

# EFFECT OF INHIBITORS ON THE ELECTROCHEMICAL CORROSION BEHAVIOR OF MILD STEEL EMBEDDED IN CONCRETE IN DILUTE SULPHURIC ACID

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## ABSTRACT

*Experiments have been performed on the electrochemical corrosion behaviour of mild steel rebars buried in concrete admixed with different inhibitors and sodium chloride salt, and exposed to dilute sulphuric acid environment. This paper reports the observed electrochemical corrosion response from the electrode potential monitoring of the reinforcing mild steel rebars during the experiments. The effect of admixed inhibitors on the compressive strengths of the used reinforced concretes are also reported. The added inhibitors provided varied degrees of protection to the embedded steel rebars. Concretes admixed with the mixture of potassium dichromate and formaldehyde, recorded some loss of compressive strengths; while the addition of formaldehyde and sodium nitrite had no effect. Potassium dichromate decreased the compressive strength of the reinforced concretes.*

## INTRODUCTION

Corrosion of steel reinforcement in concrete structures building facades, bridges and stadia exposed to different environments has now been widely recognised as an increasing problem. This entails large repair and maintenance costs <sup>(1)</sup>. Corrosion of concrete and embedded steel reinforcement in waste water collection and treatment systems costs several hundred million dollars annually in the different parts of the world. Acidic waters produced by some forms of bacteria will directly attack metal surfaces<sup>(2)</sup>.

The use of dilute sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) in this work, was in part to simulate the microbiologically induced corrosion activities by bacteria. One species that is quite common is the sulphate reducing bacteria.

These organisms are anaerobic and convert dissolved sulphur compounds, that is SO<sub>4</sub><sup>2-</sup>, to hydrogen sulphide (H<sub>2</sub>S). Carbon steel, stainless steel, copper-base alloys can be severely corroded by H<sub>2</sub>S. The aerobic sulphur bacteria - Thiobacillus can oxidise sulphur, sulphides, or sulphates to sulphuric acid. Localised pH depression as low as 1 can occur, causing severe general thinning of steels where these organisms contact the metal<sup>(3)</sup>. Investigations by Parker<sup>(3)</sup>, Thistlethwayte<sup>(4)</sup>, and others, have established the primary source of acid - forming Thiobacillus genera, specifically Th. Concretivorous and probably Th. Thiooxidans.

Protection of concrete against the microbiologically influenced corrosion and hence the dilute sulphuric acid, could be achieved by a properly designed, applied and cured protective system. Both the epoxy coating and the elastic membrane acid - proofing concrete systems are known to be fully resistant. However, the addition of a corrosion inhibitor to the concrete, is one means of protecting reinforced steel from corrosion in potentially corrosive environments. The use of inhibitors in concrete has been reviewed by Griffin<sup>(5)</sup>, Craig and Wood<sup>(6)</sup> and Treadaway and Russel<sup>(7)</sup>. An update of new advances as of 1980 was presented by Slater.

With regard to the compressive strength of the concrete admixed with inhibitors, the mechanical properties of mortars produced with sodium nitrite, potassium chromate, sodium benzoate and calcium chloride were examined by Craig and Wood<sup>(6)</sup>. A marked decrease in compressive strength was found when the inhibitors were added to the mortars. Calcium chloride, however, in contrast, increases the compressive strength when sodium nitrite and sodium benzoate were added to the concrete.

This investigation takes a look into the corrosion inhibition effect of formaldehyde, potassium dichromate, and sodium nitrite and their synergistic effect on the corrosion of reinforcing steel in concrete in dilute sulphuric acid environment. Predetermined moderate quantities of inhibitors concentrations were used; variation of inhibitor concentration will form part of the subsequent work on this subject. The mechanical properties - compressive strength effect of the admixed chemical inhibitors on the concrete was also determined. This work aims at making a contribution to the already existing knowledge in this research field. The results obtained are expected to be scientifically beneficial.

## EXPERIMENTAL PROCEDURE

### Materials preparation of Test samples:

The experiment procedure here follows the previously reported work of steel reinforced concrete in sea water<sup>(8)</sup>. Concrete blocks made of portland cement, gravel, sand and water, each one with a reinforcing steel rebar embedded in it, were used for the experiment. Each of the concrete blocks had a dimension of 160mm long, 100mm wide and 100mm thick. The formulation for the reinforced concrete specimens used, in kg/m<sup>3</sup>, was:

Cement - 320; Water - 140; Sand - 700; and Gravel - 150.

