# Comparative Study of Inhibitors on the Corrosion of Mild Steel Reinforcement in Concrete

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**ABSTRACT**

The suitability of some inhibitors in reducing corrosion of mild steel reinforcement in concrete (immersed in seawater and dilute sulphuric acid) to simulate two factors was investigated, using the potential monitoring technique. Potential readings were taken in accordance with ASTMC 109-92 and compressive strengths determined as laid down by ASTMC 39-96. Initial Voltage readings were recorded for each block and subsequent readings taken at an interval of one month for a year. The experimental results show that in seawater, admixture of potassium dichromate and formaldehyde were identified as good inhibitor for concrete mix, but it caused a substantial loss of compressive strength. Calcium nitrite on the other hand, exhibited the best inhibiting qualities with negligible effect on the compressive strength of the concrete. It is also evidence from the results, that all the inhibitors tested showed good inhibiting properties when the blocks were immersed in dilute sulphuric acid solution. It is therefore recommended that calcium nitrite be adopted for concretes expose to marine conditions and acidic environment whereas the admixture of potassium dichromate and formaldehyde is highly recommended for concrete structure exposed to acidic environments.

**Keywords:** Inhibitors, concrete, corrosion, steel reinforcement, seawater.

## 1. INTRODUCTION

The deterioration and collapse of reinforced concrete structures is a major problem in the construction industry especially in the soil in Niger Delta region of Nigeria, which are characterized by high water table levels. The cost of repairing or replacing deteriorated structures has become a major liability to government and the private sector. The primary cause of this deterioration (cracking, delamination and spalling) is the corrosion of steel reinforcing bars due to chlorides whose main source is the seawater. As a result, several measures have been developed and implemented to prevent the chloride induced corrosion of reinforcing steel rods and the resulting deterioration. Amongst these methods includes; the lowering of the water-cement ratio of the concrete, the use of epoxy-coated reinforcing steels and corrosion inhibitors. The principle of the corrosion inhibitor is to prevent the chloride ions from reacting with the steel surface and also to increase the time needed for the chloride ions to penetrate through the concrete Cover (Olasehinde, 1994; Holm, 2001). Thus, corrosion inhibitors are chemical substances, which decreases the corrosion rate when present in the corrosion system at a suitable concentration without significantly changing the concentration of any other corrosive agent (Escalante, 1990; Uhlig, 2004). There are five major commercially available corrosion inhibitors, namely: DCI (Darex Corrosion Inhibitor) – Calcium Nitrite; Sodium Nitrite; Formaldehyde, Potassium dichromate and Potassium chromate.

Several studies have been carried out on these corrosion inhibitors. Cannon and Cady(1992) and loto (2004), worked on the mechanical properties of mortars produced with sodium nitrite, potassium chromate, sodium benzoate and calcium chloride. They found a marked decrease (as high as 20 – 40%) in compressive strengths when these inhibitors were added to the mortars. In contrast calcium chloride increased the compressive strength while tensile strengths were adversely affected by sodium nitrite and sodium benzoate, but not by potassium chromate. Kompen (1997) and Macdonald (2003), also investigated inhibitors in alkaline solutions and in cement extracts. The cement extracts experiment showed that sodium nitrite inhibited corrosion in the presence of chlorides while sodium benzoate did not. Moreover corrosion initiation was delayed with sodium nitrite, with the delay increasing with inhibitor content. Rosenberg (1989) and Novokshchenov (2000), showed that calcium nitrite is not detrimental to concrete properties as it is the case for inhibitors based on sodium or potassium. A latter study by Berke and Weil (1995), Skotnick (2000) and Slater (2001) showed that under long-term accelerated testing, calcium nitrite was found to be of better quality. However, for this corrosion study, the potential techniques was used with copper-copper sulphate half-cell as the reference electrode.

But there is paucity of information on what type of corrosion inhibitor to apply in mortars and their attendant effects on concrete structures most especially in the Niger Delta region of Nigeria. Therefore the objectives of this study was to investigate;

- The suitability of the different inhibitors reducing corrosion of reinforced steel in concrete in different test media (seawater and dilute sulphunic acid)
- The effect of the different inhibitions on the mechanical properties of the prepared concrete blocks.
- The effects of admixing different inhibitors with concrete mix on the electrochemical corrosion of reinforcement steel in concrete.

