EFFECTS OF STARCH ADDITIONS IN CONCRETE ON THE PASSIVATION OF STEEL IN REINFORCED CONCRETE EXPOSED TO AGGRESSIVE ENVIRONMENTS

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ABSTRACT: *Corrosion of steel reinforcement embedded in concrete is a major cause of deterioration of reinforced concrete structure. Corrosion agents penetrate concrete due to its porous nature. This study examines the effects of cassava starch in concrete as corrosion inhibitor of reinforcement steel embedded in concrete. Starch enhances the protection of reinforcement by forming a protective film of gamma ferric oxide around the steel as well as reducing the pore spaces in concrete thereby impeding the ingress of corrosion agents. The effects of cassava starch addition, different curing types and varying concrete cover to reinforcement on the rate of corrosion of embedded reinforcing steel were investigated in the study. The result of the study shows that the use of 15% cassava starch in concrete mixtures, curing of reinforced concrete samples by sprinkling with water and a concrete cover of 40 mm improves the passivation potential of the embedded steel in concrete exposed to either chloride or sulphate environments.*

Keywords: Cassava Starch; Corrosion Inhibitor; Reinforcement Steel; Aggressive Environment; Passivation
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INTRODUCTION

The corrosion of embedded steel reinforcement in concrete is one of the most common reasons for structural failure in concrete structures. Premature deterioration of concrete structure as a result of corrosion of embedded steel reinforcement is particularly pronounced in coastal areas, and in cold climates where winter deicing chemicals are used, and in high humidity locations (David, 1999; Moskivn, 1983). The ingress of moisture, chloride ions, and or carbon dioxide through pores in concrete can initiate corrosion of steel reinforcement embedded in concrete (Mehta and Monteiro, 2008; Neville and Brook, 1990). However, concrete with its high alkalinity protect reinforcing steel by forming film of gamma ferric oxide (Addis, 2001). After initiation of corrosion, the corrosion products (iron oxides and hydroxides) develop expansive stresses that crack and spall the concrete cover (Broomfield, 2003) further exposing the reinforcement to direct environmental attack thus accelerating the deterioration of the concrete structure (Addis, 2001).

There are various corrosion inhibiting admixtures used in concrete with the aim of reducing the intrusion of chloride and sulphate containing water into concrete. The majority of these inhibitors are based on polymeric compounds, silicon chemistry, metallic stearates, or hydrophilic crystalline materials (David, 1999). The protection mechanism of the inhibitors is to block water or to reduce corrosive specie ingress into concrete. These types of admixture do not directly protect the steel rebar themselves, but impedelectrolyte ingress into concrete. Incorporating a second protection mechanism to the steel rebar itself is much desired in a well-thought admixture for the long term integrity of concrete structure (Emmons and Sordyl, 2006; Furniss, et al., 1987). Cassava starch enhances the protection of steel by forming a protective film on steel rebar while simultaneously reducing ingress of water soluble corrosive species through the concrete cover as a result of its pore blocking effect (Maciej, 2010). Limited works however exist on the use of cassava starch as a protective material against steel corrosion. For example, Sugama, et. al., (2002) employed a polyoganosiloxane-grafted potato starch and unmodified potato starch as coating to afford protection of aluminum while Abdel- halemm et al. (2008) employed a soluble starch, among other compound to improve the pitting corrosion resistance of carbon steel.

Additionally, Rosliza and Wan Nik (2009) reported that cassava starch could improve the corrosion resistance of an aluminum alloy in sea water. However, these authors did not specify the type of starch they used, the amount of functional groups present in the starch and more importantly are not added as admixture to concrete (Zhang et al., 2008; Herrero-Martinez et al., 2004; Wang et al., 1998). In the present study, an admixture developed by employing cassava starch was added to concrete mixture in varying percentages. The study is aimed at determining the optimum percentage addition of cassava starch in concrete for the corrosion inhibition of embedded steel reinforcement. Furthermore, the effects of different curing types on concrete as well as the effect of cover concrete depths on the rate of corrosion of steel in concrete were also investigated.

EXPERIMENTAL PROCEDURE

Materials

Starch: The starch used in this study was extracted from slurry of grated fresh cassava tuber. The composition of the cassava starch is as shown in Table 1.