The water - to - cement ratio (w/c) was 0.44.

Two sets of concrete blocks were made. The first set made of five specimens admixed with different inhibitors are listed below. The second set were made up of two concrete blocks without any admixed inhibitor. They were made purposely for determining strength under different curing conditions. One of the concrete blocks in the second set was cured in air for two weeks while the other was cured in water for the same period.

The first set of concrete blocks were prepared with 1:2:4 (C:S:G) - cement:sand:gravel ratio and with the different types and quantity of inhibitors and fixed quantity of sodium chloride as presented below:

1. 100g of sodium nitrite (NaNO<sub>2</sub>), and 100g of sodium chloride salt to accelerate corrosion.
2. 100g of formaldehyde plus 100g of sodium chloride salt.
3. 100g of potassium dichromate plus 100g of sodium chloride salt.
4. 50g of potassium dichromate, 100g of formaldehyde and 100g of sodium chloride salt.
5. 100g of sodium chloride salt.

All the predetermined quantity of each inhibitor, presented above, was added, in turns, to every 10kg of the concrete from which the blocks were made.

All the chemicals used were of AnalaR grade.

All the specimens were partially immersed in dilute sulphuric acid (0.2M). The block listed as specimen 5 above served as the control test sample.

The steel rebars used for reinforcement was of DIN-ST 60MM obtained from Oshogbo Steel Rolling Mill. It has the 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 rebars were cut into several pieces each with a length of 160mm and 16mm dia. An abrasive grinder was used to remove any mill scale and rust stains on the steel specimens before embedding in the concrete block

Each steel rebar was symmetrically placed across the length of the block in which it was embedded and had a concrete cover of 42mm. Only about 140mm was embedded in each concrete block. The remaining 20mm protruded at one end of the concrete block, and was painted to prevent atmospheric corrosion. This part was also used for electrical connection.

### Potential Measurement.

Each concrete test block was partially immersed in the test medium. The potential readings were obtained by placing a copper sulphate electrode firmly on the concrete block. One of the two lead terminals

of a digital voltmeter was connected to the copper sulphate electrode and the other to exposed part of the embedded steel rebar to make a complete electrical circuit. The set up of the experiment had been previously shown diagrammatically<sup>9-10</sup>. 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 7-day intervals. All the experiments were performed under free corrosion potential and at ambient temperature.

#### Determination of Specimens' Compressive Strength:

The effect of admixed inhibitors on the compressive strength of the concrete test samples was determined using the second set of concretes mentioned above. The original steel reinforced concrete test specimens, after the potential monitoring period, were removed from their respective test media and allowed to air harden for seven days.

Each of the concrete blocks was then carefully weighed, placed on a compressive fracture machine lengthwise and carefully loaded until the concrete block gently disintegrated. The maximum load before fracture commenced was noted.

#### RESULTS AND DISCUSSION

Figures 1 to 5 represent the curves of the potential vs. time for the steel reinforcement in concrete with different premixed inhibitors immersed partially in dilute sulphuric acid (0.2M). An increasing active corrosion reaction was observed in the first three weeks of the experiment achieving a potential of -500mVcse in the second and third weeks when sodium nitrite was admixed with the reinforced concrete and partially immersed in dilute sulphuric acid, (Figure 1).

The above observation was followed by a repassivation phenomenon, achieving a potential of -350mVcse in the fourth week and increasing positively to a potential of -350mVcse seventh week and slightly less in the eighth week of the experiment. The last reading in the ninth week, however, indicated an active corrosion phenomenon. The initial active

