



## **Inhibition Effect of Zinc Oxide on the Electrochemical Corrosion of Mild Steel Reinforced Concrete in 0.2M H<sub>2</sub>SO<sub>4</sub>**

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*Received 15 Dec 2015, Revised 28 Jan 2016, Accepted 2 Feb 2016*

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### **Abstract**

The inhibition effect of zinc oxide on the corrosion behaviour of embedded mild steel rebar in concrete has been investigated by potential measurement, such as pH and gravimetric (weight loss) methods. The results were further analysed using the two-factor ANOVA test. The experiments were performed using zinc oxide as an organic inhibitor in 0.2M H<sub>2</sub>SO<sub>4</sub> solution. Inhibitor concentrations of 25, 50 75, and 100% were prepared from 200g of ZnO powder, with distilled water. Potential measurements were taken using a digital voltmeter and a copper-copper sulphate electrode as the reference electrode. Compressive strength of each block sample was determined after the experiments. Weight loss values were obtained from the gravimetric method and the inhibitor efficiency was computed from the corrosion rate of each of the tested samples. Results showed that varied concentration of ZnO inhibitor and the test exposure time significantly affect both the corrosion potential of embedded steel rebar in concrete and the pH of the medium. The outcome of the ANOVA test confirmed the results at 95% confidence, and further showed that concentration of ZnO had greater effect on potential and pH measurements. Zinc Oxide inhibitor performed effectively as an inhibition agent to the corrosion of the embedded steel rebar in concrete at 25% and 50% concentrations in 0.2M H<sub>2</sub>SO<sub>4</sub> test medium. The highest inhibition efficiency was achieved at 25% concentration, the lowest inhibitor concentration used.

*Keywords:* Corrosion; Inhibition; Zinc Oxide; Reinforced Concrete; sulphuric acid

### **1.Introduction**

Reinforced concrete steel structures have been found to be exposed during their lifetimes to environmental stress such as corrosion and expansive aggregate reactions which degrades the concrete and sometimes the steel reinforcement. Furthermore, corrosion also produces pits or holes in the surface of reinforcing steel, reducing strength capacity as a result of the reduced cross-sectional area [1]. It is worth noting that researchers and engineers are continuously in search of cost-effective means for preventing and controlling the corrosion of steel reinforcement in concrete [2].

Corrosion of steel reinforcing bars is a problem in many structures such as bridges, industrial buildings, houses, high scrapers, etc. As a result, the structures fail and result into loss of lives and depletion of resources. However, corrosion in concrete can be prevented using anodic protection, cathodic protection, rebar coating or inhibitors. In this work, the effect of various predetermined constant concentration of an inhibitor on the electrochemical corrosion of mild steel reinforcement in concrete in environments (such as sulphuric acid environments) is emphasized.

Amongst inhibitors widely employed to minimize corrosion of many metallic structures in various environments are nitrates, benzoates, phosphates, chromates and borates [3]. A number of reports have dealt with the use of nitrite-based inhibitors. Studies have suggested that in order to protect steel from corrosion due to carbonation,

nitrite at a dosage of 3% should be used. Although Ca-nitrite is known to be a good inhibitor, the dosage at which it should be used for effectiveness depends on the concentration [4]. A recent work on the use of sodium nitrite on the corrosion of concrete exposed to sea water revealed that corrosion actually increases with this inhibitor in cracked concrete [4]. The inhibitive action of  $\text{Na}_2\text{PO}_3\text{F}$  has also been reported and it appeared to act as an anodic inhibitor [5]. Furthermore, mortars prepared with 0.1-0.2% Zinc oxide (ZnO) are reported to inhibit corrosion on exposure to sea water or 3% chloride solution. In this situation ZnO also acted as an anodic inhibitor. Other studies which have been carried out using ZnO inhibitor include: a comparison of the action of ZnO and  $\text{Ca}(\text{NO}_2)_2$  as rebar corrosion inhibitors [6]; to mention but a few. It is needful to say that the efficiency and usefulness of a corrosion inhibitor under one set of circumstances often does not imply the same for another set of circumstances.

Therefore, this study aims at investigating the effect of zinc oxide inhibitor as an inorganic corrosion inhibitor on the corrosion of mild steel embedded in concrete by electrochemical and gravimetric methods and by further statistically analysing the results using Analysis of Variance (ANOVA) test. In a study [7], it was revealed that the addition of ZnO in concrete manufacturing improves the processing time and the resistance of concrete against water. Zinc oxide is known [8, 9] to have high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties. Consequently, it is added into materials and products including plastics, ceramics, glass, cement, rubber, lubricants, paints, ointments, adhesive, sealants, pigments, foods, batteries, ferrites, and fire retardants, to mention but a few. Zinc oxide has been variously associated with corrosion inhibition in aqueous and acidic environments. This work was carried out using ZnO inhibitor in 0.2M  $\text{H}_2\text{SO}_4$ . The addition of sulphuric acid accelerates the corrosion of the embedded steel by providing increased sulphate ( $\text{SO}_4$ ) ions in the solution and around the reinforcing steel rebar. Fine particles of ZnO are expected to exhibit electrochemical activity of strong surface coverage to the embedded mild steel surface and thus enhancing its corrosion resistance in corrosive environments.