Table 1: Composition of Starch used in the Concrete

Moisture	Starch	Total Sugar	Lipid	Protein	Ash
16.2%	88.43%	0.14%	0.26%	0.07%	0.1%

Binder: The binder type used in the concrete is that commonly used in construction sites in Nigeria. Ordinary Portland Cement 42.5N of the Dangote brand was used as the binding agent.

Aggregates: The aggregate used are coarse aggregate (Stone), and fine aggregate (sand).The coarse aggregate is of maximum size 19mm, sourced locally from Zerock Quarry Lokoja, Kogi State, Nigeria, while the fine aggregate was obtained from river bank in Idah, Kogi State, Nigeria. The aggregate were sun dried to control moisture content during usage conforming to the requirement of BS 882 (1982). Figure 1 presents the sieve analysis result for the fine and coarse aggregate.

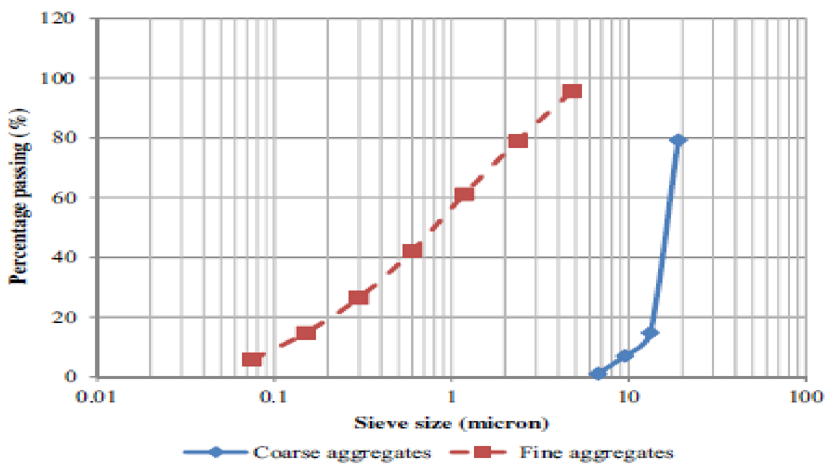

Figure 1: Sieve Analysis Graph for the Coarse and Fine Aggregate

METHODS

The test program undertaken in this study, to assess the influence of starch as an admixture in concrete is twofold. Firstly, it is to explore the effect of cassava starch on the compressive strength of concrete, and secondly, to examine the passivation effects of cassava starch addition in concrete on reinforcement steel embedded in concrete elements exposed to aggressive environments. The reinforced concrete elements were exposed to two aggressive environments – chloride and sulphate environments.

Mixing Procedure and Sample Preparation

Concrete cube samples measuring 150 X 150 X 150 mm and concrete prism measuring 100 X 100 X 150 mm were cast using each of the concrete mixture listed in Table 2. The solid materials were weight batched on a laboratory balance to the minimum accuracy. Mixing was carried out manually following these procedures:

- Mix binder uniformly with aggregate
- Introduce water gradually over a few minutes
- Mix for a further few minutes.

At the end of mixing, slump test was performed to monitor the workability.

Table 2: Mixture Proportion (kg/m^3) of the Various Concrete Used

Binder Combination	Concrete Mixture Label	Binder (kg)		Aggregates (kg)		Water Content (kg)	W/C	Slump (mm)
		Cement	Starch	Fine	Coarse			
0% CA	M0	5	0	13	24	3.20	0.6	105
5% CA	M5	5	0.25	13	24	3.20	0.6	95
10% CA	M10	5	0.50	13	24	3.20	0.6	95
15% CA	M15	5	0.75	1	24	3.20	0.6	90
20% CA	M20	5	0.10	13	24	3.20	0.6	90

The prism and cube mould were filled with concrete in single layer and hand press on a mechanical vibrating table for 20 seconds while sufficient concrete was added to fill the mould while on the table. Reinforcing steel was embedded at 20 and 40 mm cover respectively for the prism samples (see Figures 1 and 2). The samples top were smoothen and kept under polythen for 24 hours. After demoulding the concrete samples, the next day the concrete prism and cubes were divided into three groups for the purpose of curing as stated in section 2.4.