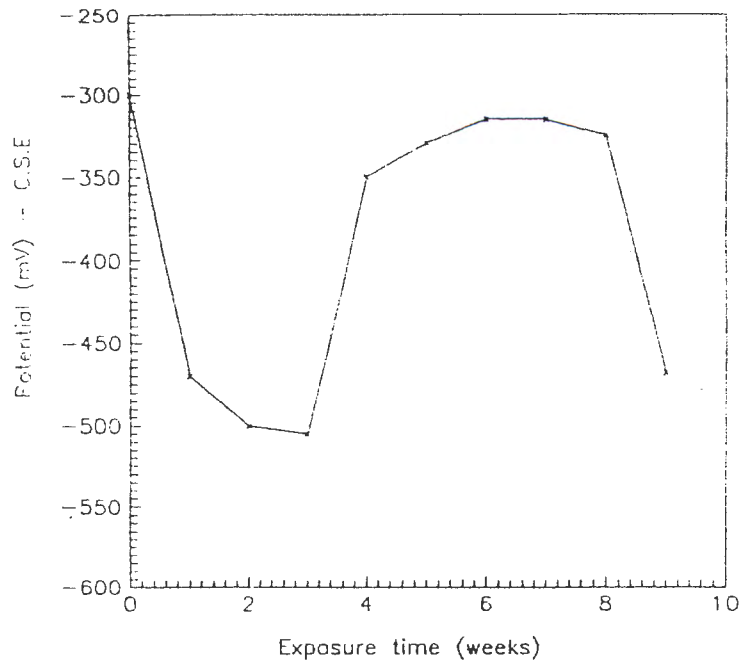


Fig.1. Potential vs. time curve for the steel reinforced concrete admixed with sodium nitrite.

Fig.1

corrosion observed could be due to the presence of strong chloride ions ( $Cl^-$ ) reacting species from the admixed sodium chloride, penetrating the hydroxide film formed around the embedded steel. During this short period, the diffusion of the sulphate ions ( $SO_4^{2-}$ ) within the concrete matrix and onto the surface of the embedded steel was expected to be minimal. The passive corrosion reaction phenomenon recorded from the fourth to the eighth (4th - 8th) week could be attributed to the further reaction of the increasing concentration of the diffused sulphate ions from the acid with the  $Ca(OH)_2$  content of the concrete. This would lead to the concentration of  $CaSO_4 \cdot 2H_2O$  (gypsum) by chemical reaction. On its own,  $CaSO_4 \cdot 2H_2O$  is an inhibitor; and when further reinforced by the sodium nitrite,  $NaNO_2$ , an admixed inhibitor, a stable inhibitive/protective film could be achieved within that period.  $CaSO_4 \cdot 2H_2O$  was also likely to have formed within the pores of concrete resulting in a reduced corrosion rate. Though the reading recorded at the ninth week indicated an active corrosion, it is difficult, however, to take that reading alone as indicating progressive or continuous active corrosion thereafter.

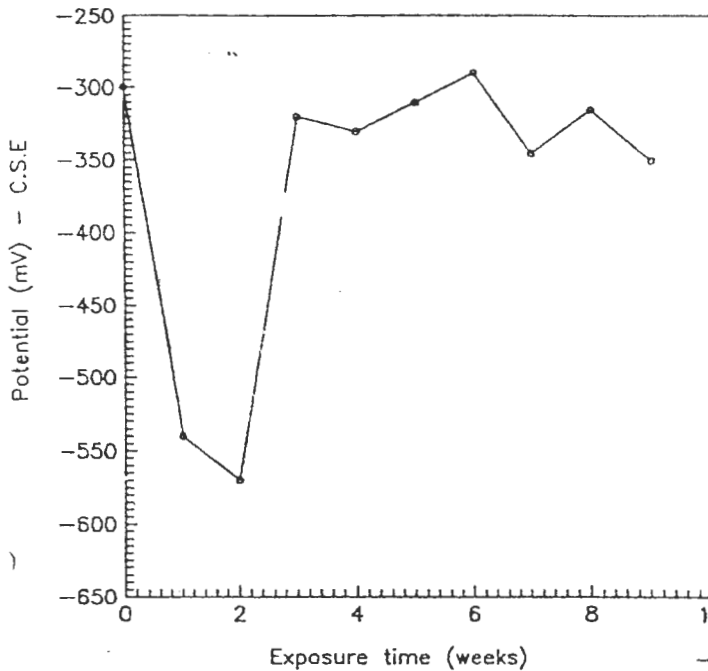


Fig. 2. Potential vs. time curve for the steel reinforced concrete admixed with formaldehyde.

Fig. 2

A phenomenal active corrosion was observed in the first two weeks of the experiment achieving a potential of -540 and -570mVcse respectively in the first and second week, (Fig.2). A repassivation of the corrosion reaction was observed from the third week to the ninth week - the end of experiment with the fluctuating potential ranging between -350mVcse (ninth week), the most negative, and -290mVcse (sixth week), the least negative. This result, during the period of third to ninth week, indicates an effective inhibitor action on the embedded mild steel. It was achieved by the reaction of formaldehyde with the diffusing sulphate ions from the dilute sulphuric acid. The chloride ions from the admixed chloride found the inhibiting protective film difficult to break within the last seven weeks of the experiment.

