EFFECT OF CORROSION INHIBITORS ON SOME MECHANICAL PROPERTIES OF CONCRETE

Ogirigbo O. R. and Iyawe O. S.
Department of Civil Engineering, Faculty of Engineering,
University of Benin, Edo State, Nigeria
*Corresponding author: *okiemute.ogirigbo@uniben.edu*

Abstract
One of the destructive conditions faced by reinforced concrete structures in marine environments is chloride-induced corrosion of steel reinforcement in the concrete. These chlorides can enter into the concrete through two means – external (via chloride ingress) and internal (via salt contaminated aggregates or mix water). This chloride-induced corrosion can be reduced by several means such as the use of large concrete covers, admixtures e.g. fly ash, slag, etc., corrosion inhibitors, coatings, cathodic protection, penetrating sealers and chloride removal. This study investigated the effect of corrosion inhibitors on concretes exposed to chloride environments. The corrosion inhibitor used was sodium nitrite (NaNO₂) and it was applied in dosages of 0, 0.5 and 1.0% of the mix water. Concrete samples were prepared for grade 25 concrete, using brine (3% sodium chloride solution) as mix water. Various tests such as slump test, compressive strength test, and pull-out test were carried out to determine the effect of the corrosion inhibitor on the properties of the concrete. From the results obtained, it was discovered that as the dosage of the corrosion inhibitor was increased from 0 to 0.5%, there was a corresponding increase in the compressive strength of the concrete. However, as the dosage was increased from 0.5 to 1.0%, there was a decrease in the compressive strength. On the other hand, it was observed that the concrete-rebar bond strength obtained from the pull-out test increased with increase in the dosage of the corrosion inhibitor. This implies that higher dosages of corrosion inhibitors can be beneficial to the resistance against corrosion of steel reinforcement, and at the same time detrimental to the strength properties of the concrete.

Keywords: Sodium nitrite, Brine, Pull-out test, Internal chlorides, Concrete, Marine environments

1.0 INTRODUCTION

Reinforced concrete is a good steel and concrete combination that has been widely used over the last decades. The steel component often regarded as rebar, provides the tensile strength; while the concrete component, which has a high alkalinity (pH ranging from 12.5 to 13.5), provides protection to the steel reinforcement in the form of a physical barrier (Vaysburd and Emmons, 2004; Shan and Xu, 2016). This physical barrier is provided by the formation

of a thin passive film around the steel reinforcement (Elfmarkova, 2015).

Chlorides may enter into concrete through two main routes – external (in the form of admixtures, de-icing salts, and via the penetration of seawater) or internal (via the use of chloride contaminated materials such as aggregates and water) (Shi *et al*., 2012; Ogirigbo, 2016). Once these chlorides enter into the concrete, they lower the pH of the surrounding concrete and this in turn results in depassivation i.e. loss of oxide or protective layer over the steel reinforcement. Over time, the exposed steel reinforcement undergoes corrosion, and according to Bastidas-Arteaga *et al*. (2011), this can affect the load carrying capacity of the concrete structure by the loss of steel reinforcement section and the loss of the concrete-steel bond.

Appropriate design and making of reinforced concrete in line with codes and standards, and well-timed maintenance of the structures are essential requirements to ensure the structures last long and are efficient in aggressive environments (Abdulrahman *et al*., 2011). However, when these requirements are not adhered to, it becomes necessary to provide preventive measures that will sustain the service life of these structures. Several preventive measures have been identified in the construction industry that can be used; they include: use of large concrete covers, admixtures, corrosion inhibitors, coatings, cathodic protection, penetrating sealers and chloride removal.

Corrosion inhibitors are chemical admixtures added to concrete in small quantities, to delay or prevent the corrosion of the embedded steel reinforcement bars. Corrosion inhibitors are also used in the repair of reinforced concrete structures exposed to corrosion attack. In such applications, they are applied on the surface of the concrete structure by spraying or painting, and allowed to penetrate into the concrete via cracks on the surface of the concrete (Roberge, 2000). As the corrosion inhibitor enters into the concrete, its molecules undergo chemical reaction with the surrounding cement paste and steel reinforcement, to reinstate the passivating layer surrounding the steel (Broomfield, 1997).

