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Effect of zinc oxide on the corrosion inhibition of mild steel embedded in concrete in 3.5% NaCl solution

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ABSTRACT

The effect of zinc oxide on the corrosion inhibition of mild steel embedded in concrete in 3.5% sodium chloride solution was investigated using potential measurement, pH and gravimetric methods. The experiments were performed using zinc oxide as the inhibitor in 3.5% NaCl solution. From 200g of ZnO powder, and using distilled water, 25, 50, 75, and 100% zinc oxide inhibitor concentrations were prepared. A digital voltmeter was used to record potential measurements. A copper-copper sulphate electrode was used as the reference electrode. After the experiments, compressive strength of each block sample was determined. Weight loss values were obtained from the weight loss method and the inhibitor efficiency was calculated from the corrosion rate of each of the tested samples. The results were further analysed using the two-factor ANOVA test. Results showed varied concentrations of ZnO inhibitor and the test exposure time significantly affected the corrosion potential of the embedded steel rebar. The inhibitor gave appreciable corrosion inhibition performance of the embedded steel rebar at 100 and 75% concentrations with the weight loss of 600 and 800mg and corrosion rates of 0.000270 and 0.000357mm/yr respectively. An inhibitor efficiency of 41.02% was achieved at 100% ZnO concentration. ANOVA analysis confirmed the results at 95% confidence.

Keywords: corrosion; inhibition; zinc oxide; reinforced concrete; sodium chloride

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INTRODUCTION

Apparently, concrete steel reinforcement corrosion seems to be a significant cause of premature failure of reinforced concrete structure worldwide. Steel reinforcement in concrete do corrode and usually results in the formation of rust which could result in appreciable increase in the volume of the original steel and thus manifests in adverse mechanical properties deterioration and performance. Usually, steel in concrete is in passive condition. At times, however, steel reinforced concrete is used in severe environments such as in the presence of sea water, sewage environment and / or deicing salts among others. The ingress of chloride, sulphate or carbonate ions into the concrete, do cause the passive protecting layer of the steel to be disrupted, resulting in corrosion. This corroding phenomenon had been reported [1, 2]

Corrosion in concrete can be prevented using cathodic protection, anodic protection, inhibitors or rebar coating. Various authors have investigated and reported the effective use of inorganic chemical compounds as inhibitors for the steel reinforcement in concrete. Chemicals such as $NaNO_2$, $LiNO_3$, Li_2CrO_4, Li_2MoO_4, Na_2MoO_4 and $Ca(NO_2)_2$

had been used by these researchers as inorganic inhibitors of mild steel in different corrosion test environments such as in steel reinforcement in concrete in chloride solutions.

This study aims at investigating the effect of zinc oxide as corrosion inhibitor of mild steel embedded in concrete by electrochemical and gravimetric methods. Zinc oxide is known to possess some very good chemical characteristics such as improvement in the manufacturing processing time and the resistance of concrete against water [8] possession of high refractive index, high thermal conductivity, binding, antibacterial and UV-protection properties [9]. Hence the chemical compound has been of multifarious beneficial industrial use. A good result in this work could be of economic and technological benefits.

MATERIALS AND METHODS

2.1 Preparation of ZnO solution

A quantity of 200g of zinc oxide (ZnO) of AnalaR grade was obtained. Four different percentage concentrations of 25, 50, 75 and 100 ZnO solutions were respectively prepared using distilled water.

2.2 Preparation of mild steel rebar

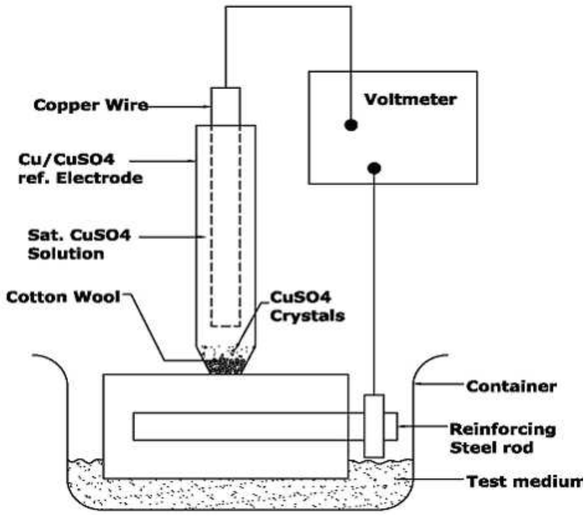
The steel rebar used for the reinforcement had chemical composition of: 0.3%C, 0.25 %Si, 1.5%Mn, 0.04%P, 0.64%S, 0.25%Cu, 0.1%Cr, 0.11%Ni, and the rest Fe. The rebar was cut into several pieces, each with a length of 120mm and 12mm diameter. The weight of each piece was taken and recorded. An abrasive paper was used to remove any mill scale and rust stains on the steel specimens before being cleaned with ethanol. The prepared steel rods were embedded in the concrete mixture just after cleaning.