## **2. Methods**

### *2.1 Preparation of ZnO solution*

200g of zinc oxide (ZnO) was obtained. From this, four different percentage concentrations of 25, 50, 75 and 100% ZnO solutions were prepared using distilled water.

### *2.2 Preparation of mild steel rebar*

The steel rebar with chemical composition of: 0.3% C, 0.25 % Si, 1.5% Mn, 0.04% P, 0.64% S, 0.25% Cu, 0.1% Cr, 0.11% Ni, and the rest Fe, was used for the reinforcement. The rebar was cut into several pieces each with a length of 120mm and 12mm diameter. The weight of each piece was taken and recorded. An abrasive paper was used to remove any mill scale and rust stains on the steel specimens before being cleaned with ethanol. Ideally, the prepared steel rods are to be kept in a desiccator but for the purpose of this experiment, they were not because the rods were used just after cleaning.

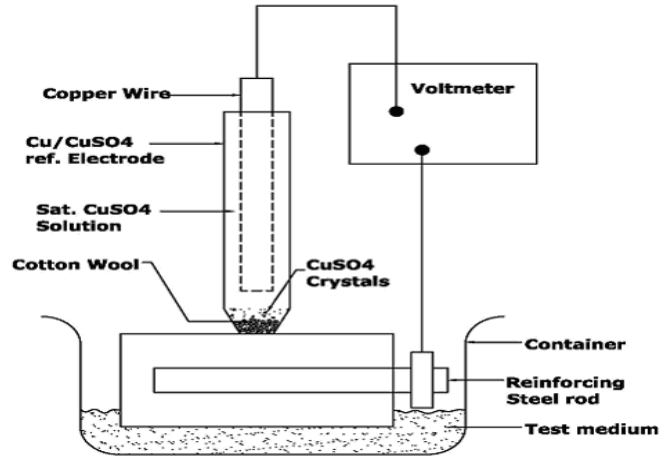
### *2.3 Preparation of concrete and the test environment*

The concrete blocks used for the experiment were made of Portland cement, Sand, Gravel and Water. They were prepared in the ratio 1:2:3 (C: S: G) – cement, sand, gravel. Each concrete block, embedded with a reinforcing steel rebar, was 100 mm long, 100 mm wide and 120 mm thick. The water cement (W/C) ratio was 0.44. Four different concentrations of 25%, 50%, 75% and 100% of the extract were used, along with the control experiment. Each steel rebar was placed symmetrically across the length of the block in which it was embedded and had a concrete cover of 50 mm (Fig.1). Only about 90 mm was embedded in each concrete block. The remaining 30mm protruded at one end of the concrete block, and was coated to prevent atmospheric corrosion. This part was also used for electrical connection. The test medium used for the investigation was 0.2M  $\text{H}_2\text{SO}_4$  solution of AnalaR grade.

0.2M Sulphuric acid was prepared by diluting 110ml of concentrated Sulphuric acid in 9,890ml of distilled water which was used as corrosion medium for reinforced concrete samples with and without inhibitor.

**2.4 Potential and pH measurements**

The procedure used followed the previously reported experimental work [10-12]. Potential measurements were taken using a digital voltmeter connected to a copper-copper sulphate electrode as shown in Fig.1. The readings were taken at three different points on each concrete block directly over the embedded steel rebar.



**Figure1:** Schematic representation of experimental set up

The average of the three readings was found and computed as the potential readings for the embedded rebar in 3 –day intervals. All the experiments were performed at ambient temperature and under free corrosion potential. The pH of the media was measured by placing a small amount of the medium in the cup of the pH meter, with the probes positioned in the sample solution.

**2.5. Compressive Strengths**

At the completion of the experimental period, compressive strength test was carried out on each block sample after weighing, with the aid of a compressive strength testing machine.

**2.6. Weight loss measurements**

Weight loss measurements were taken as described by [13]. The coupons were retrieved from their corrodent at intervals of 30 minutes progressively for 150 minutes, scrubbed with bristle brush in distilled water and then immersed in ethanol for 2 minutes to remove the corrosion product, dried in acetone and weighed. The weight loss was computed as the difference between the weight at a given time and the initial weight of the test coupon. Corrosion rate and inhibition efficiencies were calculated with the following equations [14]:

$$\%I.E = \left[1 - \frac{CR_{inh}}{CR_{BL}}\right] \times 100 \dots\dots\dots(1)$$