## 2. MATERIAL AND METHODS

### 2.1 Experimental Procedures

Concrete blocks used for the experiment were made of PortlandCement, gravel, sand and water, and were reinforced in accordance with ATMC 109-92. The dimensions of the blocks were similar each being 160mm long, 100mm wide and 1000mm thick. Two sets of concrete blocks were made. The first set of five (5) specimens were admixed with different inhibitors as listed below, and the second set of two (2) had no chemical or inhibitors admixed with the concrete, but casted purely for the purpose of determining the specimen 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 two weeks. The experiment was performed in the concrete Test Laboratory of I.T.B. Nig. Ltd, Port Harcourt.

### 2.2 Preparation of Concrete Blocks

The first set of concrete blocks were prepared with the quantity of inhibitors added as follows.

- Specimen 1**:** Prepared with a nominal mix ratio of 1:2:4 (cement, sand and gravel) plus 100g of calcium Nitrite, and 100g of sodium chloride salt to accelerate corrosion.
- Specimen 2: Nominal mix ratio of 1:2:4 (cement, sand and gravel) plus 100g of formaldehyde plus 100g of sodium chloride salt to accelerate corrosion.
- Specimen 3: Nominal mix of 1:2:4 (cement, sand and gravel) plus 100g of potassium dichromate, plus 100g of sodium chloride salt.
- Specimen 4: Prepared with nominal mix 1:2:4 (cement, sand and gravel) plus 100g of potassium dichromate, 100g of formaldehyde plus 100g of sodium chloride salt to accelerate corrosion.
- Specimen 5: Prepared with 1:2:4 (Cement, sand and gravel plus 100g of sodium chloride salt.

### 2.3 Procedure

Each specimen was made up of two concrete blocks. One partially immersed in seawater (to simulate marine environment) and the other partially immersed in dilute sulphuric acid (to simulate microbial environment), and the two concrete blocks listed as specimen 5 served as the control test piece for each corrosive solution medium.

The reinforcement steel bars were cut out from the same stock and were based on BS4466 specifications. The dimensions were 160mm long and 16mm diameter. An abrasive grinder was used to remove the mill scales and rust stains before embedding in the concrete blocks during casting. About 140mm length of each steel rod was embedded symmetrically across the width of the block, leaving the remaining 20mm protrusion for electrical connections (see fig 1). The exposed part of the steel rod was coated with paint to prevent atmospheric oxidation.

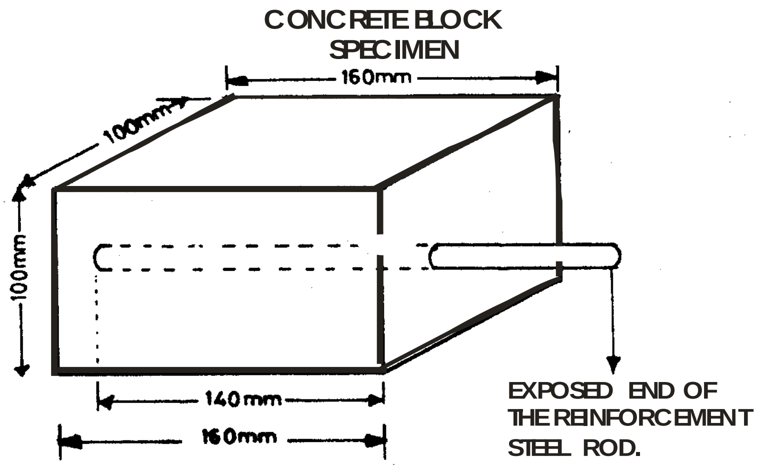


Figure 1. Concrete block specimen showing the arrangement of reinforcing steel.

Potential readings were taken by firmly placing a copper sulphate electrode on the concrete block and the lead terminals of a digital voltmeter connected to the copper rod of the copper sulphate electrode and the exposed part of the embedded steel rod to make a complete electrical circuit. The readings were taken at three different points on each concrete block and the average computed as the potential reading for the embedded steel rod. Initial voltage readings were recorded for each block and subsequent readings taken at an interval of one month for one year.

The compressive strength of the specimens were determined in accordance with ASTMC 39-96. Five blocks were tested for each batch of concrete to evaluate the effect of adding inhibitors on the compressive strength. Another set of two concrete blocks without inhibitors were prepared and cured respectively in air and water for 14 days and allowed to air hardened for another 7 days. Each concrete block was carefully weighed and placed on a compressive fracture machine lengthwise and loaded until the blocks crushes. Thus noting the maximum load before fracture commenced.