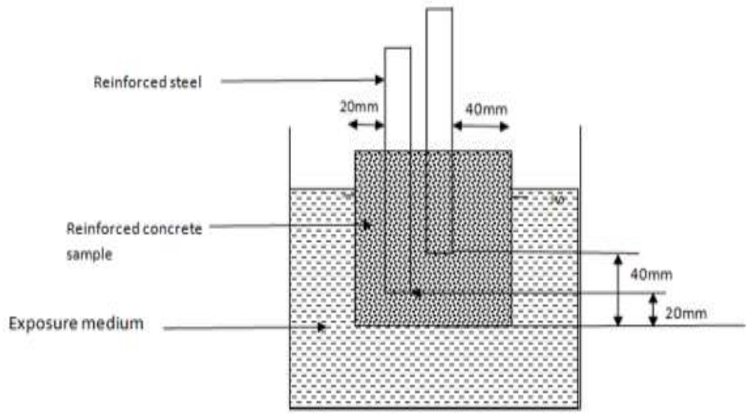

Figure 2: Sketch of Prism Sample showing Reinforcement Positioning and Exposure Arrangement in Aggressive Environments

Curing

In order to have concrete with varying strength and permeability that will replicate what is obtainable in practice and also to depict the exact situation concrete are treated to on construction site, the reinforced concrete samples were divided into 3 set after demoulding and the sets treated to the following curing conditions:

i. No curing was given to the reinforced concrete samples after demoulding. The samples were immediately exposed to the aggressive environments.
ii. After demoulding the reinforced concrete samples, they were immediately treated to 7 days moist curing. The samples were afterward exposed to aggressive environments at the end of the 7 days curing period.
iii. The reinforced concrete samples were given 7 days intermittent water sprinkling in the morning and in the evening. Samples were then exposed to aggressive environment at the end of this curing regime.

Compressive Strength Test

In order to characterize the concrete mixture in compressive strength term, 150 x 150 x 150 mm concrete cube samples were tested in compression at 28 days after casting under standard curing condition. Compressive strength was conducted to monitor the quality of the produced concrete as well as the effect of starch addition. The compressive strength test was carried out for each percentage of starch addition to cement to know the effect of cassava starch on compressive strength of concrete, and for each replacement, concrete cubes were cast and allowed to set for 24 hours. After which the concrete cube were demoulded and placed in curing tank filled with water for 28 days. At the end of the moist curing period the concrete cube were removed from the curing tank and wiped dry. After which each of the cube is centrally placed in the universal testing machine and an axial load was applied gradually until failure, and the compressive strength was then determined.

Corrosion Rate Test

Corrosion monitoring test on the reinforced concrete prisms were carried out at an interval of 5 days via the half-cell corrosion measuring method using multimetre and digital voltmeter. The rate of steel corrosion was assessed by measuring the corrosion potential, since it is qualitatively associated with the steel corrosion rate. The potential difference between a standard portable half-cell, normally a copper/copper sulphate (cu/cuso$_4$), but zinc reference electrode was used in this study. The standard reference electrode (zinc electrode) was suspended in the solution via the retort stand. The reinforced concrete samples were half submerge in the solution (see Figure 3). The reference electrode is connected to the negative end of the voltmeter and the steel reinforcement embedded in the concrete to the positive end and the reading is recorded (see Figure 4).

Figure 3: Picture showing Reinforced Concrete Prisms Samples in the Different Aggressive Environments (A-NaCl solution, B-H_2SO_4 solution)

Figure 4: Picture showing Corrosion Readings been taken from Concrete Samples

RESULTS AND DISCUSSION

Compressive Strength Results

The results for the compressive strength obtained for the concrete cubes at 28 days are presented graphically in Figure 5, which show the compressive strength and percentage of cassava starch addition in the different concrete mixtures. From the figure it was observed that, there was a slight decrease in the compressive strength of the concrete mixture as the percentage of cassava starch addition increases. The overall decrease in the ultimate strength of concrete samples with cassava starch addition compared to control samples (i.e 0% starch) could be due to poor extent of hydration caused by the low hydraulic activity index of the cassava starch (Aremu, 2004).