$$CR(= gh^{-1}cm^{-2}) = \Delta W / AT \dots\dots\dots(2)$$

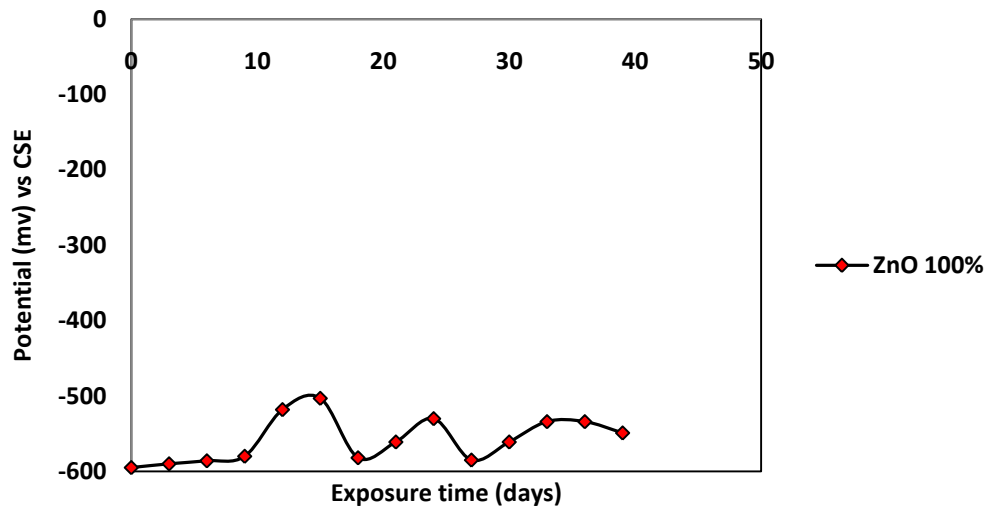
**3. Results and Discussion**

Where  $CR_{inh}$  and  $CR_{BL}$  are the corrosion rate of mild steel in presence and absence of the inhibitor, respectively.  $A$  is area of coupon in  $cm^2$ ,  $T$  is the period of immersion in hours and  $\Delta W = W_1 - W_2$ ; where  $W_1$  is the initial weight of mild steel and  $W_2$  is its final weight.

**3.1 Potential Measurement**

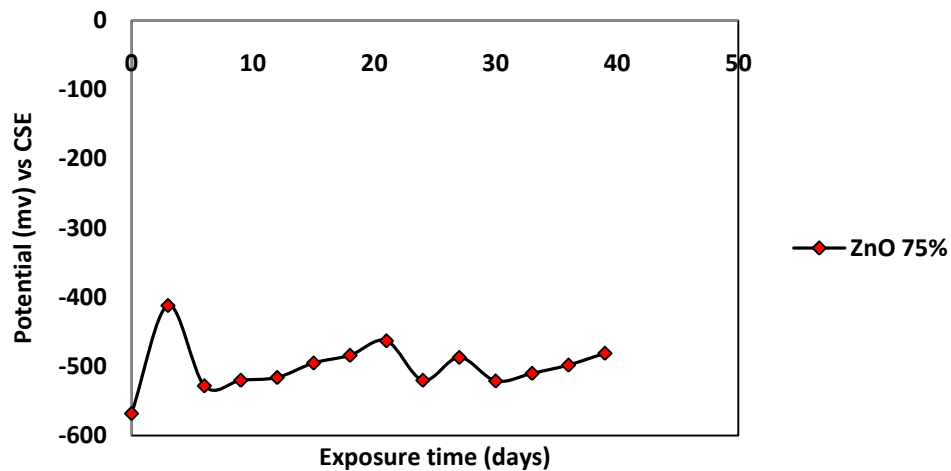
For the four different concentrations of 25%, 50%, 75% and 100% ZnO mixed with the concrete test samples, the results obtained are presented in the curves of Figs. 2 – 6. At the concentration of 100%, Fig. 2, there were active corrosion reactions for most part of the experiment. Although, fluctuations were observed beginning from

the 11<sup>th</sup> day, the corrosion reactions remained in active state that ranged between -503 and -595mV. Obviously, at this concentration the extract could not be described as being protective.



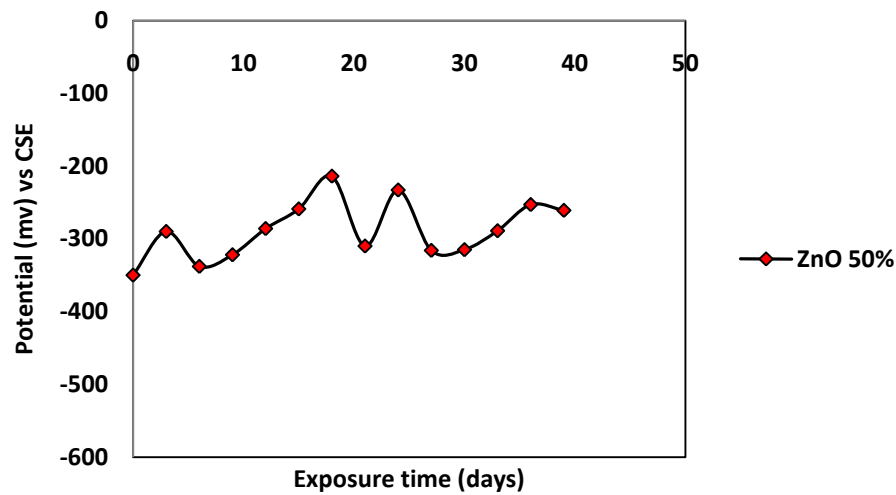
**Figure 2:** Variation of potential with time for mild steel reinforcement in concrete mixed with 100% concentration ZnO inhibitor and partially immersed in 0.2M H<sub>2</sub>SO<sub>4</sub> solution.

