

EFFECT OF INHIBITOR CONCENTRATION IN ITS ADMIXTURE WITH FIXED AMOUNT OF SODIUM CHLORIDE ON THE ELECTRO-CHEMICAL CORROSION OF MILD STEEL REINFORCEMENT BARS

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ABSTRACT

Electrochemical potential monitoring experiments have been performed on the mild steel rebars embedded in concrete admixed with two different inhibitors in variable concentrations and sodium chloride salt, and exposed to 0.5M dilute sulphuric acid and sea water environments. The electrode potential of the reinforcing steel rebar in the concrete was monitored during the experiments and this paper reports the observed electrochemical response. Neither the various concentrations of sodium nitrite inhibitor nor that of the sodium benzoate alone could provide any effective protection to the embedded steel. The combination of the two inhibitors, however, gave synergistic protective effect at some concentrations in the two different test media.

INTRODUCTION

In a recent paper,⁽¹⁾ the effect of various pre-determined constant concentration of some inhibitors on the electrochemical corrosion of mild steel reinforcement in concrete in sea water was reported. Due to the importance of steel reinforced concrete as one of the most widely used materials of construction throughout the world, an attempt has been made in this work at looking into the effect of variation of sodium nitrite and sodium benzoate inhibitors' concentrations on the electrochemical corrosion behaviour of the embedded steel in concrete in two different test media - dilute sulphuric acid and sea water.

Use of inhibitors as one of the means of protecting reinforced steel from corrosion in potentially corrosive environments has long been recognized. Various authors,⁽²⁻⁸⁾ have reviewed and/or worked on this research subject at different times. However, further work still needs to be done as a means of contributing to the already existing knowledge on this research field.

The sea water environment used in this work was to simulate the marine corrosion effects. Sea water with the high sodium chloride content plus the other constituent ions, is very corrosive to ferrous materials in particular. The sulphuric acid was used to simulate the bacterial or microbial environment. Sodium chloride was added to the concrete mix to accelerate the corrosion of the embedded steel by providing increased chloride ions in the matrix and particularly around the reinforcing steel rebar.

EXPERIMENTAL PROCEDURE

Preparation of Concrete Block Samples:

Concrete blocks made of Portland cement, sand, gravel and water, each with a reinforcing steel rebar embedded in it were used for the experiment. Each concrete block was 160mm long, 100mm wide, and 100mm thick. All the blocks were prepared with 1:2:4 (C:S:G) - cement; sand; gravel ratio. The formulation for the reinforced concrete specimens used, in Kg/m³, was: Cement 320; Water 140; sand 700 and Gravel 1150. The water/cement (W/C) ratio was 0.44.

Thirteen sets of blocks comprising two specimens which were cast with different inhibitor concentrations admixed. The percentages quoted below for each of the admixed inhibitors and the sodium chloride were computed, basing them on every 10Kg weight of the concrete from which the blocks were made. All the chemicals used were AnalAR grade. The sets were prepared as presented below:-

1. 10% sodium chloride and no inhibitor.
2. 5% Sodium nitrite and 10% sodium chloride
3. 10% sodium nitrite and 10% sodium chloride
4. 15% sodium nitrite and 10% sodium chloride
5. 20% sodium nitrite and 10% sodium chloride
6. 5% sodium benzoate and 10% sodium chloride
7. 10% sodium benzoate and 10% sodium chloride
8. 15% sodium benzoate and 10% sodium chloride
9. 20% sodium benzoate and 10% sodium chloride
10. 20% sodium nitrite, 5% sodium benzoate and 10% sodium chloride
11. 15% sodium nitrite, 10% sodium benzoate and 10% sodium chloride
12. 10% sodium nitrite, 15% sodium benzoate and 10% sodium chloride
13. 5% sodium nitrite, 20% sodium benzoate and 10% sodium chloride.

