



# Journal of Applied Sciences

ISSN 1812-5654

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## Corrosion of Steels in Steel Reinforced Concrete in Cassava Juice

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**Abstract:** The corrosion of two types of construction steels, ST60Mn and RST37-2\*, in a low cyanide concentration environment (cassava juice) and embedded in concrete had been studied. The ST60 Mn was found to be more corrosion resistant in both ordinary water and the cassava juice environment. The cyanide in cassava juice does not attack the steel but it provides an environment of lower pH around the steel in the concrete which leads to breakdown of the passivating film provided by hydroxyl ions from cement. Other factors such as the curing time of the concrete also affect the corrosion rates of the steel in the concrete. The corrosion rate of the steel directly exposed to cassava juice i.e., steel not embedded in concrete is about twice that in concrete. Long exposure of concrete structure to cassava processing effluent might result in deterioration of such structures. Careful attention should therefore be paid to disposal of cassava processing effluents, especially in a country like Nigeria where such processing is now on the increase.

**Key words:** Corrosion, steel, cassava, cassava juice, reinforced concrete, cyanide

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### INTRODUCTION

Corrosion which is the interaction of metals with the environment occurs in various forms and there are many variable factors that influence its initiation and rates. Corrosion may be initiated because of the existence of one set of conditions, but may subsequently progress because of another. Due to the very rampant destruction of metals by corrosion it has become everybody's concern. The loss of metals and the cost implications of corrosion are quite high in any society. Corrosion leads to failure in plants, infrastructure, machines, etc. and this can be costly to repair. Corrosion is recognized as one of the most serious problems in our modern societies and the resulting losses each year are in the hundreds of billions of dollars. Studies carried out have shown that the cost of corrosion ranges from 1 to 5% of Gross National Product (GNP) in countries such as US, Japan, UK and Germany ([www.galvanizeit.com](http://www.galvanizeit.com); [www.corrosion-doctors.org](http://www.corrosion-doctors.org); [www.keronite.com](http://www.keronite.com), Batchelor *et al.*, 2002; [www.nims.go.jp](http://www.nims.go.jp)).

Corrosion studies have become extensive and multidisciplinary in order to minimize its adverse effects on nation's economies. One of such areas in recent years that have generated much concern is in the area of steel reinforced concrete. Concrete structures such as bridges, dams, buildings, tunnels, offshore oil platforms, packing garages, etc. all contain reinforcing steels. These steels are usually attacked by certain aggressive agents making them lose their integrity, thereby rendering them incapable

of satisfactorily performing their intended functions. The economic loss and damage caused by the corrosion of the reinforcing steel in concrete makes it arguably the largest single infrastructural problem facing industrialized countries. Studies (Tullmin, 2005; Mehta and Burrows, 2001) have shown that the corrosion of reinforcing steel was not the only cause of all structural deficiencies; it is however a significant contributor and has therefore become a matter of major concern. Damage to the reinforcing steel has been identified as the main mechanism of degradation of steel-reinforced concrete.

The environment provided by good quality concrete to steel reinforcement is one of high alkalinity (pH 12-13) due to the presence of the hydroxides of sodium, potassium and calcium produced during the hydration reactions. The bulk of surrounding concrete acts as a physical barrier to many of the steel's aggressors. In such an environment steel is passive and any small breaks in its protective oxide film are soon repaired.

Once corrosion sets in on the reinforcing steel bars, it proceeds in electrochemical cells formed on the surface of the metal and the electrolyte or solution surrounding the metal. Each cell consists of a pair of electrodes (the anode and the cathode) on the surface of the metal, a return circuit and an electrolyte. Basically, on a relatively anodic spot on the metal, the metal undergoes oxidation (corrosion), which is accompanied by production of electrons and subsequent dissolution. These electrons move through a return circuit, which is a path in the metal itself to reach a relatively cathodic site on the metal, where

these electrons are consumed through reactions involving substances found in the electrolyte. In reinforced concrete, the anode and the cathode are located on the steel bars, which also serve as the return circuit, with the surrounding concrete acting as the electrolyte.

Though steel in concrete as a composite material is the one that is attacked, the factors that affect corrosion reinforced concrete can be grouped in two viz:

- Factors associated with steel itself due to its composition microstructure and contamination of the steel surface
- Factors associated with concrete itself; these are (a) porosity and permeability which determine whether aggressive external ions can get to the steel surface. The more permeable the concrete is, the easier it is for ions to migrate inside. (b) chemical composition of cement which together with water determine alkalinity of the environment (c) aggregate (d) admixture and (e) workmanship.