Corrosion inhibitors are classified based on their mode of protection. Some protect by influencing the anodic reaction, while some protect by influencing the cathodic reaction. Others have the capacity to influence both the anodic and cathodic reactions (Broomfield, 1997; Hansson *et al*., 1998). Examples of corrosion inhibitors commonly used in the construction industry are nitrates, phosphates, chromates, benzoates, borates (Konno *et al*., 1982; Isaacs *et al*., 2002) and nitrites which are commonly used in reinforced concrete structures (Montes *et al*., 2004; Sideris and Savva, 2005; Anna *et al*., 2006).

Nitrites have been reported to be one of the most effective corrosion inhibitor that can be used to protect the steel in concrete (Okeniyi *et al*., 2014; Gao *et al*., 2015; Shi *et al*., 2017). When used as corrosion inhibitors, they have the ability to delay the time to failure of the passivating layer surrounding the steel, and thus slow down the rate of corrosion of the embedded steel reinforcement (Tang, 2017). Several studies e.g. Liu *et al*. (2005), have shown that rapid setting will occur in cement paste when the content of calcium nitrite or magnesium nitrite is 4%. For potassium nitrite, rapid setting will occur at a content of 2%; while for lithium nitrite, sodium nitrite and bismuth nitrite, rapid setting will only occur at high contents of 10%. Amongst the various types of nitrites, sodium nitrite and calcium nitrite appear to be the ones mostly used in the construction industry. As regards sodium nitrite, a study by Garc´es *et al*. (2011) showed that it had the potential of accelerating the occurrence of alkali-aggregate reaction, especially when used in high proportions. On the other hand, calcium nitrite has been shown to have excellent rust resistance ability and

accelerated early strength development, but can also reduce the setting time and increase shrinkage, when used in high proportions (Ormellese *et al*., 2009).

The use of corrosion inhibitors in the Nigerian construction industry is not very common, and it is well known that there are certain areas in Nigeria where the use of salt contaminated materials for concreting may be unavoidable, e.g. the coastal areas. In such instances, one way to ensure that the service lives of the concrete structures are not affected by corrosion of the embedded steel reinforcement, may be to use corrosion inhibitors as admixtures. However, very few studies have looked at the impact the use of corrosion inhibitors will have on concrete containing chlorides that may have been introduced into the concrete either as hydration accelerating admixtures or via the use of chloride contaminated materials. This study aims to look at the effect of corrosion inhibitors on some of the properties of concrete containing chlorides.

2.0 MATERIALS AND METHODS

2.1 Materials
The materials used in carrying out the study are as follows:

2.1.1 Cement
The cement used for the study was procured from a local vendor. It had a strength grade of 42.5 and conformed to the specifications given in BS EN 196-1:2005.

2.1.2 Aggregates
The fine aggregate used for the study was obtained from a quarry site at Ugbioko community at Edo State. Sieve analysis conducted on it placed it at Zone II, with a maximum particle size of 4.75 mm. Grading of the fine aggregates conformed to BS EN 12620:2002+A1. The coarse aggregate used was crushed granite, with particle size ranging from 14 – 20 mm, and a specific gravity of 2.59.

2.1.3 Water
Potable water as obtained from the University's main water supply was used for the study.

2.1.4 Corrosion inhibitor
The corrosion inhibitor used for the study was sodium nitrite ($NaNO_2$). It was obtained from the Chemistry Laboratory in the University of Benin, Benin City, Nigeria, in solid form and diluted to the required concentration.

2.1.5 Steel reinforcement bar (Rebar)
The steel reinforcement bars used for the study was obtained from the Production Engineering Laboratory in the University of Benin, Benin City, Nigeria. The size of the rebar used was 12 mm and it was cut and bent into nine (9) pieces.

2.2 Preparation of mix water
Brine was used as the mix water for casting the concrete. The solution was prepared by mixing 30g of salt to 1 litre of water. This has similar chloride concentration as that of Atlantic seawater (Hewlett, 2004). The diluted corrosion inhibitor solution was added to the brine at different percentages of 0%, 0.5% and 1% of the mix water, and mixed thoroughly to obtain an even solution.