At the extract concentration of 75% (Fig. 3), a fluctuating and passive corrosion reaction that ranged between -568 and -412mv was achieved. This indicates passive corrosion reactions which could be described as strong since the values were not apparently close to the active corrosion reactions. Nevertheless, in comparison, the extract concentration at 75% showed better corrosion inhibition performance than that of 100% ZnO

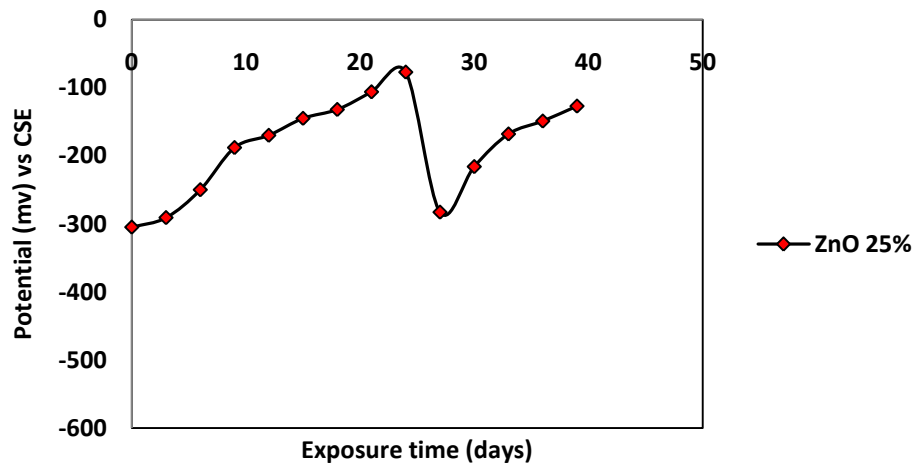


**Figure 3:** Variation of potential with time for mild steel reinforcement in concrete mixed with 75% Concentration ZnO inhibitor and partially immersed in 0.2M H<sub>2</sub>SO<sub>4</sub> solution.

At the extract concentration of 50%, fluctuating but passive corrosion reactions were achieved throughout the experiment for a potential range of -350 to -214mV. A comparison of the inhibitor performance at 50% concentration with 75 and 100% concentrations showed more passive corrosion reactions, hence, a lesser tendency towards active corrosion. As a result, at 50% concentration, the inhibitor could be described as more protective.



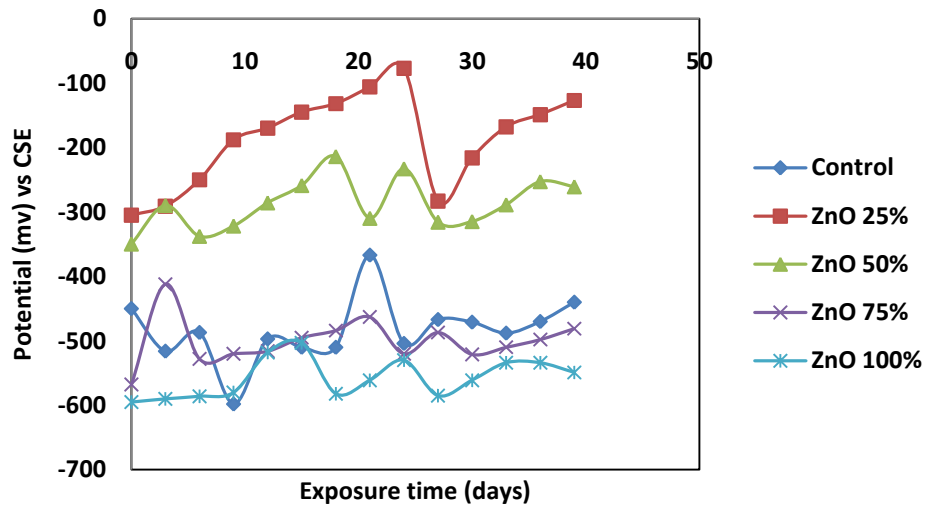
**Figure 4:** Variation of potential with time for mild steel reinforcement in concrete mixed with 50% Concentration ZnO inhibitor and partially immersed in 0.2M H<sub>2</sub>SO<sub>4</sub>solution.



**Figure 5:** Variation of potential with time for mild steel reinforcement in concrete mixed with 25% concentration ZnO inhibitor.