Potassium dichromate inhibitor did not show any initial inhibitive effect, (Figure 3). The initial potential -587mVcse indicates an active corrosion. It achieved a potential of -633mVcse in the first one week. The sudden drastic repassivation in the second week achieving a potential of -587mVcse in the third week could be attributed to the inability of the inhibitor to form a stable protective film on the

embedded steel during this period. A repassivation was observed in the fourth week achieving a potential of -379mVcse and this continued to -275mVcse in the sixth week where a complete repassivation could be said to have occurred. Though with fluctuating potentials, the embedded steel remained in the passive state throughout the experimental period with the most negative potential being -342mVcse in the seventh week. This is an indication that the potassium dichromate inhibitor later formed a more stable protective chemical complex by reacting with the diffusing  $SO_4^{2-}$  ions from the acid and the  $Ca(OH)_2$  from the concrete.

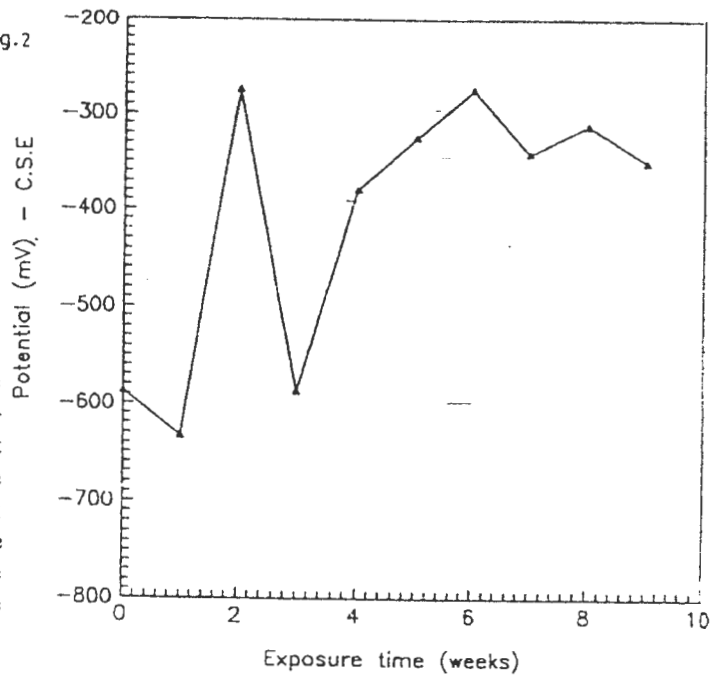


Fig. 3. Potential vs. time curve for the steel reinforced concrete admixed with potassium dichromate.

Fig. 3

A mixture of formaldehyde and potassium dichromate inhibitors gave the embedded steel some measure of protection in the first two weeks when the reinforced concrete was partially immersed in dilute sulphuric acid as presented in Fig.4. The active corrosion reaction, from the second to the fourth week was not drastic. A repassivation was observed from fourth to the sixth week, after which an active corrosion was observed to the ninth week. The synergistic effect of the inhibitors was noticed up to the seventh week (-322mVcse) except in the fourth week where a poten-

tial of  $-427\text{mVcse}$  was achieved. However, the potentials of  $-505$  and  $-516\text{mVcse}$  achieved respectively in the eighth and ninth week showed that the combined inhibitors effect are not very long lasting on the embedded steel immersed in dilute sulphuric acid medium in the presence of admixed sodium chloride.