2.3 Sample preparation and curing
Three concrete mixes was used for this study. These were designated as C0%, C0.5% and C1.0% (as shown in Table 1). The C0% mix did not contain any corrosion inhibitor, while the C0.5% and C1.0% contained 0.5% and 1.0% dosage of corrosion inhibitors respectively. The mixes were designed to have a 28-day strength of 25 MPa.

The various constituents (cement, water and aggregates) were weighed separately and placed in the concrete mixer. After mixing, the concrete was placed into 100

mm cube moulds. For concrete samples to be used for pull-out test, rebars were inserted into the cast concrete in the moulds, to a depth of 50 mm. Thereafter, the moulds were covered with thin polythene sheets and left to cure under air in the laboratory for at least 24 hours (Figure 1), after which the cubes were demoulded and taken to the curing room.

Due to the fact that the concrete cubes were mixed with brine water, they had to be cured separately so as not to contaminate the control concrete cubes (i.e. the C0% mix) in the curing bath. Fifteen (15) concrete cubes having

0% dosage of corrosion inhibitor were cured separately in a different bath, while the remaining 30 concrete cubes (15 of 0.5% and 15 of 1.0 % dosage of corrosion inhibitor) were cured in a separate curing bath. Curing was done for 28 days.

The concrete cubes for compressive strength test were brought out from the curing baths after 3, 7, 21 and 28 days; while the concrete cubes for pull-out tests were brought out from the curing baths after 28 days of curing.

Table 1: Mix proportion of the different materials

	Mix designation		
	C0%	C0.5%	C1.0%
Water/cement ratio	0.51	0.51	
Cement (kg/m^3)	412	412	412
Fine aggregate (kg/m^3)	619	619	619
Coarse aggregate (kg/m^3)	1149	1149	1149
Water (kg/m^3)	210	210	210
Corrosion inhibitor (g)	0	19	38

(a)   (b)
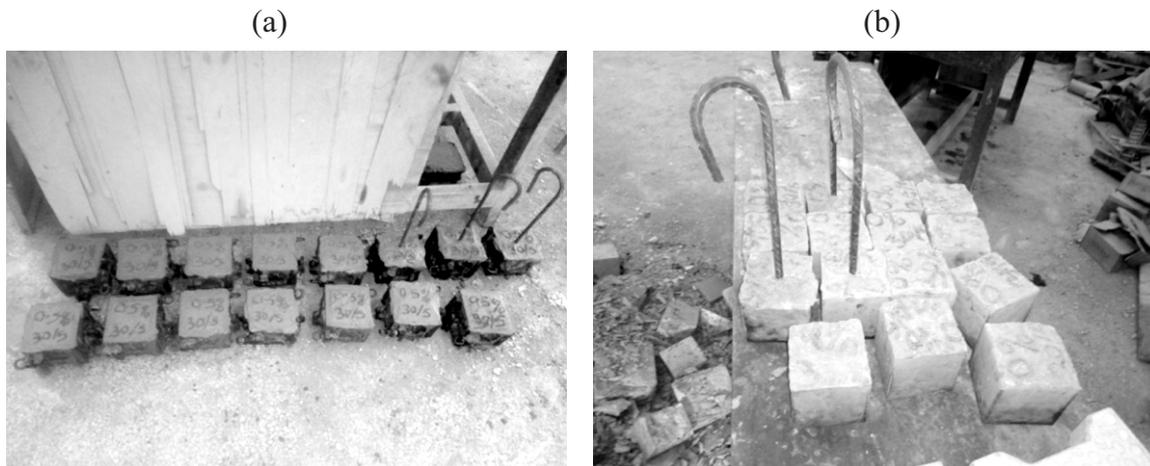
Figure 1: (a) Concrete cubes left to cure under air for 24 hours (b) Concrete cubes after de-moulding

2.4 Test methods

2.4.1 Slump test
After mixing, a portion of the concrete was poured into the slump cone to determine the slump value in accordance with EN 12350-2:2002. This was used to assess the impact of the corrosion inhibitor on the workability of the concrete.