For ZnO concentration at 25%, passive corrosion reactions was achieved from -305mV on the first day to -127mV on the last day of the experiment. Increasingly passive reactions were subsequently maintained until the end of the experiment. This concentration gave good corrosion inhibition performance and in comparison with 75% and 50% concentrations, the optimum value for the extract inhibition performance was obtained with 25% concentration.

Fig. 6 provides the overall zinc oxide corrosion inhibition performance profile for the mild steel embedded in concrete and partially immersed in 0.2M H<sub>2</sub>SO<sub>4</sub> test medium. Here it could be confirmed again that the best inhibition performance in this work is with the extract with 25% concentration. In addition, 50%ZnO concentration performed better than the control experiment in which there was no inhibitor addition. The general observation/inference here is that ZnO inhibitor could provide reasonable measure of corrosion inhibition of mild steel in concrete in the sulphuric acid environment within the all other experimental conditions used, particularly at 25% concentration.



**Figure 6:** Variation of potential with time for mild steel reinforcement in concrete mixed with 25, 50, 75 and 100% concentrations ZnO inhibitor and partially immersed in 0.2M H<sub>2</sub>SO<sub>4</sub> solution.

### 3.2 Statistical Analysis

The scatter plots show a fluctuating decrease and increase in potential with respect to time; average stability was attained from the 30th day. It can also be deduced that 25%ZnO and 50%ZnO exhibited optimal performance while 75%ZnO and 100%ZnO showed the least performance in corrosion inhibition.

Two-factor single level experiment ANOVA test (F-test) was used to evaluate the separate and combined effects of ZnO concentration and exposure time on the corrosion potential of the mild steel reinforcement in 0.2M H<sub>2</sub>SO<sub>4</sub> solution. The F-test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples. The Sum of squares was obtained with equations 3-5 [15].

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \dots\dots\dots(3)$$

Sum of Squares among rows (concentration of VA):

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \dots\dots\dots(4)$$

Total Sum of Squares:

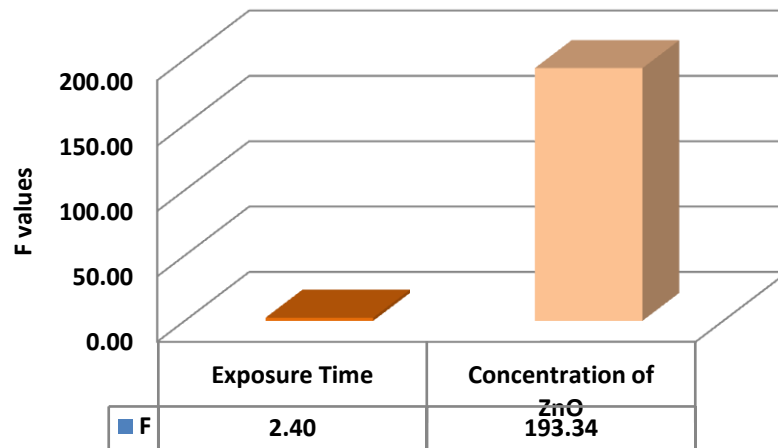
$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \dots\dots\dots(5)$$

The calculation using the ANOVA test is tabulated (Table 1) as shown.

On the basis of the results in Table 1, it can be concluded with 95% confidence that varied concentration of ZnO inhibitor and exposure time significantly affects the corrosion potential of the test medium (Fig.7). The effect of ZnO concentration was highly significant.

**Table 1:** Summary of ANOVA analysis for potential measurements

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	56441.44	13	4341.65	2.40	1.91
Concentration of ZnO	1401282.49	4	350320.62	193.34	2.55
Residual	94219.91	52	1811.92		
Total	1551943.84	69			



**Figure 7:** Influence of exposure time and ZnO concentration on corrosion potential

### 3.3. pH Measurements

The results obtained for the different concentrations (25, 50, 75 and 100%) of ZnO inhibitor are presented in Table 2. The reinforced concrete blocks recorded pH values which its acidity decreased from 3.07 from the beginning of the experiment to 2.44 at the end in a period of 39 days. The trend was not the same for all the different per cent concentrations of inhibitor addition. For ZnO at 25% concentration addition, the acidity increased from 1.54 – 1.78. At 50% concentration, it increased from 1.57 – 1.94; at 75% concentration, it increased from 1.52 – 1.75; and at 100%, from 1.54 – 1.93. This increase in acidity could be due to the reactions between the concrete constituents, ZnO, the H<sub>2</sub>SO<sub>4</sub> test environment and the reactions at the steel/environment interface for the steel reinforced concrete blocks.

Though minimal, one clear correlation of this increasing acidity value with potential readings was that with the increasing acidity, there was a tendency towards increasing passive potential values, that is, more positive values of potentials, though sometimes with random fluctuations, particularly with some of the concentrations of ZnO inhibitor.