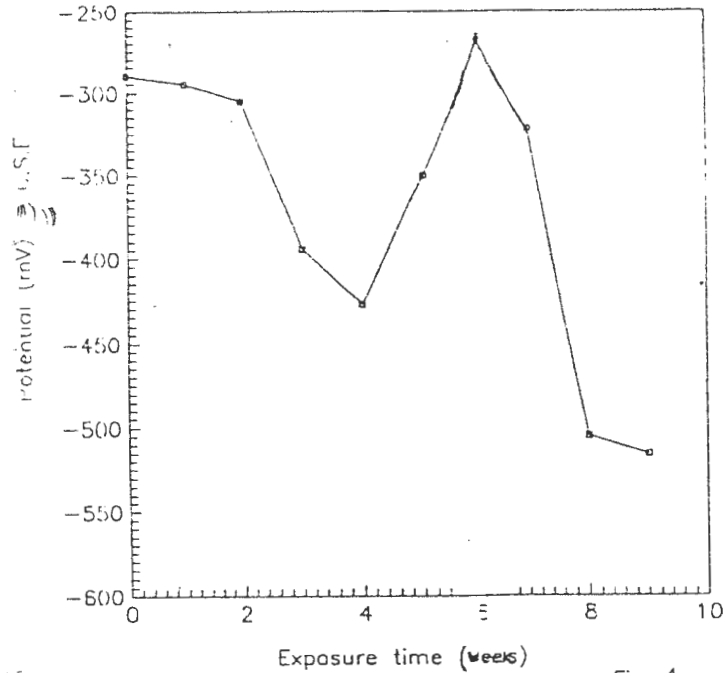


Fig. 4. Potential vs. time curve for steel reinforced concrete admixed with a mixture of formaldehyde and potassium dichromate.

Fig. 4.

Even without any admixed inhibitor, and with the added NaCl, the embedded steel in concrete immersed in dilute sulphuric acid, (Fig.5), presented a passivating corrosion phenomenon. This started with an initial potential of  $-456\text{mVcse}$  and achieving a potential of  $-260\text{mVcse}$  in the second week. As explained earlier, the reaction of  $\text{Ca}(\text{OH})_2$  and  $\text{H}_2\text{SO}_4$  (the diffusing sulphate ions) to form gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) within the concrete matrix could be responsible for the passivating phenomenon. Halogens are, however, known<sup>(11)</sup> to inhibit corrosion to some extent in acid solutions. Chloride ions had been found to lower the rate of attack on steel by  $\text{H}_2\text{SO}_4$ <sup>(11)</sup>. The passivation observed here could therefore be attributed, in part, to the chloride ions content (from NaCl) of the concrete. An active corrosion reaction was observed, thereafter, from the second to the fourth

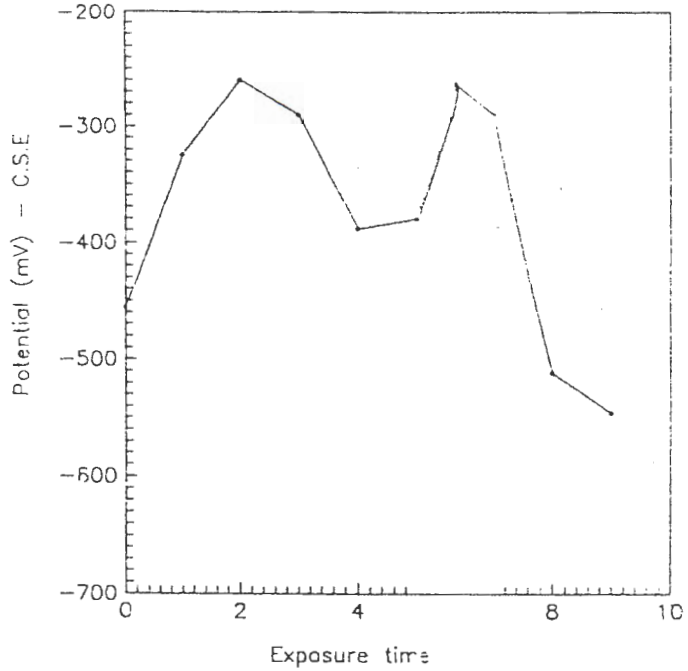


Fig. 5. Potential vs. time curve for steel reinforced concrete without admixtures (only).

Fig. 5.

week. A repassivation process occurred from the fourth to the sixth week. The chloride content of the concrete actually caused, in combination with some other factors such as oxygen and carbon dioxide of the air diffusing into the concrete's matrix, the active corrosion mentioned above, and from the sixth to the ninth week of the experiment. However, the partial inhibiting effect of chloride ions in dilute sulphuric acid would have reduced the active corrosion reaction. The combined curves for Figures 1 to 5 are presented in Figure 6. This is done to compare the effectiveness of the various inhibitors used under this particular environment and experimental conditions.