Set 1 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 :

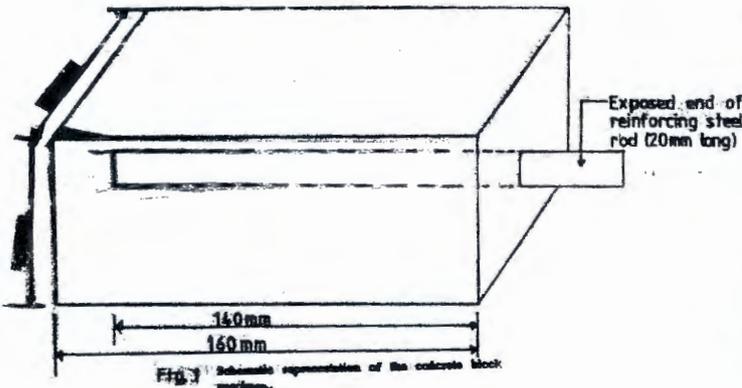
0.3% C, 0.25% Si, 1.5% Mn, 0.04% P, 0.64% S, 0.25% Cu, 0.1% Cr, 0.11% Ni, and the rest Fe.

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 strains on the steel specimens before embedded in the concrete block.

Each steel rebars 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. Fig. 1. This part was also used for

the water (from the Atlantic coast of Lagos), and dilute sulphuric acid (0.5M) which simulates microbial environment was used as test media.



Potential Measurement:

Each concrete block was partially immersed in their respective test medium such that the liquid level was just below the exposed reinforcing steel but not making any contact with it. The potential readings were obtained by placing a copper sulphate electrode firmly on the concrete block, Fig. 2. One of the two lead terminals of a digital voltmeter was connected to the copper sulphate electrode and the other to the exposed part of the embedded steel rebar to make a complete electrical circuit. 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 5-day intervals for a period of 80 days. All the experiments were performed under free corrosion potential and at ambient temperature.

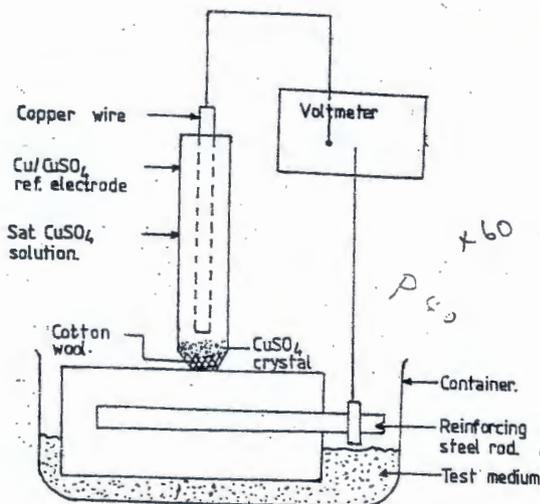


Fig.2. Schematic representation of experimental set-up.

RESULTS AND DISCUSSION

5%, 10%, 15% and 20% by wt. sodium nitrite and 10% by wt. sodium chloride:

The curves of potential (mean) vs. time of exposure for the steel reinforced concrete admixed with 5% sodium nitrite and 10% sodium chloride by weight and partially immersed in 0.5M sulphuric acid and sea water respectively, are presented in Fig. 3.

Both media showed continuous corrosion throughout the experimental period. However, in the first 20 days, the sulphuric acid medium exhibited fairly constant potential before experiencing a sharp drop in the 25th day achieving a potential of -700mVcse. This phenomenon might be due to the depassivation by sulphate and chloride ions of the film formed by the complexes due to the reaction between sodium nitrite and the alkaline concrete constituents. At the potential of -700mV on the 25th day, corrosion of the reinforcing steel rebar was expected to occur or to have occurred. A low negative potential of between -650 and -700mVcse prevailed between the 25th day and the 50th day, beyond which the corrosion potential gradually increased positively to the end of the experiment. This seemed to be a repassivation phenomenon.

The sea-water medium showed a fluctuating corrosion potential between -479 and 600mVcse throughout the period. This observation could be due to the unstable nature of the film formed around the steel rebar resulting from the complexes produced by the reactions between the concrete mix, sodium nitrite and sodium chloride. In general, the sodium nitrite inhibitor could not be regarded as being effective here at the percent concentration used.

Fig. 4 shows the curves of mean corrosion potential vs time of exposure for the steel reinforced concrete block specimens admixed with 10% sodium nitrite and 10% sodium chloride by weight and partially immersed in sulphuric acid and sea water respectively.