2.3 Preparation of concrete and the test environment

A locally obtained Portland cement used in this work consisted of the following composition: CaO (64%), SiO_2 (23%), Al_2O_3 (4.5%), Fe_2O_3 (2%), and sulphate (3.5%). The test concrete blocks were made of Portland cement, Sand, Gravel and Water. The blocks were prepared in the ratio 1:2:4 (C: S: G) – cement, sand, gravel. Each concrete block was 100 mm long, 100 mm wide and 120 mm thick and was embedded with a reinforcing steel rebar. The water cement (W/C) ratio was 0.44. Along with the control experiment, four different concentrations of 25, 50, 75 and 100% respectively of the ZnO were used. 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 as presented in Fig.1. About 90 mm of the rebar was embedded in each concrete block; the remaining 30mm protruded at one end of the concrete block. The protruded portion of the rebar was coated to prevent atmospheric corrosion and a part of this portion was used for electrical connection. A test medium of 3.5% NaCl solution was used for the investigation. The 3.5% NaCl solution was prepared by diluting 35 grams of NaCl in 10,000ml of distilled water. This was used as corrosion test medium for the reinforced concrete samples - with inhibitors and for those without inhibitor**.**

2.4 Potential and pH measurements

The procedure here also followed the previously reported experimental work [10 - 11]. As shown in Fig.1, each concrete block sample was partially immersed in the 3.5% chloride solution test medium. The potential voltages were recorded with a digital voltmeter by connecting to a copper-copper sulphate electrode used as the reference electrode. The readings were taken at three different points on each concrete block directly over the embedded steel rebar. The average of the three readings was computed as the potential reading for the embedded rebar in 3 –day intervals. All the experiments were performed at free corrosion potential and at ambient temperature.



(3.5 % NaCl solution)
Fig. 1: Schematic representation of experimental set up

A pH meter was used to measure the pH of the test media by placing the probe connected to the meter in a small amount of each of the test media in a cup with the sample solution.

2.5 Compressive Strengths
At the completion of the experimental period, compressive strength test was performed with the use of a compressive strength testing machine.

2.6 Weight- loss measurements
The rebar pieces were first weighed in turns before embedding in concrete. After the corrosion and compression tests each of the rebar was again weighed after cleaning. The weight loss was computed as the difference between the weight of each rebar at the end of the experiment (final weight) and the initial weight of the test coupon. Corrosion rates and inhibition efficiencies were calculated with the following equations:

The percentage inhibitor efficiency, P, for each of the corrosion rate results obtained for every experimental reading was calculated from the relationship:

P =100[1 – W2/W1] ………………………………………………………1
Where, W1 and W2 are, respectively the corrosion rates in the absence and presence of the predetermined concentration of the inhibitor.

The corrosion rate was calculated from:

Corrosion rate - CR (mmpy) = Weight loss (W) x 87.60/ATD …………2

Where A = area of test specimen in cm^2, T is the period of immersion in hours, and D is the metal density. CR mm/yr (mmpy)

RESULTS AND DISCUSSION

3.1 Potential Measurement
Presented in the curves of Figs. 2 – 6 are the results obtained for the four different concentrations of 25, 50, 75 and 100% ZnO respectively, mixed with the concrete test samples. At the concentration of 100%, Fig. 2, for the first nine days, decreasing passive corrosion reactions were observed. Subsequently, the corrosion reactions remained at the potential voltage range of -436 and -326mV from the 9^{th} day until the 21^{st} day. A sudden spike towards the more passive state though temporary, was observed on the 24^{th} day. Subsequently, the corrosion reactions remained

passive in the potential voltage range of -282 and -408mV until the end of the experiment. Obviously, a comparison of the corrosion reactions at this concentration of ZnO with the control test shows that inhibition was achieved to a great extent.

At the extract concentration of 75% (Fig. 3), a fluctuating and passive corrosion reaction that ranged between -356 and -485mV was achieved in the first 9 days. This indicates passive corrosion reactions which could be described as weak since the values were apparently close to the active corrosion reactions.