### The Concrete's Compressive Strength.

The analysis of compressive fracture load data for the steel reinforced concrete test samples immersed in dilute sulphuric acid are presented in Fig. 7. All the five specimens used for the monitoring experiment and partially immersed in dilute sulphuric acid had compressive strength values that were substantially higher than the compressive strength of the specimen cured in water. When compared with the specimens cured in air, values less than the compressive

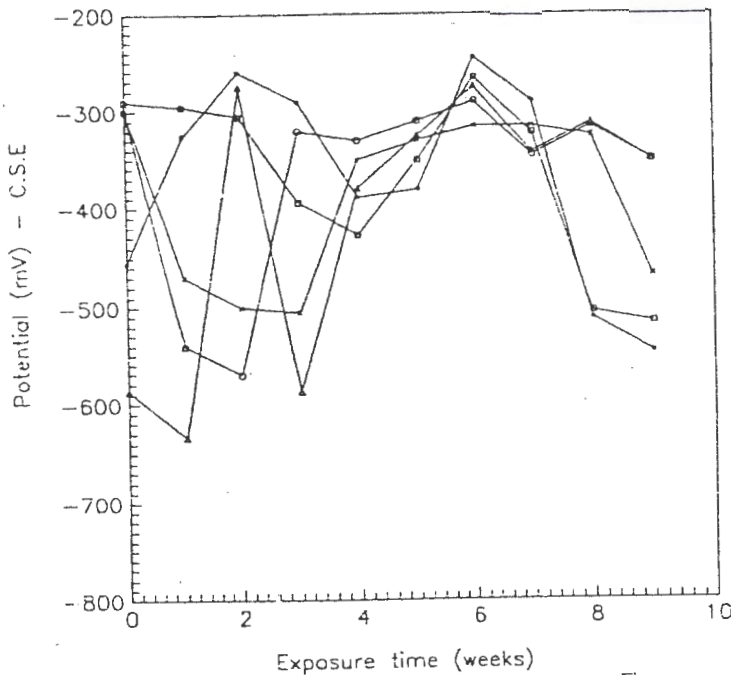


Fig. 6. Potential vs. time curves for the steel reinforced concretes admixed with the various inhibitors used.

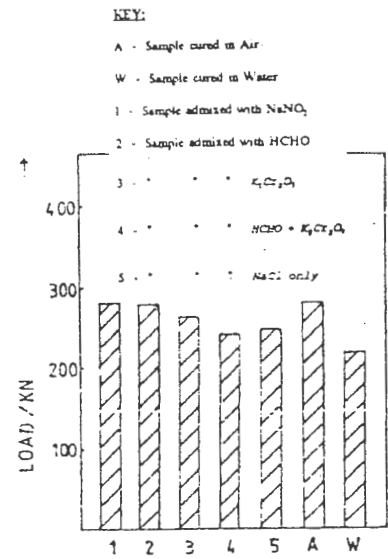


Fig. 7. Histogram of compressive fracture load for the reinforced concrete test samples immersed in dilute sulphuric acid.

strengths of the specimens cured in air were obtained for the specimens admixed with potassium dichromate and sodium chloride; a mixture of potassium dichromate, formaldehyde and sodium chloride, and the specimen admixed with chloride only. The specimen admixed with sodium nitrite and sodium chloride had the same compressive strengths as the specimen cured in air. In general, the sulphate ion content of the acid could be deleterious to the concrete. Apart from the fact that acidic waters corrode concrete by direct attack on calcium carbonate constituents, sulphate ions are known<sup>(12)</sup> to attack directly the tricalcium aluminate constituents of the concrete (Cement Bacillus), - requiring increasingly resistant grades as the sulphate ion content increases. This is not encountered in sea water, however. In the selection of inhibitors for use in reinforced concrete for corrosion prevention, it is pertinent to be cautious taking into consideration, strengths of the concrete blocks.

**CONCLUSION:**

1. All the inhibitors used, inhibit the corrosion of all the embedded rebars to varying extent when the blocks were exposed to dilute sulphuric acid.

2. Sodium nitrite and formaldehyde inhibitors had no effect on the compressive strength of the concrete blocks exposed to dilute sulphuric acid while potassium dichromate decreased the strength.

3. Sodium chloride salt alone admixed with concrete gave an increase in compressive strength and it gave a passivating effect when the concrete block was exposed to dilute sulphuric acid. Halogen ions are known to inhibit corrosion to some extent in acid solutions.

4. The overall effectiveness of the inhibitors could not be fully determined due to the non-variation of the inhibitors' concentration.

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