Continuous corrosion reactions were observed in both test media. More passivating initial potentials occurred when compared with that of Fig. 3. The drop in corrosion potential in the first 10 days for the two test media might be due to the unstable nature of the film formed by the complexes formed within the alkaline concrete matrix around the embedded steel rebar by the chloride and sulphate ions. The fact that the steel rebar was scraped before embedding in the concrete also contributed to the initial active interfacial reaction.

After the 10th day there was a continuous repassivation corrosion reaction throughout the rest of the experimental period for the test in sea water, achieving a potential of -380 mVcse in the 30th day and up to the 40th day for the

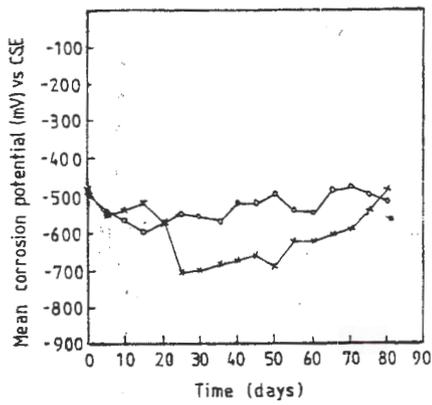


Fig. 3. Variation of corrosion potential with time for mild steel reinforcement in concrete with 5% by wt. sodium nitrite and 10% by wt. sodium chloride in sea water (o) and dilute sulphuric acid (x).

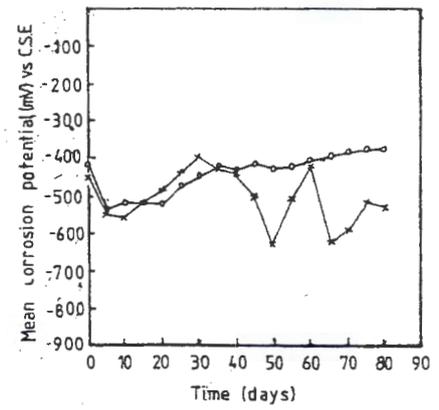


Fig. 4. Variation of corrosion potential with time for mild steel embedded in concrete with 10% by wt. sodium nitrite and 10% by wt. sodium chloride in sea water (o) and dilute sulphuric acid (x).

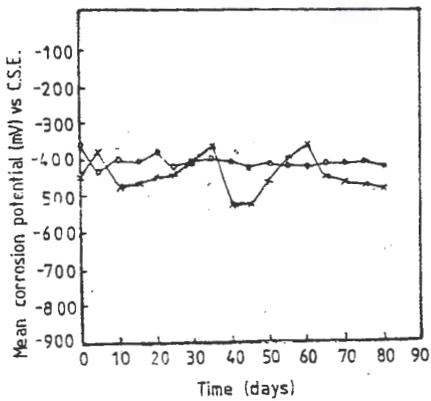


Fig. 5. Variation of corrosion potential with time for mild steel reinforcement in concrete with 15% by wt. sodium nitrite and 10% by wt. sodium chloride in sea water (o) and sulphuric acid (x).

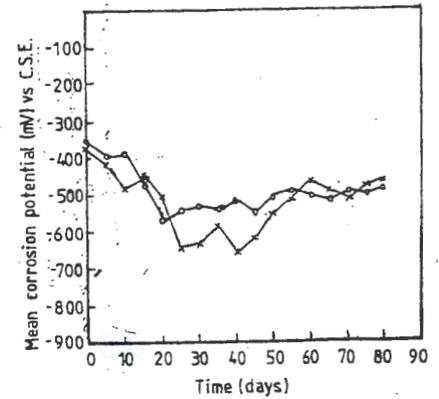


Fig. 6. Variation of corrosion potential with time for mild steel reinforcement in concrete with 20% by wt. sodium nitrite and 10% by wt. sodium chloride in sea water (o) and sulphuric acid (x).

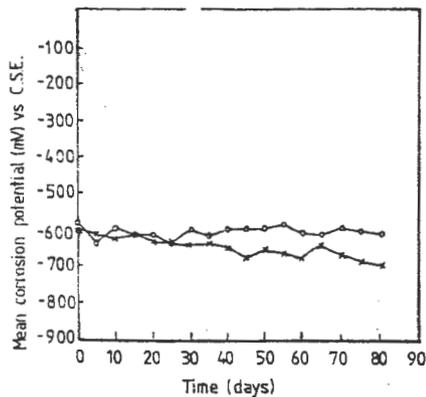


Fig. 7. Variation of corrosion potential with time for mild steel reinforcement in concrete with 5% by wt. sodium benzoate and 10% by wt. sodium chloride in sea water (o) and chl. sulphuric acid (x).