**Table 2:** pH readings of admixed ZnO inhibitor with 0.2M H<sub>2</sub>SO<sub>4</sub> solution

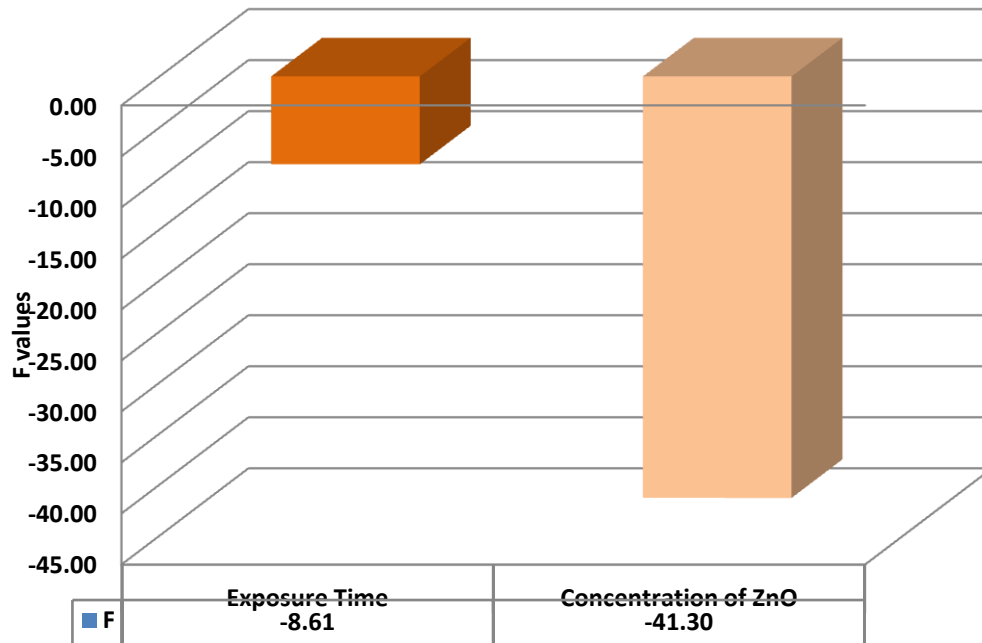
Day	Control	ZnO 100%	ZnO 75%	ZnO 50%	ZnO 25%
0	3.07	1.54	1.52	1.57	1.54
3	1.95	1.80	1.85	1.95	2.10
6	3.24	2.29	1.84	2.29	2.09
9	2.52	2.27	2.09	2.00	1.88
12	1.93	1.72	1.67	1.86	1.65
15	2.35	1.83	1.82	1.98	1.71
18	2.12	2	1.79	2.27	1.87
21	2.33	1.77	1.75	2.35	1.55
24	1.98	1.92	1.98	1.64	1.66
27	2.45	1.66	1.67	1.65	1.66
30	1.57	1.79	1.78	1.79	1.82
33	1.95	1.77	1.79	1.87	1.9
36	2.19	1.68	1.79	1.7	1.57
39	2.44	1.93	1.75	1.94	1.78

The scatter plot of pH values against exposure time show an almost linear relationship between the variables at all ZnO concentration levels. This shows that at varied concentration of ZnO inhibitor in solution, there are fluctuations in pH as exposure time varies. The effect of these variables on the pH of the solution was further confirmed with the ANOVA test using equations (3) – (5) as stated earlier. The results are displayed in Table 3.

**Table 3:** Summary of ANOVA analysis for pH measurements

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	1.70	13	0.13	-8.61	1.91
Concentration of ZnO	2.51	4	0.63	-41.30	2.55
Residual	-0.79	52	-0.02		
Total	3.42	69			

On the basis of the results shown in Table 3, it can be concluded with 95% confidence that the concentration of Zinc oxide and exposure time has no significant effect on the pH of the test environment (Fig. 8).



**Figure 8:** Influence of exposure time and ZnO concentration on pH of test environment

### 3.3 Compressive Strengths of Test Samples

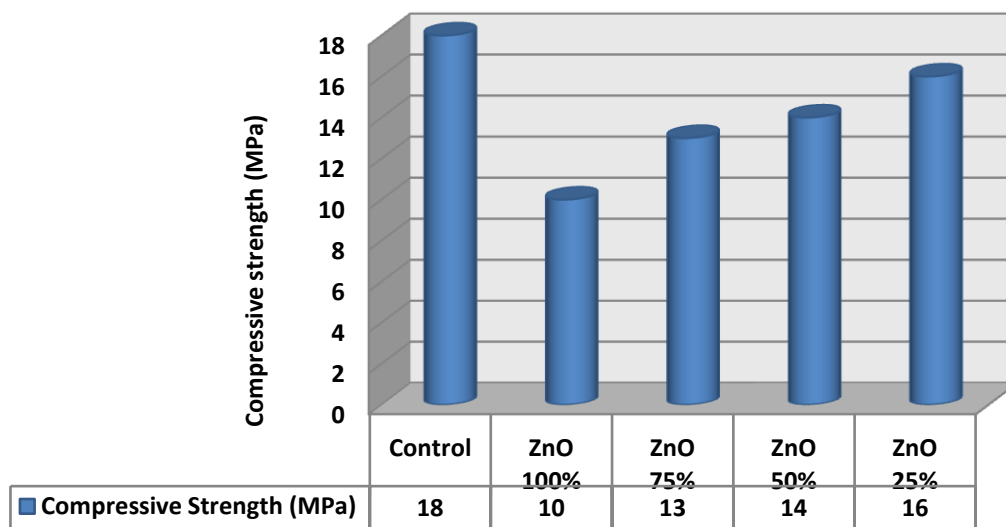
The compressive strength of the samples measured after the corrosion tests are shown in Table 4.