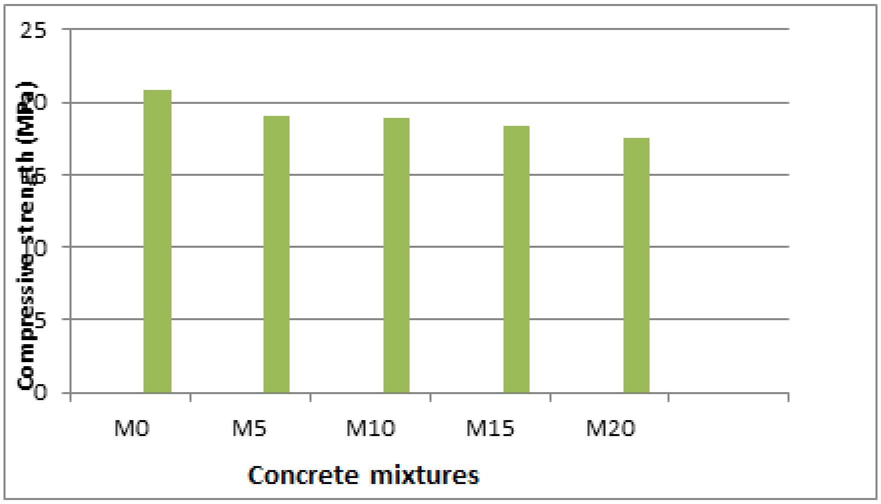

Figure 5: Compressive Strength (MPa) Versus Percentage Addition of Starch

Corrosion Rate Results

The results for the corrosion rate of the reinforced concrete prism samples are presented graphically in Figures 6 to 9. In the figures, the rate of corrosion of the embedded reinforcing steel are plotted against the exposure duration. The results are then presented and discussed based on the following influencing factors; effects of varying cassava starch addition, effects of curing type, effects of cover concrete and effects of exposure environment on the rate of corrosion.

Effect of Varying Cassava Starch Addition on Corrosion Rate

From Figure 6, the result show that the electrode potential of the reinforcement embedded in the concrete with no starch, increased slightly at early age. This indicates that the protective film was been developed on the embedded reinforcement steel during this period. After 40 days of exposure, a sharp drop in the electrode potential was observed; this was probably due to breakdown of the protective film by the aggressive environment.

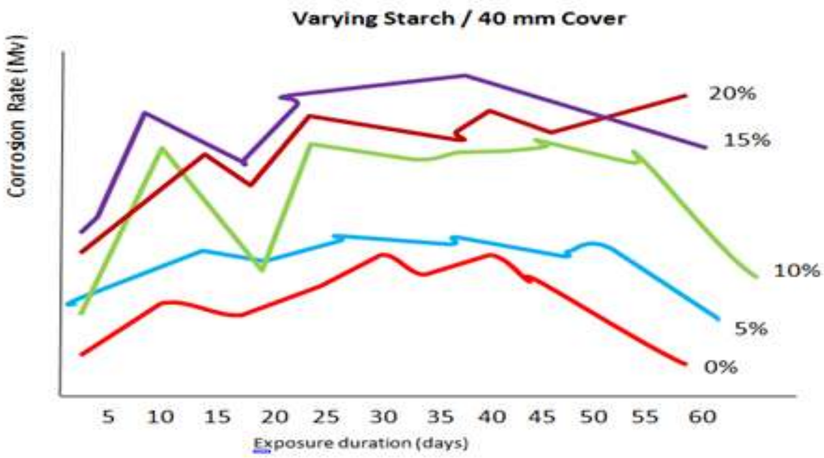

Figure 6: Corrosion Rate versus Exposure Duration for the Varying Percentage of Starch Addition

The test sample with 5% starch addition produced a progressive increase in electrode potential in the first 25 days of exposure (see Figure 6). This indicated that the protective film developed during this period could be as a result of starch addition in the concrete which probably offered a slight resistance to ingress of the chloride ions which block the pores of the concrete. Between 30 and 45 days it was observed that no change in the electrode potential occurred, this is an indication that a strong film has formed around the steel reinforcement. After 45 days, there was progressive breakdown of the protective film up till 60 days. Such breakdown could be attributed to the fact that the amount of starch admixture in the concrete could no longer hinder the movement of chloride ions or sulphate to the reinforcing steel.