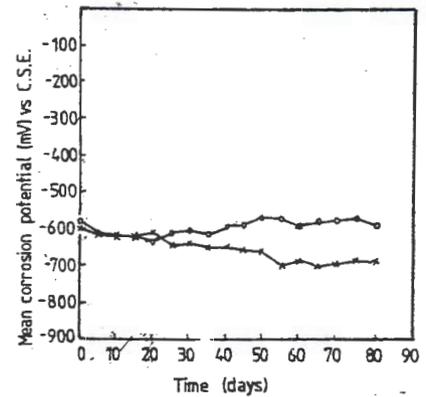


Fig. 8. Variation of corrosion potential with time for mild steel reinforcement in concrete with 10% by wt. sodium benzoate and 10% by wt. sodium chloride in sea water (o) and dil. sulphuric acid (x).

test in sulphuric acid before the occurrence of the fluctuating depassivation and repassivation for the rest of the period of the experiment. Apparently, there was decrease in the active corrosion reactions when the 10% sodium nitrite was used as compared with the 5% sodium nitrite. It was particularly more effective in the sea water than the dilute sulphuric acid test environment.

The curves of the corrosion potential (mean) vs exposure time for the steel reinforced concrete block specimens admixed with 15% sodium nitrite and 10% sodium chloride by weight and partially immersed in sulphuric acid and sea water respectively, are presented in Fig. 5.

No significant active corrosion reaction was observed in the sulphuric acid test medium except during the 40th to the 50th day of the experiment and slightly from the 60th to the 80th day. In the sea water environment, there were very slight potential fluctuations of depassivation and repassivation corrosion reactions. The range of corrosion potential was between 346 and 426Vcse. The steel/test environment interfacial reaction was minimal. This could be attributed to the increasing effective inhibiting action of the increased percentage of the sodium nitrite inhibitor in this test medium. Though there was improved active corrosion inhibition, the sodium nitrite inhibitor could be observed here to be less effective in the sulphuric acid medium when compared with the sea water test environment. The range of corrosion potential in the sulphuric acid test medium was between 367 and 528mVcse.

The curves of the corrosion potential (mean) vs exposure time for the steel reinforced concrete block specimens admixed with 20% sodium nitrite and 10% by wt. sodium chloride and partially immersed in the sulphuric acid and sea water media respectively, Fig. 6, did not show any improved inhibiting effect when compared with the results in Fig. 5. Though fluctuating, an active corrosion reaction occurred in each of the two test media until the 20th and 25th day before a fluctuating repassivation corrosion reactions occurred till the end of the experiment. The increased active corrosion reactions for the 20% by wt. sodium nitrite when compared with the 15% by wt. sodium nitrite in both test media, till about the 40th day of the experiment, is difficult to explain. From an initial corrosion potential of -383mVcse, the test in the sulphuric acid medium achieved a negative potential of -645 mV and -655 mVcse on the 30th and 40th days, respectively. The test in the sea water started with an initial potential of -362mVcse and achieved a potential of -546 mVcse on the 25th day. Addition of 15% sodium nitrite to the concrete therefore appeared to give an optimum inhibiting result in these two test media.

5%, 10%, 15% and 20% by weight sodium benzoate and 10% by weight sodium chloride

The initial potentials ranged between 364 to 595 mVcse, when 5% to 20% by wt. sodium benzoate and 10% by wt. sodium chloride as written above were added to the concrete block specimens and partially immersed in sulphuric acid and sea water test media, Figs. 7 - 10. With little range of potential fluctuations, the test in the sea water medium did not show any further increase in negative potential, but in the sulphuric acid, the potentials increased slightly negatively throughout the experimental period for all percentage of sodium benzoate inhibitor addition. The inference from the result is that sodium benzoate used could not inhibit effectively corrosion of the embedded steel rebar in the concrete in the two test environments. Sodium benzoate is a non-oxidizing inhibitor. Non-oxidizing inhibitors are known⁽⁹⁾ to be only effective at higher concentrations, since part of their function is to buffer the solution on the alkaline side of neutrality.