**Table 4:** Compressive strengths of test samples

Concentration	Compressive Strength (MPa)
Control	18
ZnO 100%	10
ZnO 75%	13
ZnO 50%	14
ZnO 25%	16



It was necessary to investigate the effect of inhibitor concentration on compressive strength of concrete due to its relative importance in concrete applications. The highest compressive strength of 15MPa was obtained at 25% ZnO inhibitor concentration. Lower concentration of Zinc Oxide yielded higher compressive strength (Fig. 9). This signifies that higher ZnO concentration has a negative effect on the compressive strengths of the samples in 0.2M H<sub>2</sub>SO<sub>4</sub> environment. Similarly, potential measurements showed higher ZnO concentrations resulting in more active corrosion reactions.



**Figure 9:** Influence of concentration of ZnO inhibitor on compressive strength of test samples

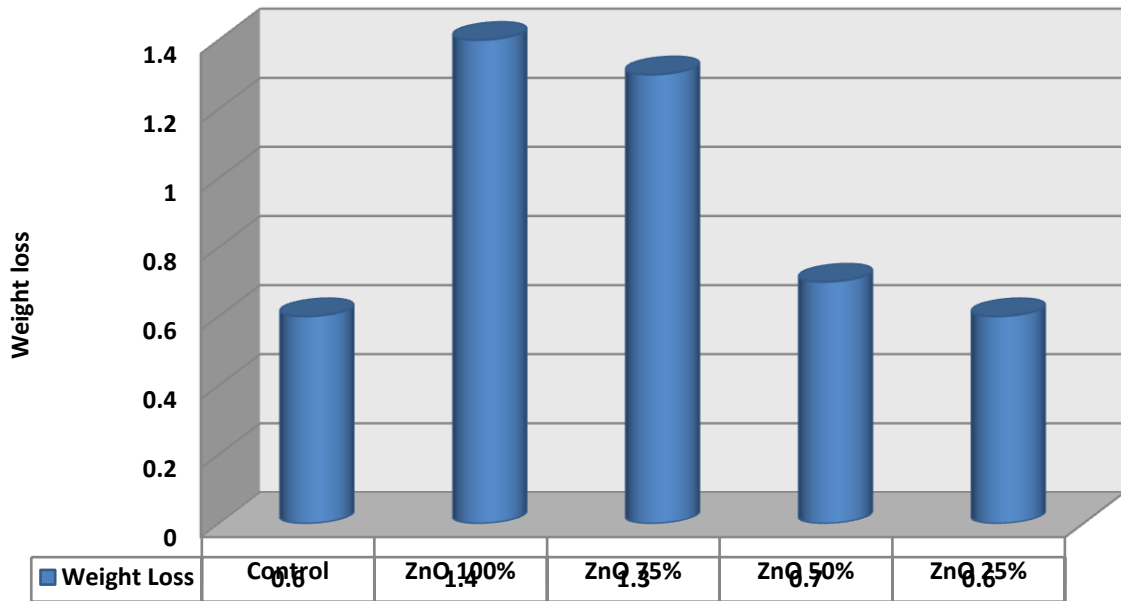
### 3.4 Weight Loss and Inhibitor Efficiency

The table of results for the weight loss, corrosion rate and the inhibitor efficiency is presented in Table 5. The results presented in Table 5 bear a very close relationship with the results of potential measurement. The inhibitor at 25% concentration had the lowest weight loss (0.6g); a corrosion rate of  $27.0 \times 10^{-5}$  mm/yr and with an inhibitor efficiency of 41.02%. This value was followed with 50% ZnO concentration with a weight loss value of 0.7g; a corrosion rate of  $29.7 \times 10^{-5}$  mm/yr and an inhibitor efficiency of 35.23%. The 75 and 100% inhibitor concentrations showed relatively very low values of inhibitor efficiency. The lowest inhibitor efficiency of -37.63 was recorded with the 100% ZnO concentration. This has a tendency of accelerating corrosion instead of inhibiting it. This phenomenon is a characteristic of inhibitor when the appropriate concentration value is not used.

The variation of weight loss based ZnO concentration is shown in Fig.10.