This observation could be linked to the presence of starch mixture in the concrete. The change in concrete composition by the starch was probably such that after the chloride ions might have catalyzed the breakdown of the passivating film on the steel, the hydroxyl (OH) group in the structure of the admixture particularly the soluble α-amylose were replaced by the chloride ions instead of recycled. The free hydroxyl group released created more passivity in the concrete medium thereby raising the electrode potential of the embedded steel (Furniss, et. al, 1987).

The electrode potential of the test sample with 10% starch addition though similar to the 5% addition, fluctuated between -1029.9 and 1028mv throughout the exposure period. This could be attributed to the higher amount of starch in the concrete, which offered a higher resistance to the free movement of the chloride ions through the concrete. The admixture also created higher change in decomposition of the concrete's chemistry (Stark, 1989).The test sample with 15% starch addition has passivating effect throughout except between 15 and 20 days when there was slight loss of protective film which was quickly repaired. This observation indicate the beginning of the required amount of starch addition necessary to enhance good surface passivation of mild steel embedded in concrete. The same phenomenon was observed for the test sample containing 20% starch addition, which showed depassivation only between 15 and 20 days and thereafter showed high level of film repair for the rest of the exposure time. The implication of these two results is that the addition of 15 and 20% starch in concrete reduced the permeability of the concrete. Emmons, (1994) in his study had suggested that such an addition would enhance higher rate of interchange of chloride ions, sulphate, and hydroxyl group within the structure of the starch and the concrete mediums.

Effect of Various Curing Type on Corrosion Rate

The electrode potential of the reinforcement steel embedded in the concrete samples given 7 days continuous moist curing is higher compared to samples cured by intermittent sprinkling of water at intervals for 7 days (see Figure 7). This behavior is similar for all the different percentages of starch addition to concrete. Thus, only the result for the 10% starch addition is presented here. The higher electrode potential experienced by these samples is as a result of the dense pore structure of the concrete, thus providing resistance to the ingress of aggressive agents into the concrete. Reinforcing steel embedded in the concrete samples given no curing presented the least electrode potential. This is as a result of the poor micro structures developed by the concrete. However, the trends observed for all the samples are similar, with initial increase in the electrode potential up to 55 days before decreases are been noted. Again, similar situations were observed for the different aggressive environments the samples were exposed to and for the different percentage replacement of starch.

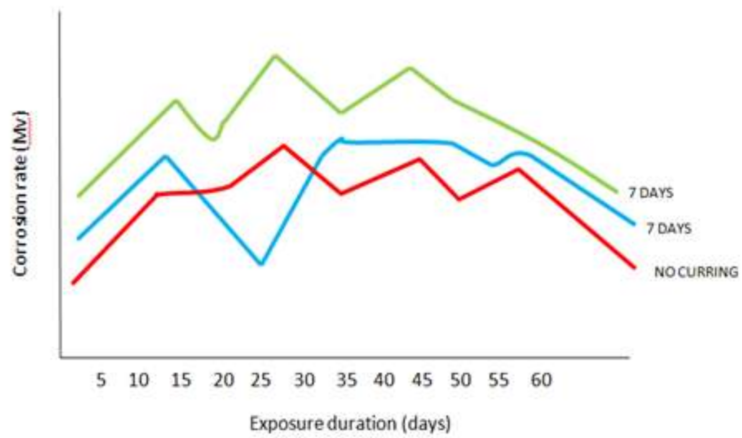

Figure 7: Corrosion Rate versus Exposure duration for the Different Curing Types

Effect of Cover Concrete on Corrosion Rate

The electrode potential for the reinforcing steel embedded in concrete sample with a cover concrete depth of 40mm is lower compare to the concrete samples with a cover depth of 20mm (see Figure 8). This observation is similar for the different percentage of starch additions and also similar for the different curing types and exposure environments. Hence, only results for the 10% starch additions, 7 days moist curing and for the sulphate environment is presented here. The cover concrete thickness has a remarkable effect on rebar corrosion due to the penetration depth the aggressive media has to pass through to depassivated the steel. However, the rate of corrosion of the reinforcing steel, once it has started, is independent of the concrete cover thickness.