The present study is about the corrosion of steel in reinforced concrete in cassava juice. The study is being undertaken for the following reasons:

- Present in abundant supply in Nigeria is cassava (*Manihot esculanta*), which is a source of one of the most popular foods (Garri) in the country. Cassava is a shrubby, tropical, perennial plant that is not well known in the temperate zone ([www.wam.umd.edu/~mathewsc/Cassava.html](http://www.wam.umd.edu/~mathewsc/Cassava.html)). Nigeria is the highest producer of cassava in the world (Oke, 2005). Efforts are being geared towards exporting processed cassava products rather than the raw forms leading to expanded cassava producing industry and consequential increase in cassava effluent discharge into the environment. Various studies have been carried out on this cassava in order to reduce its toxicity (Anonymous, 2003; Bradbury, 2003). Cassava contains the cyanogenic glucosides linamarin and lotaustralin, which produce hydrocyanic acid when the action of the enzyme linamarase is initiated by crushing or otherwise changing the cellular structure of the plant (Conn, 1969). The concentration of hydrocyanic acid in cassava tubers ranges from 10-490 mg kg<sup>-1</sup> tuber (Onwueme, 1978; Oke, 2005) and the tubers and leaves of cassava can produce 20-250 mg HCN per 100 g of fresh tissues (Montgomery, 1969).
- More uses have now been found for cassava, apart from being source of food, through various researches carried out in recent times and the

processing of the crop is now on the increase. The waste water from the processing is known to contain cyanide and is thought that when it comes in contact with structures, it might cause more damage through corrosion. Disposal of the waste water is now a serious concern. There is also concern about the durability of the agro-processing equipment and the civil structures such as bridges and buildings that come in contact with agro-fluids. All these have led to research activities and studies to find solutions to problems arising from contact of agro-fluids with machineries and disposal of agro-fluid containing effluents (Loto and Atanda, 1998; Silva *et al.*, 2006; Boucherit Tebib, 2005; Jekayinfa *et al.*, 2005 (a, b); Rajendran *et al.*, 2005; Sudhakar and Singh, 2004).

- Some studies that were carried out earlier on this subject were inconclusive and therefore more studies have to be done to elucidate the corrosion mechanism of mild steel in cassava juice.

The aim of the present study is to assess the corrosion of structural steels used for building structures in Nigeria and hence deduce from the results (I) the mechanism of corrosion in the presence of cyanide ions in an environment and (ii) the suitability of the two types of steel in Nigeria as reinforcement in concrete structures.

## MATERIALS AND METHODS

**Materials:** The main materials used for this study were RST37-2 and ST60 Mn, two structural steels commonly used in Nigeria. The specimens were obtained from standard stock and the chemical compositions of the steel samples are as given in Table 1. The cassava juice was sourced from cassava processing sites in farms around the Obafemi Awolowo University Community, Nigeria.

Other materials are elephant brand Portland cement, the composition of which is illustrated in Table 2. The aggregates used were obtained from the left over of building project in the school. Cu/CuSO<sub>4</sub> reference electrode and the voltmeter were used.

Table 1: Chemical analysis of steel samples

Element	RST37-2	ST60Mn
Carbon	0.12-0.17	0.35-0.42
Silicon	0.18-0.28	0.20-0.30
Manganese	0.40-0.60	0.90-1.20
Phosphorus	0.04	0.04
Sulphur	0.04	0.25
Copper	-	0.10
Chromium	-	0.10
Nickel	-	0.10
Iron	Balance	Balance

Table 2: Composition of portland cement

Component	Composition (%)
Tricalcium silicate	55
Dicalcium silicate	18
Tricalcium aluminate	11
Tetracalcium aluminoferrate	7
Na <sub>2</sub> O	0.21
CaO	0.4
Others	8.39

Table 3: Embedded steel samples, curing time and the environment for the concrete samples

Concrete samples	Steel sample	Curing time (days)	Environment
A	RST37-2	28	Cassava juice
B	RST37-2	28	Ordinary water
C	RST37-2	21	Cassava juice
D	RST37-2	21	Ordinary water
E	ST60Mn	28	Cassava juice
F	ST60Mn	28	Ordinary water
G	ST60Mn	21	Cassava juice
H	ST60Mn	21	Ordinary water