20% by wt. Sodium nitrite, 5% by wt. sodium benzoate and 10% by wt. sodium chloride:

The variation of corrosion potential with time curves for the mild steel rebar embedded in concrete with 20% by wt. sodium nitrite, 5% by wt. sodium benzoate, and 10% by wt. sodium chloride in both sea water and sulphuric acid test media is presented in Fig. 11. The corrosion potentials recorded for the test in sulphuric acid medium ranged between -230 mVcse and 330 mVcse. Within this range, the steel rebar could be said to be under passive conditions. The corrosion potential increased gradually, though with little fluctuations, to the end of the experiment. The effectiveness of the combined inhibitors as mentioned above is thus very significant. Though more negative in corrosion potentials, the corrosion reactions of the steel reinforcement in the sea water environment was also effective. The effectiveness of the combined inhibitors under the test environments would be due to their synergistic effect.

15% by wt. sodium nitrite, 10% by wt. sodium benzoate and 10% by wt. sodium chloride:

The curves of mean corrosion potential vs. exposure time for the steel reinforced concrete block specimens admixed with 15% by wt. sodium nitrite, 10% by wt. sodium benzoate and 10% by wt. sodium chloride and partially immersed in sulphuric acid and sea water test environments are presented in Fig. 12.

Throughout the experimental period the corrosion potentials ranged between 240 mV and 360 mVcse with little depassivation and repassivation corrosion reactions' fluctuations. Within this potential ranges, the embedded steel rebar could be said to be within a reasonable passive range where no any amount of significant active corrosion occurred. Compared with the individual results that emanated from the

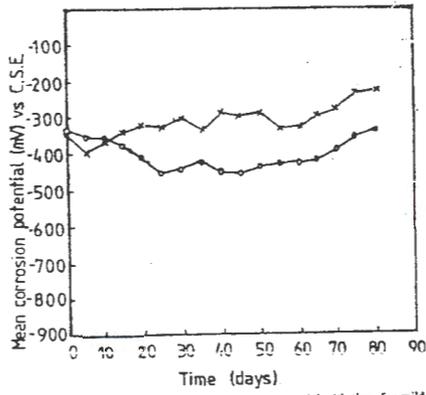


Fig. 11. Variation of corrosion potential with time for mild steel reinforcement in concrete with 20% by wt. sodium nitrite, 5% by wt. sodium benzoate, and 10% by wt. sodium chloride in both sea water (o) and sulphuric acid (x).

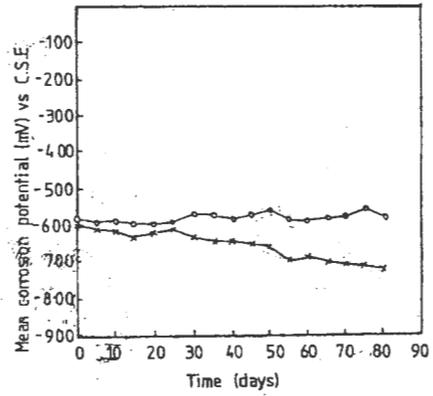


Fig. 9. Variation of corrosion potential with time for mild steel reinforcement in concrete with 15% by wt. sodium benzoate and 10% by wt. sodium chloride in sea water (o) and dilute sulphuric acid (x).

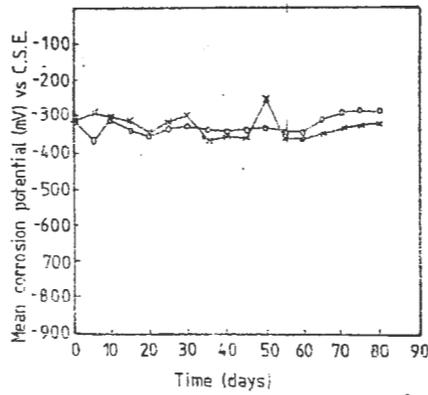


Fig. 12. Variation of corrosion potential with time for mild steel reinforcement in concrete with 15% by wt. sodium nitrite, 10% by wt. sodium benzoate and 10% by wt. sodium chloride in sea water (o) and dilute sulphuric acid (x).