2.4.2 Compressive strength test

Compressive strength was determined on triplicate samples at specific ages of 3, 7, 21 and 28 days, to study the effect of the corrosion inhibitor on the early and later strength of the concrete. At the test age, the concrete cubes were brought out from their respective curing environment, surface dried (as applicable), and weighed before testing. The compressive strength (in MPa) was taken as the average failure load (in kN) divided by the cross sectional area of the concrete cube (in mm^2), as shown in Equation 1 below:

$$P = \frac{F}{A} \qquad (1)$$

where:

P   Compressive strength in Mpa

F   Failure load in kN

A   Cross sectional area of concretecube in mm^2

2.4.3 Pull-out test

After 28 days of curing, samples for the pull-out test were brought out from the curing room for testing. Testing was done using a tensile machine. The concrete sample was placed in a concrete bracket (as shown in Figure 2a) to enable the tensile machine to have adequate grip on the concrete sample and on the rebar, and to ensure effective pulling of the rebar out of the concrete. Thereafter, a tensile force was applied onto the rebar by pulling it upwards. The force at which cracks appeared on the concrete, at the region around the rebar, was recorded as the bond strength of the concrete-rebar bond.

(a)   (b)

Figure 2: (a) Concrete bracket for holding concrete cubes (b) concrete cubes after testing showing cracks at interface between concrete and rebar

3.0 RESULTS AND DISCUSSION

3.1 Slump test

The result obtained from the slump test is shown in Table 2. From the result, it can be seen that as the dosage of the corrosion inhibitor was increased from 0 to 0.5%, there was an increase in the slump value from 240

mm to 256 mm, corresponding to an increase of about 7% in the workability of the concrete. However, on further increase of the dosage of the corrosion inhibitor to 1.0%, there was a decrease in the slump from 256 mm to 240 mm. Similar findings were also reported in the study by Ogirigbo *et al*. (2016), where they investigated the effect of sodium nitrite as a corrosion inhibitor on the workability and strength development of concrete. In their study, it was observed that as the dosage of the corrosion inhibitor was increased from 0.0% to 0.3%, there was an increase in the workability of the concrete mixes; however, at higher dosages of 0.6% and 1.0%, there was a corresponding decrease in the workability of the concrete mixes. This may be due to the increase in the alkali-aggregate reaction that usually occurs when sodium nitrite is used as a corrosion inhibitor, as stated by Gaidis (2004) and Garc´es *et al*. (2011).

Table 2: Effect of corrosion inhibitor on workability

Mix	Slump (mm)
C0%	240
C0.5%	256
C1.0%	240

3.2 Compressive strength

Figure 3 shows the average compressive strength of all the mixes. From the figure, it can be seen that the addition of 0.5% of corrosion inhibitor resulted in an increase of about 6.5% in the early age (3 day) strength, as compared to the control mix (C0% mix). After 28 days, the difference between the strength of the C0.5% mix and the C0% mix was seen to increase to about 10%. This agrees with the results obtained by O'Reilly *et al*. (2013), where a 12% increase in compressive strength was observed for mixes containing corrosion inhibitors. In contrast, as the dosage of the corrosion inhibitor was increased to 1.0%, a deteriorating effect was observed in the strength. There was a decrease in the compressive strength of about 11% and 7% for the compressive strength at 3 days and 28 days respectively, for the C1.0% mix as compared with the C0% mix. Similar findings were also reported by Gaidis (2004) and Ogirigbo *et al*. (2016), where it was also observed that an increase in the dosage of corrosion inhibitor resulted in a decrease in the compressive strength. The reason for this can also be attributed to increased alkali-aggregate reaction, which is well known to cause a reduction in the compressive strength of concrete.
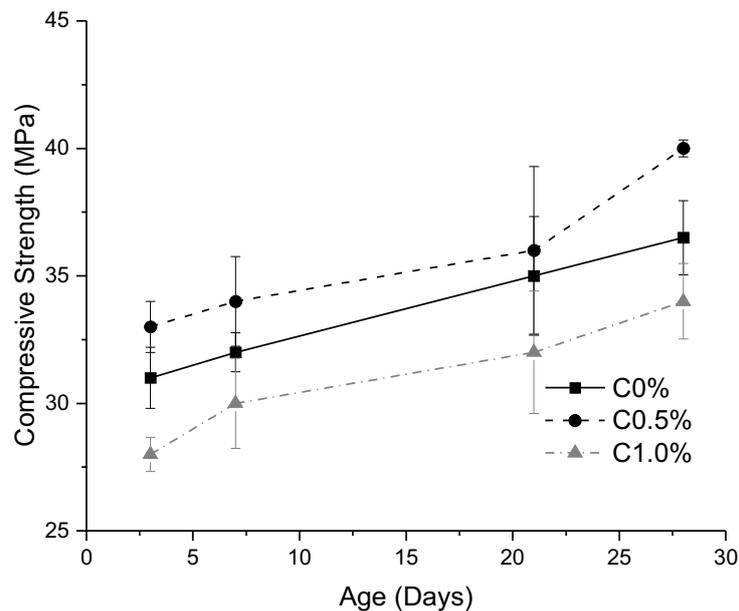
Figure 3: Effect of corrosion inhibitor on compressive strength of all mixes