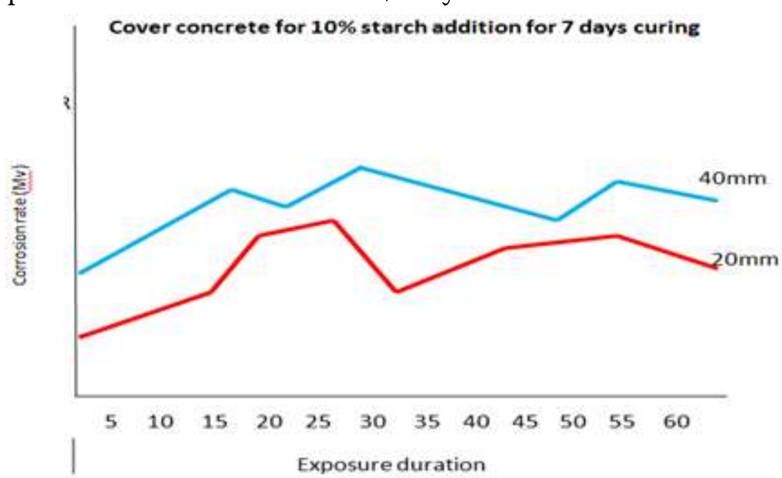

Figure 8: Corrosion Rate versus Exposure Duration for Different Cover Concrete

Effect of Exposure Environment on Corrosion Rate

Both the sulphates and chlorides environment increases the corrosion rates of the embedded steel reinforcement. But the effect of sulphate on embedded steel in concrete given 7 days continuous moist curing is pronounced compared to the concrete samples in the chloride environment (see Figure 9). However, the rate at which the aggressive environment induce corrosion depend on it concentration and the depth of the concrete cover. This is evident in the fact that samples with 20 mm cover has higher corrosion rate compared with samples with 40 mm cover concrete. The type of curing given to the samples and the percentage addition of starch in concrete also influences the rate of corrosion. However, the figure below only presented the effect of corrosion for the different aggressive exposure tested for the 40mm cover concrete samples given 7 days continuous moist curing.

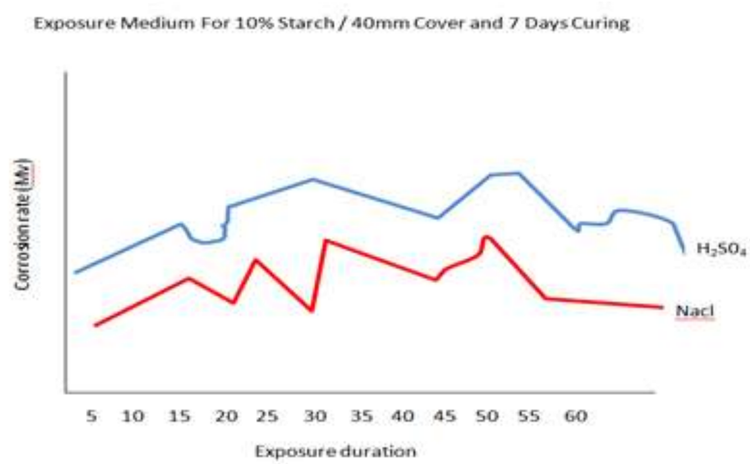

Figure 9: Corrosion Rate versus Exposure duration for 10% Starch Addition in Concrete

CONCLUSION

From the results of this investigation presented above, the under listed conclusions can be made:

- The use of 15 and 20% cassava starch addition in concrete improve the passivation potential of reinforcing steel embedded in concrete samples exposed to either chloride or sulphate environment.
- The corrosion rate of reinforcing steel was high for the 20mm cover concrete than for 40mm cover

concrete, this is because the lower the cover the higher the penetration time for the aggressive agents to get to the reinforcement.

- Corrosion rate of the embedded steel was less for all the reinforced concrete samples exposed to chloride environment, compared to the sulphate environment. This shows that sulphate is more aggressive to reinforcement corrosion.
- The reinforcement steel embedded in concrete samples that were given no curing before exposure to the aggressive environments, presented the highest rate of corrosion. While the least rate of corrosion was noticed in reinforcement steel embedded in concrete given 7 days continuous moist curing. This shows that curing of concrete is very important for reinforced concretes durability performance.

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