**Materials preparation:** A concrete mix was made which comprised elephant brand Portland cement, sand as fine aggregate, gravel as coarse aggregate and water. The cement-sand-gravel ratio used was 1:2:4. Eight steel embedded concrete slabs were cast with four each for RST37-2 and ST60 Mn steel samples. The specimens each with a radius of 7 mm and a length of 20 cm were pickled in hot dilute hydrochloric acid solution for about 10 min at around 60°. The steel samples were rinsed in water and dried before insertion. Only about 17 cm of each steel was embedded while the remaining 3 cm protruded out at one end of the slab to facilitate electrical connection during the taking of reading. The concrete slabs have uniform dimensions of 20×10×15 cm. After remolding, the concrete slabs were cured in water for 21 and 28 days to reduce porosity and permeability.

Two each of RST37-2 and ST60Mn embedded concrete slabs were placed in the environment under study for the corrosion of the embedded steels. The four slabs immersed in water were used as control experiment. The embedded steel sample, curing time and the environment exposed to for the slab samples are as shown in the Table 3.

In addition, the pickled steel samples were directly exposed to the environment and the corrosion monitored for ten consecutive days.

**Potential measurement:** To measure corrosion potential, the experimental set up is as shown in Fig. 1.

The experiment was conducted with each concrete slab partially immersed in the medium. A distance is maintained between the exposed end of the steel rod and the medium to ensure the solution did not make contact with it. This is necessary because such a contact

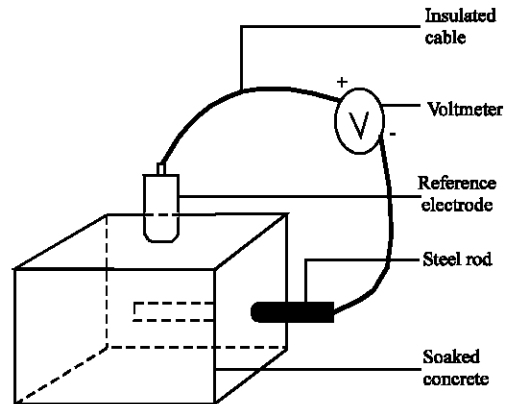


Fig. 1: Experimental set up

might result in reaction between the steel and environment which might affect the accuracy of the results.

To obtain readings, a copper/copper sulphate reference electrode was placed on the concrete slab. The circuit was completed by connecting an insulated flexible cable of the half-cell to a voltmeter and another cable to a hole drilled on the exposed end of the steel specimen. Readings were taken on both sides of each slab and the average potential calculated.

In addition, the potential readings for the pickled steel samples directly exposed to the environment were taken for ten consecutive days. Similarly, the potential measurements were done relative to Cu/CuSO<sub>4</sub> reference electrode.

## RESULTS AND DISCUSSION

It is clear from the results of this research that the corrosion potentials/rates of the RST37-2 are higher than those of ST60 Mn as shown in Fig. 2-8. This can be explained in terms of their composition and microstructure. As shown in Table 1, ST60 Mn has carbon in excess (about 0.35-0.42%) than RST37-2 (0.12-0.17%). It must be realized that galvanic corrosion process is not, necessarily, conditional on the contact between two dissimilar metals. The formation of anodic and cathodic sites may occur in the same metal, due to local variations in its composition, stress level, oxygen supply, etc., anodic and cathodic sites develop, sometimes, at very short intervals, to give what is usually referred to as galvanic microcells (Soroka, 1994) (Fig. 9). In low carbon steels, these microcells can be illustrated as shown here: In addition, area ratio (the *area ratio* of the anode: cathode) is an important variable affecting the dissolution

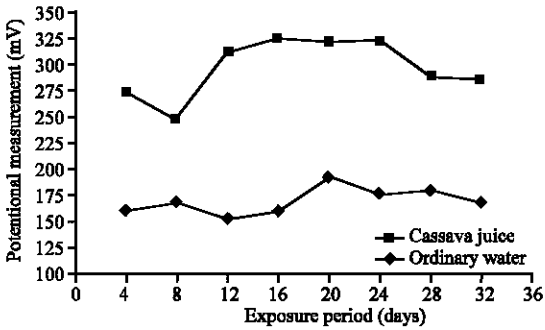


Fig. 2: Potential vs exposure period for RST37-2 in cassava juice for three and four week of curing