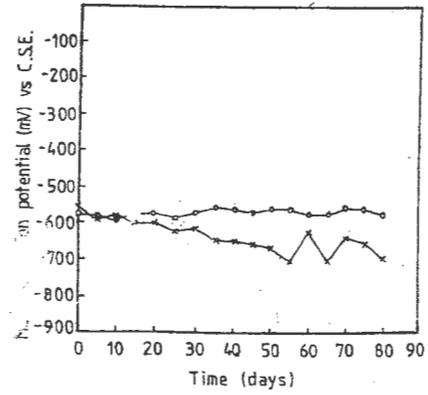


Fig. 10. Variation of corrosion potential with time for mild steel reinforcement in concrete with 20% by wt. sodium benzoate, and 10% by wt. sodium chloride in both sea water (o) and sulphuric acid (x).

use of sodium nitrite and sodium benzoate in turns, the effective inhibiting results obtained here would definitely be due to synergism of the two inhibitors working together. The two inhibitors at the concentrations used would have formed a very stable protective film, in complex with concrete constituents, around the embedded steel rebar and thereby disallowing the penetration of chloride and sulphate ions to the steel surface to cause corrosion reactions.

10% by wt., sodium nitrite, 15% by wt. sodium benzoate, and 10% by wt. sodium chloride.

When 10% by wt. sodium nitrite, 15% by wt. sodium benzoate and 10% by wt. sodium chloride were admixed with steel reinforced concrete test specimens and partially immersed in sulphuric acid and sea water test media, Fig. 13, the corrosion reactions became slightly more active than observed in Fig. 12. The corrosion potentials still ranged between 310mV and 515mVcse throughout the experimental period. The inhibiting effectiveness of the combined inhibitors has been reduced though there was increase in the amount of sodium benzoate added compared with that of Fig. 12. However, there was at the same time, a further reduction in the sodium nitrite concentration. It could thus be referred that sodium nitrite had more inhibiting effect despite their synergistic action. The sea water environment appeared to be more corrosive.

5% by wt. sodium nitrite, 20% by wt. sodium benzoate and 10% by wt. sodium chloride:

With the above concentrations of inhibitors and sodium chloride, there was further active corrosion of the embedded steel rebar in concrete in both test media as indicated by the corrosion potentials, Fig. 14. The test specimens in sulphuric acid medium however, was far more corrosive than in the sea water indicating lack of passivity by the inhibitors' protective film in that test environment. The chloride and sulphate ions would have penetrated the film barrier by diffusion. In the sea water test environment, the specimens maintained a passive corrosive reaction from the 15th day of the experiment to the end. Again, the very low sodium nitrite concentration in the concrete would have contributed significantly to the loss of steel rebars, passivity in the concrete, in spite of the increased concentration of the sodium benzoate.

10% by wt. sodium chloride and no inhibitor

Fig. 15 shows the curves for the mean corrosion potential vs. time of exposure for the steel rebar reinforced concrete block specimens admixed with 10% by wt. sodium chloride and partially immersed in sulphuric acid and sea water test environments respectively.

Both curves remained in the active corrosion potential range throughout the experimental period; ranging between 600

mV and 680 mVcse. There was no inhibitor added and that could account for the non-passive nature of the corrosion reactions. The chloride and sulphate ions had put the potential range in an active corrosion reactions range throughout.

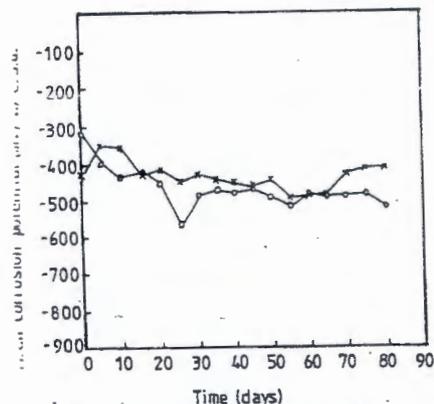


Fig.13 Variation of corrosion potential with time for mild steel reinforcement in concrete with 10% by wt. sodium nitrite, 15% by wt. sodium benzoate, and 10% by wt. sodium chloride in sea water (o) and sulphuric acid (x).

