole in hydrochloric acid," *Electrochimica Acta*, vol. 52, no. 24, pp. 6811–6820, 2007.

- [29] ASTM International, *ASTM C192/192M-02. Standard Practice for Naking and Curing Concrete Test Specimens in the Laboratory*, ASTM International, West Conshohocken, Pa, USA, 2005.
- [30] X. Zhou, H. Yang, and F. Wang, "Investigation on the inhibition behavior of a pentaerythritol glycoside for carbon steel in 3.5% NaCl saturated $\text{Ca}(\text{OH})_2$ solution," *Corrosion Science*, vol. 54, no. 1, pp. 193–200, 2012.
- [31] M. M. Mennucci, E. P. Banczek, P. R. P. Rodrigues, and I. Costa, "Evaluation of benzotriazole as corrosion inhibitor for carbon steel in simulated pore solution," *Cement & Concrete Composites*, vol. 31, no. 6, pp. 418–424, 2009.
- [32] J. O. Okeniyi, O. A. Omotosho, O. O. Ajayi, O. O. James, and C. A. Loto, "Modelling the performance of sodium nitrite and aniline as inhibitors in the corrosion of steel-reinforced concrete," *Asian Journal of Applied Sciences*, vol. 5, no. 3, pp. 132–143, 2012.
- [33] O. A. Omotosho, C. A. Loto, O. O. Ajayi, and J. O. Okeniyi, "Aniline effect on concrete steel rebar degradation in saline and sulfate media," *Agricultural Engineering International: CIGR Journal*, vol. 13, no. 2, Manuscript no. 1830, 17 pages, 2011.
- [34] H.-W. Song and V. Saraswathy, "Corrosion monitoring of reinforced concrete structures: a review," *International Journal of Electrochemical Science*, vol. 2, no. 1, pp. 1–28, 2007.
- [35] S. G. Millard, D. Law, J. H. Bungey, and J. Cairns, "Environmental influences on linear polarisation corrosion rate measurement in reinforced concrete," *NDT & E International*, vol. 34, no. 6, pp. 409–417, 2001.
- [36] ASTM, "Standard test method for half-cell potentials of uncoated reinforcing steel in concrete," ASTM C876-91 R99, ASTM International, Conshohocken, Pa, USA, 2004.
- [37] G. E. Abdelaziz, A. M. K. Abdelalim, and Y. A. Fawzy, "Evaluation of the short and long-term efficiencies of electro-chemical chloride extraction," *Cement & Concrete Research*, vol. 39, no. 8, pp. 727–732, 2009.
- [38] S. Jäggi, H. Bohni, and B. Elsener, "Macrocell corrosion of steel in concrete-experimental and numerical modelling," in *Proceedings of the Eurocorr*, Riva di Garda, Italy, 2001.
- [39] W. J. McCarter and Ø. Vennesland, "Sensor systems for use in reinforced concrete structures," *Construction and Building Materials*, vol. 18, no. 6, pp. 351–358, 2004.
- [40] V. S. Sastri, *Green Corrosion Inhibitors: Theory and Practice*, John Wiley & Sons, Hoboken, NJ, USA, 2011.
- [41] ASTM International, "Standard guide for applying statistics to analysis of corrosion data," ASTM G16-95 R04, ASTM International, West Conshohocken, Pa, USA, 2005.
- [42] P. R. Roberge, "Statistical interpretation of corrosion test results," in *Corrosion: Fundamentals, Testing, and Protection*, S. D. Cramer and B. S. Covino Jr., Eds., vol. 13A of *ASM Handbook*, pp. 425–429, ASM International, Materials Park, Ohio, USA, 2003.
- [43] J. O. Okeniyi, " $\text{C}_{10}\text{H}_{18}\text{N}_2\text{Na}_2\text{O}_{10}$ inhibition and adsorption mechanism on concrete steel-reinforcement corrosion in corrosive environments," *Journal of the Association of Arab Universities for Basic and Applied Sciences*, 2014.
- [44] R.-D. Reiss and M. Thomas, *Statistical Analysis of Extreme Values*, Birkhäuser, Basel, Switzerland, 3rd edition, 2007.
- [45] J. O. Okeniyi and E. T. Okeniyi, "Implementation of Kolmogorov-Smirnov p-value computation in Visual Basic: implication for Microsoft Excel library function," *Journal of Statistical Computation and Simulation*, vol. 82, pp. 1727–1741, 2012.
- [46] D. Izquierdo, C. Alonso, C. Andrade, and M. Castellote, "Potentiostatic determination of chloride threshold values for rebar depassivation: experimental and statistical study," *Electrochimica Acta*, vol. 49, no. 17-18, pp. 2731–2739, 2004.
- [47] J. O. Okeniyi, C. A. Loto, and A. P. I. Popoola, "Electrochemical performance of *Anthocleista djalensis* on steel reinforcement corrosion in concrete immersed in saline/marine simulating environment," *Transactions of the Indian Institute of Metals*, vol. 67, no. 6, pp. 959–969, 2014.
- [48] J. O. Okeniyi, S. O. Okpala, O. M. Omoniyi, I. O. Oladele, C. A. Loto, and A. P. I. Popoola, "Methods of ASTM G16 and conflicts in corrosion test data: case study of NaNO_2 effectiveness on steel-rebar corrosion," *Canadian Journal of Pure and Applied Sciences*, vol. 7, no. 13, pp. 2589–2597, 2013.
- [49] N. S. Berke and M. C. Hicks, "Predicting long-term durability of steel reinforced concrete with calcium nitrite corrosion inhibitor," *Cement & Concrete Composites*, vol. 26, no. 3, pp. 191–198, 2004.
- [50] J. H. Bungey, S. G. Millard, and M. G. Grantham, *Testing of Concrete in Structures*, Taylor & Francis, New York, NY, USA, 4th edition, 2006.