## 3. RESULTS AND DISCUSSION

Table 1. Potential readings for specimen 1,with calcium nitrite and sodium chloride.

| | In seawater | In dil. $H_2S0_4$ |
|---|---|---|
| Time (months) | Voltage reading(-mV) | Voltage reading (-mV) |
| Initial | 38 | 21 |
| 1 | 75 | 23 |
| 2 | 90 | 25 |
| 3 | 110 | 50 |
| 4 | 100 | 52 |
| 5 | 112 | 73 |
| 6 | 115 | 68 |
| 7 | 125 | 75 |
| 8 | 130 | 92 |
| 9 | 132 | 75 |
| 10 | 150 | 110 |
| 11 | 150 | 115 |
| 12 | 200 | 152 |

Table 1 shows the corrosion potential against the exposure time (months) for the steel reinforced concrete with premixed calcium nitrite and sodium chloride in seawater and dil.suphuric acid respectively. The results shows a fairly constant potential within the monitoring period and the values obtained falls within the range of accepted passive condition of –200mV to –350mV (ASTMC 106-92) The potentials obtained from the seawater fell within the range of –38mV to –200mV as against –21mV to –152mV of that from the dil.sulphuric acid.The significanceof these low potentials is that corrosion may be delayed. Comparing these results, it is observed that, in seawater the protective film formed on the steel rod inhibited only for a short period, whereas in dilute sulphuric acid, the film provided a more effective barrier against further corrosion of steel rod. This could be attributed to the continuos diffusion of chlorine ions through the concrete matrix and depassivating the protective layer on the reinforcement steel. These results are in agreement with that of Kompen (1997) and Rosenberg (1989).

Table 2. Potential readings for specimen 2,with formaldehyde and sodium chloride.

| | In seawater | In dil. $H_2S0_4$ |
|---|---|---|
| Time (months) | Voltage reading(-mV) | Voltage reading (-mV) |
| Initial | 100 | 100 |
| 1 | 120 | 128 |
| 2 | 132 | 140 |
| 3 | 115 | 138 |
| 4 | 160 | 120 |
| 5 | 140 | 110 |
| 6 | 148 | 140 |
| 7 | 105 | 100 |
| 8 | 122 | 100 |
| 9 | 128 | 120 |
| 10 | 128 | 120 |
| 11 | 157 | 200 |
| 12 | 228 | 210 |

Table 2 is a measure of the corrosion potentials of steel reinforced concrete blocks with premixed formaldehyde and sodium chloride in the tow different test media. In seawater the potential readings varies between –100mV and –228mV as against –100mV and –230mV in dilute sulphuric acid. The readings tend to fluctuate up to the 7$^{th}$ month of monitoring. This phenomenon may be due to the reaction of the concrete mix, the premixed formaldehyde and sodium chloride stifled the electrochemical corrosion of the reinforcement. The results in the two different tests media are in accordance with previous investigators. They also fall within range recommended by ASTMC 109-92.

Table 3. Potential readings for specimen 3.with potassium dichromate and sodium chloride.

| | In seawater | In dil. $H_2S0_4$ |
|---|---|---|
| Time (months) | Voltage reading(-mV) | Voltage reading (-mV) |
| Initial | 100 | 100 |
| 1 | 100 | 118 |
| 2 | 129 | 112 |
| 3 | 141 | 120 |
| 4 | 130 | 199 |
| 5 | 110 | 172 |
| 6 | 150 | 205 |
| 7 | 170 | 180 |
| 8 | 122 | 150 |

| | | |
|---|---|---|
| 9 | 160 | 160 |
| 10 | 160 | 200 |
| 11 | 162 | 168 |
| 12 | 225 | 222 |

Table 3 shows the corrosion potentials against time for steel reinforced concrete blocks with premixed potassium dichromate and sodium chloride in the two test media. It can be observed that the minimum and maximum potentials in seawater are – 100mV and –225mV respectively. This is an indication that potassium dichromate inhibitors plays a vital role in the corrosion of steel reinforcement in saline conditions. Similarly, in dilute sulphuric acid, potential readings of between –100mV and –222mV were observed indicating good inhibiting qualities that fell within the recommended range. The results are also in concordance with that of Cannon and Cady (1992).