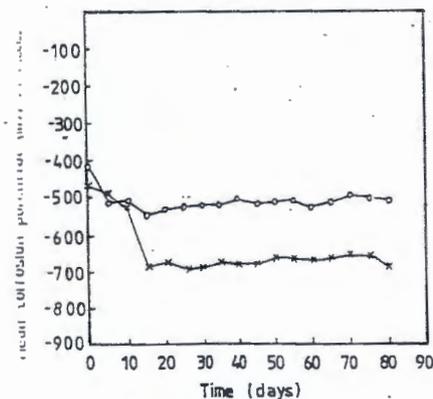


Fig.14. Variation of corrosion potential with time for mild steel reinforcement in concrete with 5% by wt. sodium nitrite, 20% by wt. sodium benzoate, and 10% by wt. sodium chloride in both sea water (o) and sulphuric acid (x).

CONCLUSION

1. Sodium Nitrite (NaNO_2) inhibitor alone did not provide effective inhibition to the corrosion of the embedded steel rebar in concrete, in both the sulphuric acid and sea water test media. However, a more stifling action of the progressive active corrosion reactions was shown in the sea water test environment.
2. Sodium benzoate inhibitor alone was also not effective in providing passivity for the steel rebar embedded in concrete and partially immersed in the sulphuric acid and sea water test media. The magnitude of the negative potentials recorded confirmed this inhibitor to be very less effective

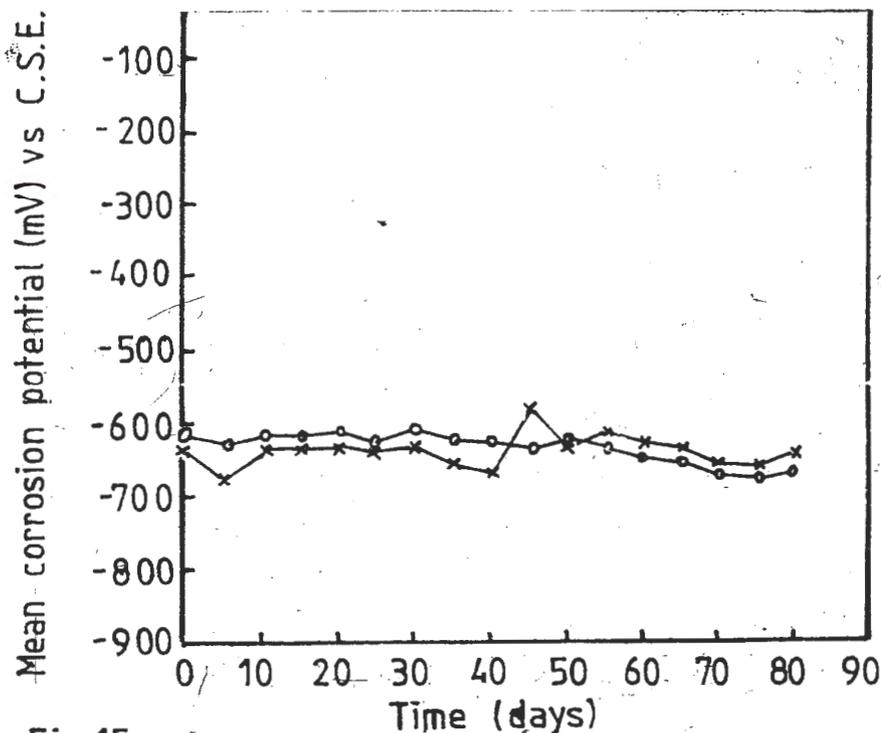


Fig.15. Variation of corrosion potential with time for mild steel reinforcement in concrete with 10% by wt. sodium chloride and no inhibitor in sea water (o) and sulphuric acid (x).

than the sodium nitrite in the two test environments.

3. The combination of the two inhibitors at the concentrations of 15% by weight sodium nitrite and 10% by wt. sodium benzoate; and 20% by wt. NaNO_2 and 5% by wt. sodium benzoate provided the optimal protective effect by synergism in the two test media. The two different concentrations could therefore be said to be the most suitable inhibitor concentrations for the steel reinforced concrete structures that will be exposed to dilute sulphuric acid (representing simulated microbial environment) and sea water (marine) environment.
4. The most negative potentials and hence the most active corrosion reactions of the embedded steel rebar in concrete in the two test media were obtained in the order: sodium benzoate > sodium nitrite > sodium nitrite + sodium benzoate.

ACKNOWLEDGEMENT

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