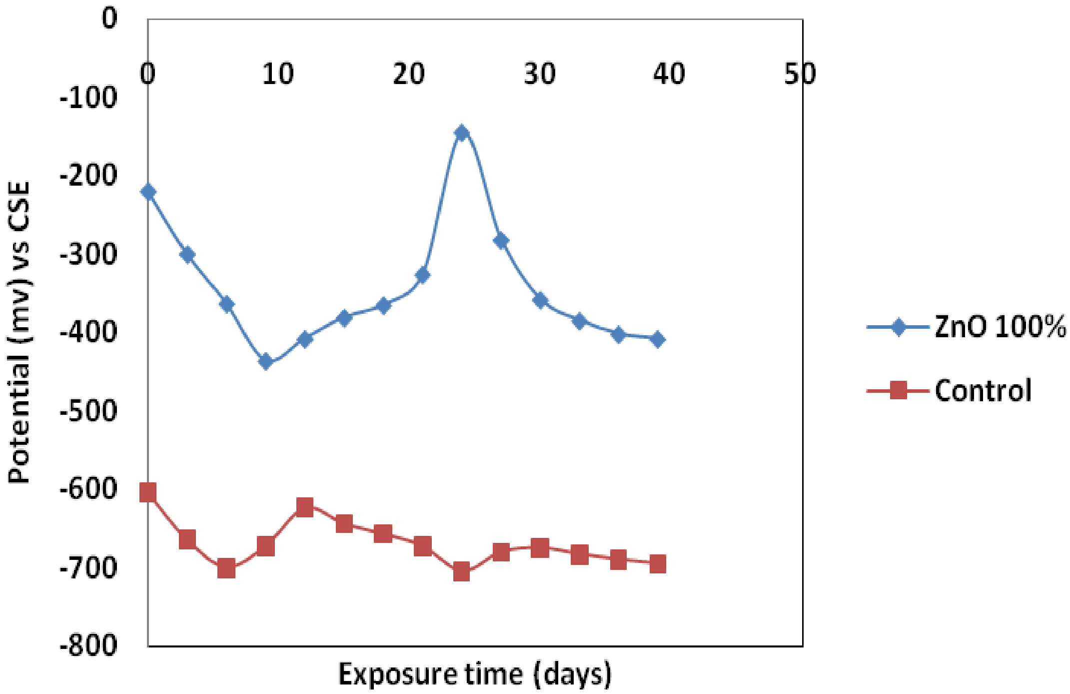


Fig. 2: Potential versus time curves for mild steel reinforcement in concrete mixed with 100% concentration of ZnO and partially immersed in 3.5% NaCl solution

Passive corrosion reactions remained within this potential range until the end of the experiment. However, in comparison with the control experiment, the extract concentration at 75% showed some measure of corrosion inhibition performance which was not as high as that of 100% ZnO.

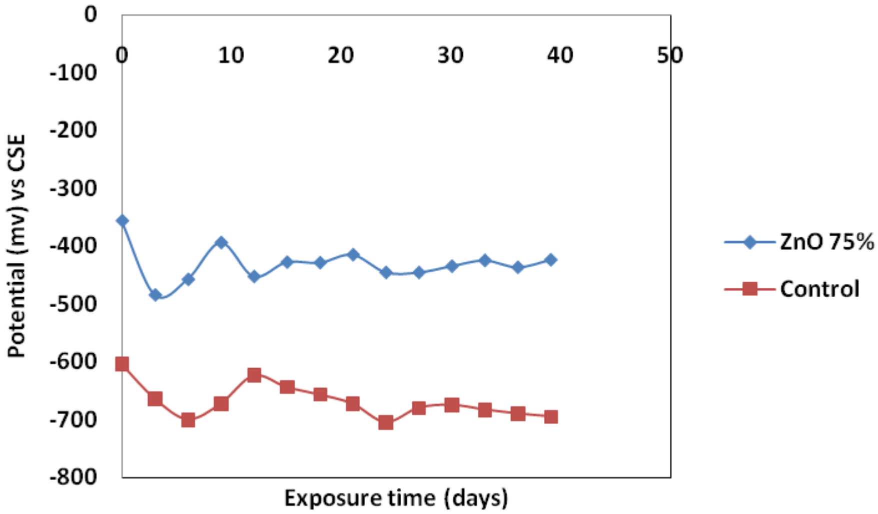


Fig. 3: Variation of potential with time for mild steel reinforcement in concrete mixed with 75% concentration ZnO inhibitor and partially immersed in 3.5M NaCl solution

At the extract concentration of 50% (Fig.4), potential fluctuations of decreasing passive and increasing active corrosion reactions were achieved throughout the experimental period for potentials ranging from -451 to -648mV. A comparison of the inhibitor performance at 50% concentration with 75 and 100% concentrations showed more active corrosion reactions, hence, a lesser tendency towards passive corrosion.