3.3 Concrete-rebar bond strength

The average concrete-rebar bond strength as obtained from the pull-out test conducted on the 28 days old samples is shown in Figure 4. The lowest bond strength was recorded in the control mix, while the highest bond strength was recorded for the mix containing 1.0% dosage of the corrosion inhibitor. The bond strength of the C0.5% mix was about 11.5% higher than that of the control mix (C0% mix); whereas, that of the C1.0% mix was about 38% higher than that of the control mix. The presence of chlorides in the mix water is bound to have initiated some form of localised rebar corrosion, and this might have resulted in the low bond strength observed in the control mix. The addition of the corrosion inhibitor to the mix might have resulted in some form of inhibition or slowing down of the corrosion process; hence, the higher bond strength values observed in the mixes containing corrosion inhibitors. As against what was observed in the slump and compressive strength results, increasing the dosage of the corrosion inhibitor resulted in a corresponding increase in the concrete-rebar bond strength. While a difference of about 11.5% was observed between the C0% mix and the C0.5% mix, a difference of about 24% increase was observed between the C0.5% mix and the C1.0% mix. This underlines the effect of the corrosion inhibitor in counteracting the corrosion process.
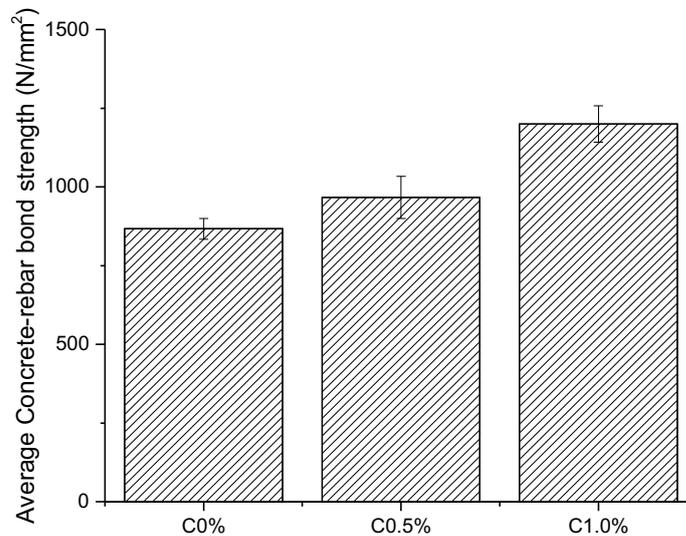
Figure 4: Effect of corrosion inhibitor on concrete-rebar bond strength

CONCLUSION

This study investigated the effect of sodium nitrite as a corrosion inhibitor on the compressive strength and bond strength of concrete. Based on the results obtained, the study has shown that the use of sodium nitrite as a corrosion inhibitor for concrete can enhance the compressive strength properties of the concrete, when used in low dosages of 0.5% and below. At higher dosages greater than 0.5%, it will result in a reduction of the compressive strength. The addition of sodium nitrite as an admixture can also enhance the concrete-rebar bond strength of concrete. This is particularly significant for concretes containing chloride-contaminated materials. The higher the amount of sodium nitrite added, the higher the bond strength

Overall, one may conclude that the appropriate dosage of sodium nitrite to be used as a corrosion inhibitor will depend largely on the application. For instances involving reinforced concrete structures, where concrete-rebar bond strength may be of more importance, dosages up to 1.0% per mix water can be applied; whereas for other normal applications, dosages up to 0.5% can be used.

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