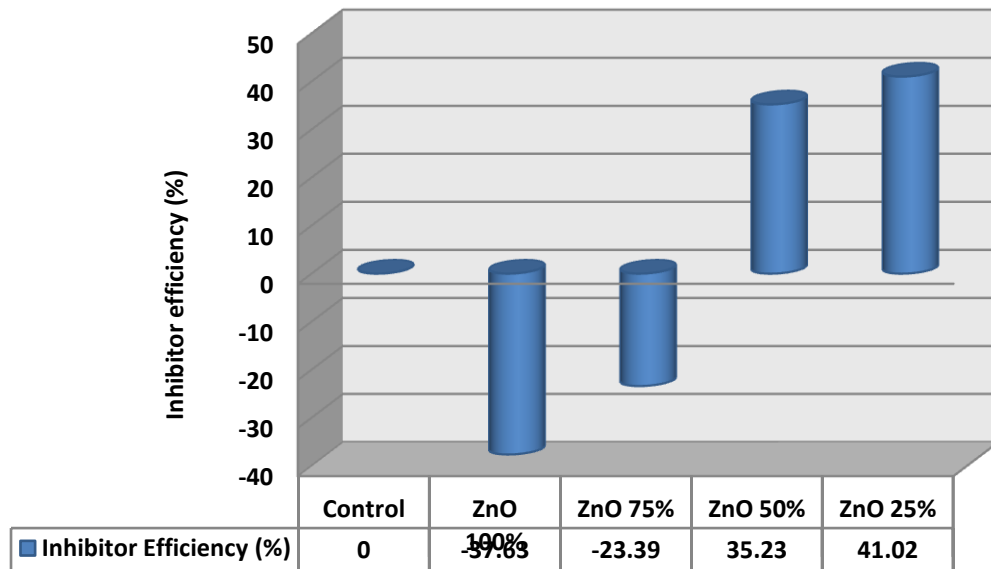
**Table 5:** Weight loss and inhibition efficiency of mild steel in mixed ZnO with 0.2M H<sub>2</sub>SO<sub>4</sub> medium

Inhibitor Concentration	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	Inhibitor Efficiency (%)
Control	110	109.4	0.6	0.000275	
ZnO 100%	112	110.6	1.4	0.000630	-37.63
ZnO 75%	116	114.7	1.3	0.000565	-23.39
ZnO 50%	119	118.3	0.7	0.000297	35.23
ZnO 25%	112	111.4	0.6	0.000270	41.02



**Figure10:** Influence of concentration of ZnO on Weight loss of samples

The least weight loss, 0.6, was obtained at ZnO concentration of 25%. Since the weight loss of the control test was 0.6, this signifies that corrosion inhibition was more effective with lower concentration of Zinc Oxide inhibitor whilst higher concentration of the same resulted into accelerated corrosion rate.



**Figure11:** Influence of concentration of Zinc Oxide Inhibitor Efficiency

Fig. 11 shows clearly the concentrations of Zinc Oxide with the highest and lowest inhibitor efficiencies. The highest efficiency is 41.02% obtainable with 25% ZnO while the lowest efficiency is -37.63% obtainable with 100% ZnO.

In summary, the experiment was performed using zinc oxide as inhibitor in the concrete and 0.2M H<sub>2</sub>SO<sub>4</sub> solution test environment. Sulphuric acid is a very strong acid and the ion, SO<sub>4</sub><sup>2-</sup>, has a very strong tendency to

cause severe corrosion/degradation of mild steel even in the concrete environment. There was acceleration of corrosion reactions, on addition of this acid, of the embedded reinforcing steel rebar. The  $\text{SO}_4$  ions of the acid broke the passivity of the concrete test environment. The zinc oxide behaved characteristically like effective chemical inhibitor, acting as anodic inhibitor, in providing a measure of inhibition while maintaining strong concrete compressive strength. The inhibitor maintained appreciable measure of inhibitive effectiveness.

## Conclusions

From the experimental results obtained and the analysis of the same, the following conclusions can be drawn:

1. The severity of corrosion on concrete is increased in sulphuric acid environments.
2. Zinc oxide (ZnO) inhibitor was effective as a chemical inhibitor to the corrosion of the embedded steel rebar in concrete at 25% and 50% concentrations in 0.2M  $\text{H}_2\text{SO}_4$  test medium.
3. The higher the concentration of ZnO used, the less effective was the corrosion inhibition performance achieved in the tests.
4. The concrete compressive strength was appreciably maintained by the use of zinc oxide within the percentage concentrations used for the corrosion inhibition though slightly weakened with increase in ZnO concentration.
5. At 95 percent confidence level, ANOVA test showed that varied concentration of zinc oxide inhibitor and exposure time significantly affect the corrosion potential of embedded steel rebar in concrete.

**Acknowledgement**-The authors acknowledge the laboratory investigation contribution of Miss Oluwanipinni O. Oladoyinbo, and also, the Department of Mechanical Engineering, Covenant University, Ota for the provision of research facilities for this work.

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