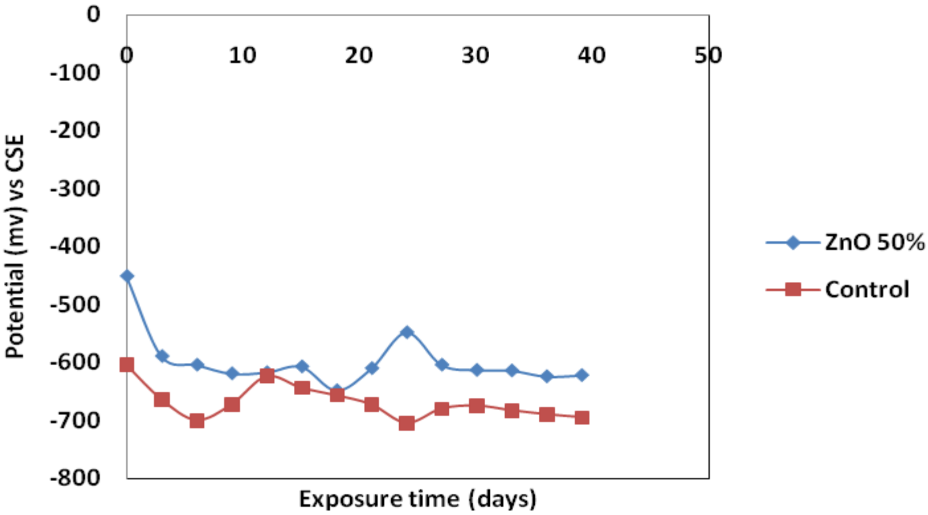


Fig. 4: Potential - time curves for mild steel reinforcement in concrete mixed with 50% concentration ZnO and partially immersed in 3.5% NaCl solution

At 50% concentration, the inhibitor could be described as less protective.

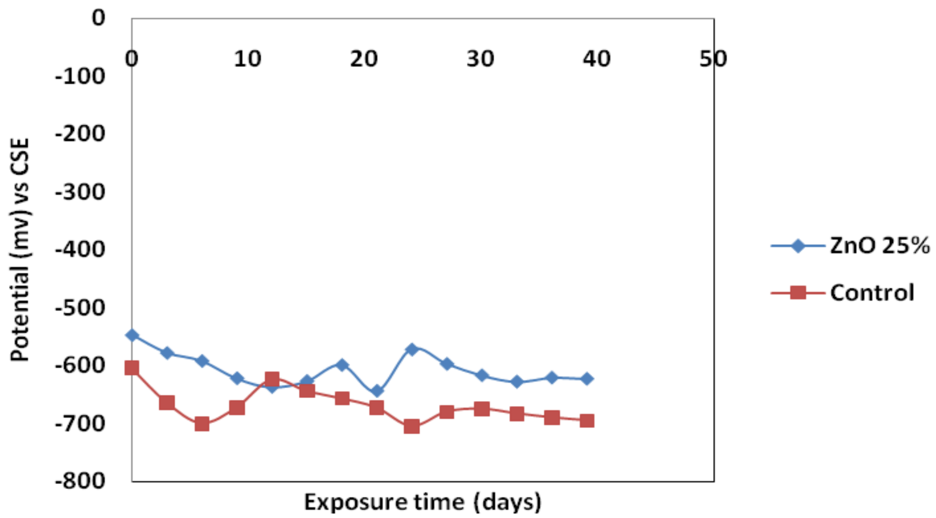


Fig. 5: Potential versus time curves for mild steel reinforcement in concrete mixed with 25% concentration of ZnO and partially immersed in 3.5% NaCl solution

For 25% ZnO concentration as presented in Fig. 5, decreasing passive corrosion reactions was achieved from -547 mV on the first day to -644 mV on the last day of the experiment. This concentration also gave very minimal corrosion inhibition performance and in comparison with 100%, 75% and 50% concentrations, the optimum value for ZnO inhibition performance was obtained with 100% concentration.

The overall zinc oxide corrosion inhibition performance profile for the mild steel embedded in concrete and partially immersed in 3.5% NaCl test medium is presented in Fig. 6. It could also be confirmed here again that the best inhibition performance in this work is with 100% and 50% ZnO concentrations respectively. In addition, 50%, and 25% ZnO concentrations performed better than the control experiment in which there was no inhibitor addition. The general observation is that ZnO as an inhibitor could provide reasonable measure of corrosion inhibition of mild steel in concrete in the chloride environment, particularly at 100% concentration.