Table 4. Potential readings for specimen 4,with potassium dichromate,formaldehyde and sodium chloride.

| | In seawater | In dil. $H_2S0_4$ |
|---|---|---|
| Time (months) | Voltage reading(-mV) | Voltage reading (-mV) |
| Initial | 80 | 0 |
| 1 | 88 | 70 |
| 2 | 90 | 78 |
| 3 | 88 | 60 |
| 4 | 122 | 140 |
| 5 | 118 | 156 |
| 6 | 118 | 140 |
| 7 | 206 | 140 |
| 8 | 200 | 156 |
| 9 | 216 | 250 |
| 10 | 231 | 246 |
| 11 | 231 | 250 |
| 12 | 220 | 212 |

Table 4 is a measure of the corrosion potentials for steel reinforced concrete blocks with premixed potassium dichromate, formaldehyde and sodium chloride in the two test media. The result shows that in the two different test media, combining the two inhibitors yielded better results than when singly used in the first six months of monitoring . Though at the end of 12 months both results still fell within the recommended range and in conformity with that of Cannon and Cady (1992).

Table 5. Potential readings for specimen 5,with sodium chloride.

| | In seawater | In dil. $H_2S0_4$ |
|---|---|---|
| Time (months) | Voltage reading(-mV) | Voltage reading (-mV) |
| Initial | 100 | 100 |
| 1 | 120 | 100 |
| 2 | 126 | 110 |
| 3 | 210 | 142 |
| 4 | 120 | 134 |
| 5 | 222 | 205 |
| 6 | 248 | 229 |
| 7 | 248 | 220 |
| 8 | 248 | 332 |
| 9 | 294 | 350 |
| 10 | 360 | 358 |
| 11 | 375 | 350 |
| 12 | 490 | 430 |

Table 5 shows corrosion potentials for the steel reinforced concrete block with premixed sodium chloride in the test media. Results obtained from the seawater varies between –100mV and –490mV. This value is higher than that recommended by ASTMC 109-92 (i.e. –200mV to –350mV). It therefore indicates a very high probability of corrosion. Similarly, potential readings obtained from the dilute sulphuric acid media also varies between –100mV and –430mV which is also higher than the recommended values. The breakdown of protective film may be attributed to the diffusion of chloride ions into the concrete matrix which is destructive to passivity in the absence of inhibitors.

Table 6. Compressive strength of the specimens.

| Specimen | Load (MPa) Seawater | Load (Mpa) In dil. $H_2S0_4$ |
|---|---|---|
| 1 | 60 | 62 |
| 2 | 58 | 55 |
| 3 | 31 | 29 |
| 4 | 25 | 33 |
| 5 | 40 | 47 |

Table 6 gives the compressive strengths of the five different specimens. Results show that, the highest compressive strengths were observed in concrete containing calcium nitrite and formaldehyde at 28 days of age. Both of these mixtures had compressive strengths approximately 50 and 45% foe seawater and 31 and 17% $H_2SO_4$. These results are in agreement with that of Cannon and Cady (1992) and Berke and Weil (1995). In contrast a mixture of potassium dichromate and formaldehyde caused a loss in the compressive strength the concrete blocks.

## 4. CONCLUSION

A comparative study of some commercially available corrosion inhibitors were conducted in the concrete test laboratory of I.T.B. Nigeria Ltd., Port Harcourt with a view to determine the suitability of the different inhibitors in different test media (seawater and dilute sulphuric acid) and also ascertain the effects of the inhibitors on the mechanical properties of the prepared concrete blocks. The concrete blocks used for the experiment were made in accordance with ATMC 109-92 and the reinforced steel bars cut based on BS 4466 specifications. The compressive strength of the specimen were determined in accordance with ASTMC 39-96. However, for this corrosion study, the potential technique was used with copper-coper sulphate half-cell as the reference electrode. Potential readings were taken for a period of 12months.

The experimental results show that, in seawater, admixture of potassium dichromate and formaldehyde were identified as a good inhibitor for concrete mix, but it caused a substantial loss of compressive strength while calcium nitrite exhibited the best inhibiting qualities with no effect on the compressive strength of the concrete blocks. Hence calcium nitrite is recommended as the best inhibitor for concrete structures that will be exposed to marine conditions. It is evidence from the results, that all the inhibitors used showed good inhibiting properties to the embedded steel rods when immersed in dilute sulphuric acid, calcium nitrite and formaldehyde had no negative effect on the compressive strength of the concrete blocks. The calcium nitrite and the mixture of potassium dichromate and formaldehyde were the most effective inhibitors in the two media studied. Hence they are recommended for concrete structures that will be subjected to acidic environment.

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