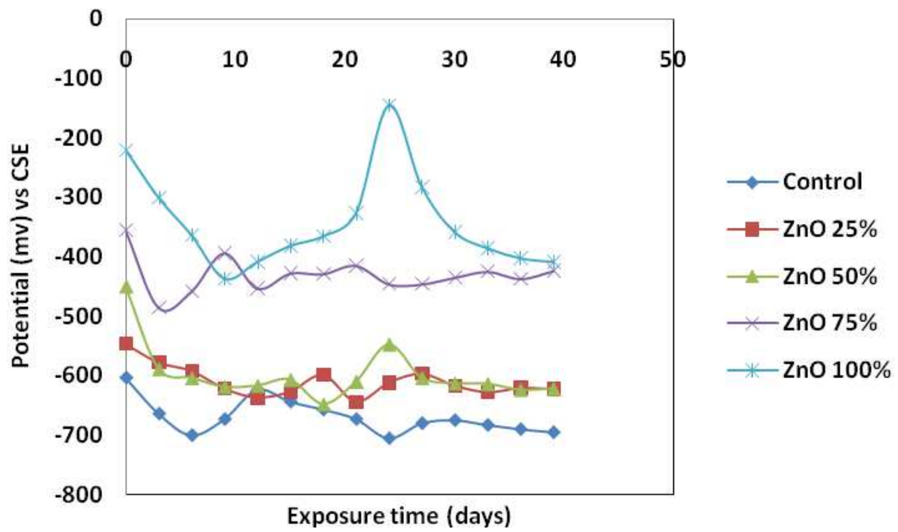


Fig. 6: Potential - time curves for mild steel reinforcement in concrete mixed with varied concentrations of ZnO and partially immersed in 3.5% NaCl solution

Statistical Analysis using ANOVA

The scatter plots show a fluctuating decrease and increase in potential values with respect to time. An average stability was achieved from the 30th day of the experiment. It could also be observed that 100% ZnO and 75% ZnO concentrations exhibited optimal performance of corrosion inhibition while 50% and 25% ZnO concentrations showed the least performance.

To evaluate the separate and combined effects of ZnO concentration and exposure time on the corrosion potential of the mild steel reinforcement in 3.5% NaCl solution, the two-factor single level experiment ANOVA test (F-test) was used ((Figs. 7 and 9-12). The amount of variation within each of the samples relative to the amount of variation between the samples was examined with F-test. The Sum of squares was obtained with equations (3) - (5), [12]

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

Sum of Squares among rows (concentration of ZnO):

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

Total Sum of Squares:

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

The calculation using the ANOVA test is presented in Table 1.

Table 1: ANOVA analysis for potential measurements

Sources of Variation	SS	Df	MS	F	Significance F
Exposure Time	69047.50	13	5311.35	3.53	1.91
Concentration of ZnO	1055149.06	4	263787.27	175.30	2.55
Residual	78246.14	52	1504.73		
Total	1202442.70	69			

The inference from the results in Table 1, is that with 95% confidence, the varied concentration of ZnO inhibitor and exposure time significantly affects the corrosion potential of the test medium (Fig.7). The effect of variable ZnO concentrations was significant.

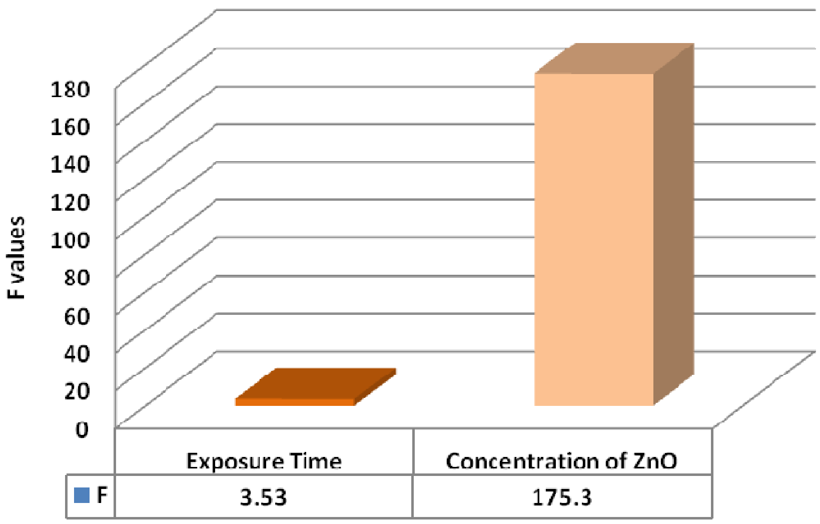


Fig.7: Influence of exposure time and ZnO concentration on corrosion potential

3.2 pH readings

Table 2 shows the results obtained for the different concentrations (25, 50, 75 and 100%) of ZnO inhibitor. The recorded pH values of the reinforced concrete blocks test environment gave decreasing acidity from 10.17 at the beginning of the experiment to 8.95 at the end in a period of 39 days. A similar trend was observed for all the different per cent concentrations of inhibitor addition.

The acidity for ZnO at 25% concentration addition, decreased from 10.72 to 9.46. At the concentration of 50%, the acidity decreased from 10.61 – 9.49; and at 75% concentration, it decreased from 10.89 – 9.38; and at 100%, from 10.96 – 9.37. This decrease in acidity could be due to the reactions between the concrete constituents, ZnO, the NaCl test environment and the reactions at the steel/environment interface for the steel reinforced concrete blocks.
One clear correlation of this decreasing acidity value with potential readings is that there was a tendency towards increasing active potential values when acidity was decreasing, that is, more negative values of potentials were obtained; though sometimes with random fluctuations, in particular with some of the ZnO inhibitor concentrations.

Table 2: pH readings of admixed ZnO inhibitor with 3.5M NaCl solution

Day	Control	ZnO 100%	ZnO 75%	ZnO 50%	ZnO 25%
0	10.17	10.96	10.89	10.61	10.72
3	8.65	10.47	10.41	10.49	10.31
6	10.05	10.54	10.3	10.1	10.11
9	9.02	9.93	9.83	9.75	9.68
12	8.7	9.75	9.67	9.61	9.56
15	8.61	9.79	9.77	9.73	9.72
18	8.89	9.89	9.81	9.86	9.81
21	9.18	9.86	9.77	9.88	9.84
24	8.73	9.43	9.36	9.5	9.44
27	9.38	9.83	9.77	9.84	9.82
30	8.6	9.15	9.16	9.32	9.33
33	8.45	10.05	9.63	9.59	9.73
36	9.23	9.67	9.67	9.77	9.75
39	8.95	9.37	9.38	9.49	9.46

The plot of pH values against exposure time (Fig.8) gave curves that are almost in linear relationship with the variables at all ZnO concentration levels.

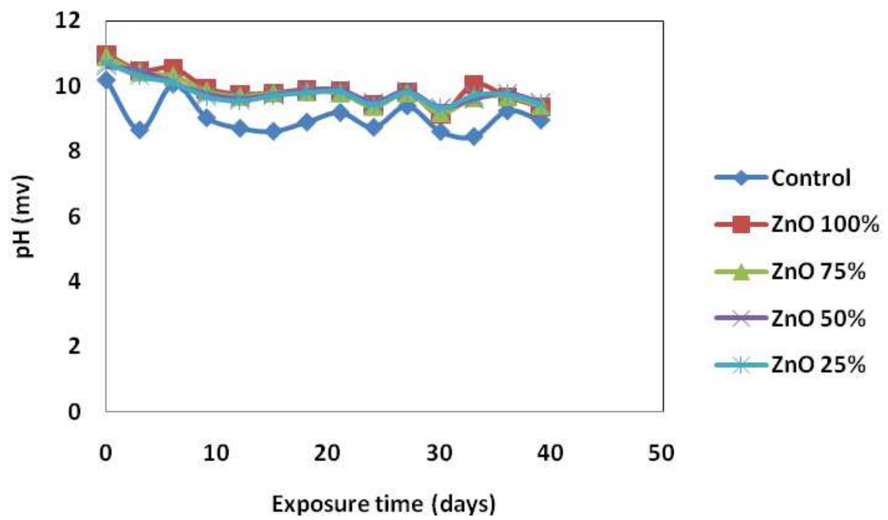


Fig. 8: Curves of pH with time for mild steel reinforcement in concrete partially immersed in 3.5% NaCl solution

These results show that at varied concentrations of ZnO inhibitor in solution, there were 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 presented in Table 3.

Table 3: ANOVA analysis for pH measurements

Source of Variation	SS	Df	MS	F	Significance F
Exposure Time	10.67	13	0.82	-0.12	1.91
Concentration of ZnO	7.16	4	1.79	-0.25	2.55
Residual	-365.41	52	-7.03		
Total	-347.58	69			

As shown in Table 3, it can be said that with 95 percent confidence the concentration of zinc oxide and exposure time have no significant effect on the pH of the test environment (Fig. 9).

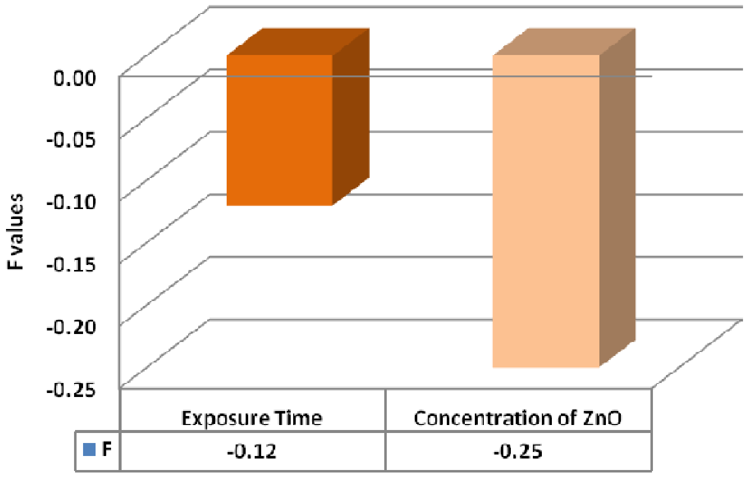


Fig. 9: Effect of exposure time and ZnO concentration on pH of test environment

3.3 Compressive Strengths of Test Samples

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

Table 4: Compressive strengths

Concentration of ZnO (%)	Compressive Strength (MPa)
Control	15
100	21
75	18
50	18
25	14

As presented in Table 4, it could be seen that the highest compressive strength of 21MPa was obtained at 100% ZnO inhibitor concentration. Lower concentration of Zinc Oxide yielded lower compressive strength (Fig. 10). This means that lower ZnO concentration has a negative effect on the compressive strengths of the samples in 3.5M NaCl environment. Similarly, potential measurements showed lower ZnO concentrations resulting in more active corrosion reactions.

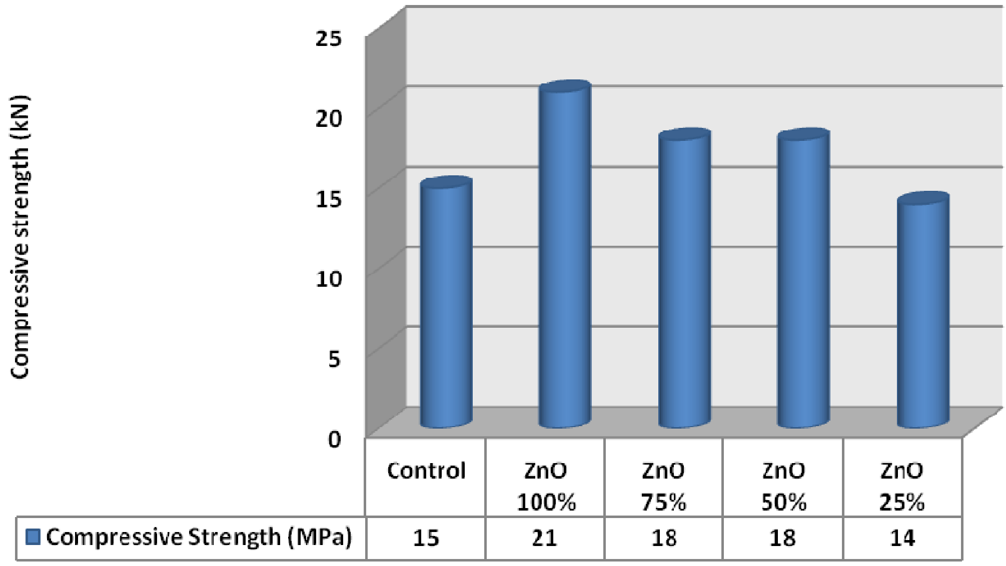


Fig. 10: Effect of ZnO inhibitor concentrations on compressive strength of test samples

3.4 Weight Loss and Inhibitor Efficiency

Presented in Table 5 are results for the weight loss, corrosion rate and the inhibitor efficiency. These results presented bear very close relationship with the results of potential measurement. The lowest inhibitor efficiency of 5.08 was achieved with the 25% ZnO concentration. The least weight loss of 0.6g was achieved with the ZnO inhibitor concentration of 100%. The recorded corrosion rate was 27.0 x 10^{-5} mm/yr and with an inhibitor efficiency of 41.02%. The 75% ZnO concentration with a weight loss value of 0.8g; a corrosion rate of 35.7 x 10^{-5} mm/yr and an inhibitor efficiency of 22.05% was next in corrosion inhibition performance in this test. The 50% inhibitor concentrations showed relatively low value of inhibitor efficiency. This tends to accelerate corrosion instead of inhibiting it.

Table 5: Weight loss and inhibition efficiency of mild steel in mixed ZnO with 3.5M NaCl medium

Zinc oxide Concentration	Initial Weight (g)	Final Weight (g)	Weight Loss (g)	Corrosion Rate (mm/yr)	Inhibitor Efficiency (%)
Control (Without ZnO addition)	110	109.4	0.6	0.000275	
ZnO 100%	112	111.4	0.6	0.000270	41.02
ZnO 75%	113	112.2	0.8	0.000357	22.05
ZnO 50%	114	113.1	0.9	0.000398	13.08
ZnO 25%	116	115	1	0.000435	5.08

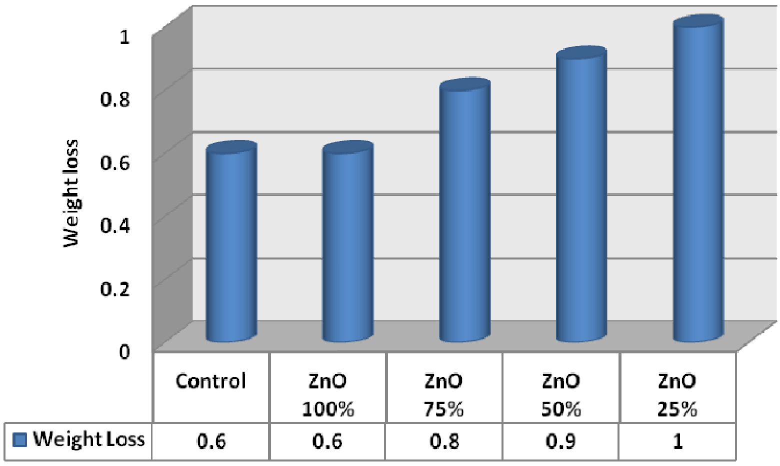


Fig.11: Concentration effect of ZnO on weight loss of test samples

Presented in Fig. 11 is the effect of ZnO concentrations on weight loss of test samples. The ZnO concentration of 100% recorded the least weight loss value of 0.6. The fact that the weight loss of the control test was 0.6, indicates that corrosion inhibition was more effective with higher concentration of zinc oxide inhibitor in 3.5M NaCl environment while lower concentration of the same resulted into accelerated corrosion rate.

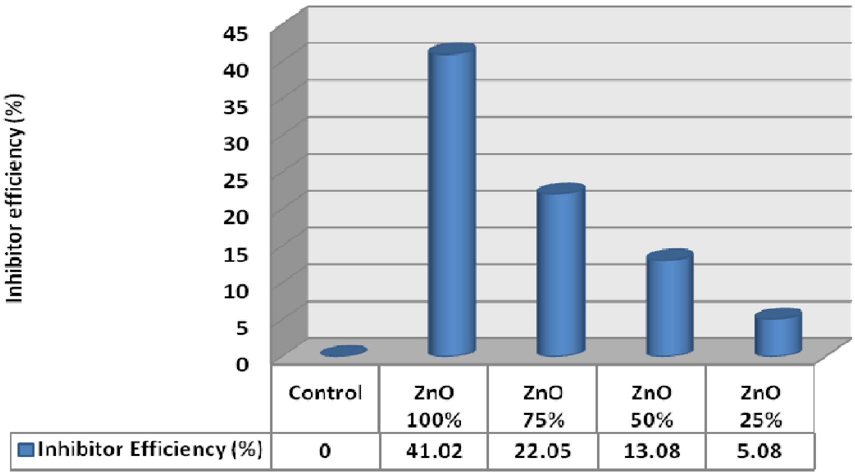


Fig.12: Influence of concentration of Zinc Oxide Inhibitor Efficiency

From Fig. 12, the highest efficiency obtained with the use of 100% ZnO concentration is 41.02%. The lowest inhibitor efficiency of 5.08% is obtained with the 25% ZnO concentration.

In summary, the NaCl ion, Cl^-, (from the 3.5% NaCl solution test environment) has a very strong tendency to cause severe corrosion of mild steel. The addition of this saline environment, therefore, accelerated the corrosion of the embedded reinforcing steel rebar. 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.

CONCLUSION

➢ Zinc oxide (ZnO) gave appreciable inhibition to the corrosion of the embedded steel rebar in concrete at 100% and 75% concentrations in 3.5% NaCl test medium.

- The corrosion inhibition performance was comparatively better with the higher concentrations of ZnO, particularly at the 75 and 100% concentrations.
- The concrete compressive strength was not adversely affected by the use of zinc oxide within the percentage concentrations used for the corrosion inhibition.
- At 95 percent confidence level, ANOVA analysis showed that varied concentrations of zinc oxide and exposure time affect the corrosion potential values significantly. The recorded effect was not significant for the pH of the chloride test medium.

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