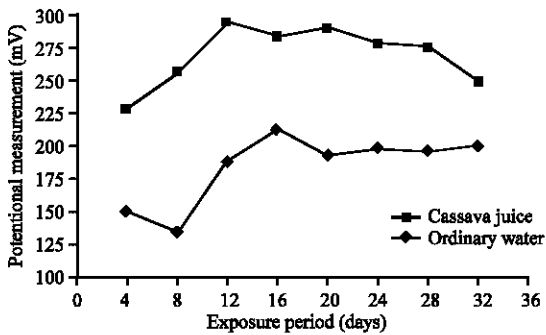


Fig. 3: Potential vs exposure period for ST3760Mn in cassava juice and ordinary water environment

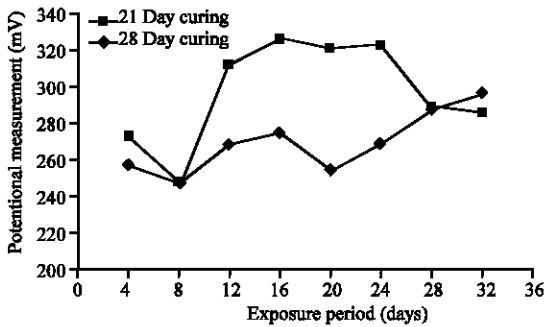


Fig. 4: Potential vs exposure period for RST37-2 in cassava juice for three and four week of curing

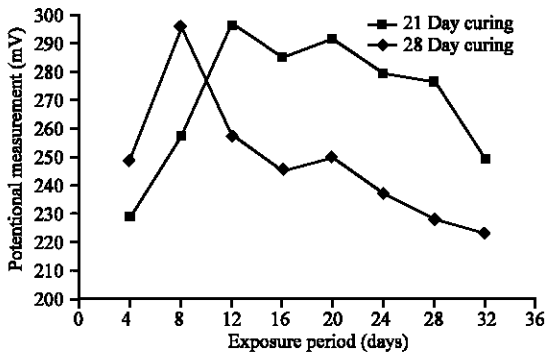


Fig. 5: Potential vs exposure period for ST60Mn in cassava juice for three and four week of curing

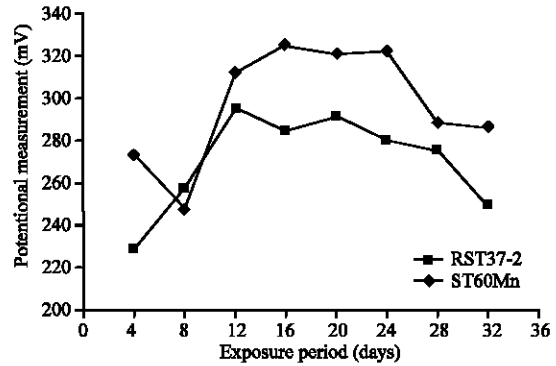


Fig. 6: Potential vs exposure period for RST37-2 and ST60Mn for three weeks of curing

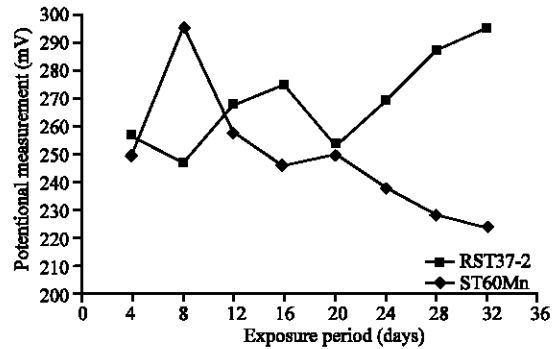


Fig. 7: Potential vs exposure period for RST37-2 and ST60Mn for four weeks of curing

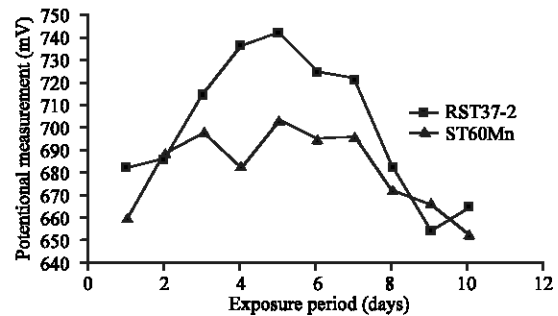


Fig. 8: Potential vs exposure period for RST37-2 and ST60Mn directly exposed to cassava juice

current density (and hence corrosion rate) pertaining to the anode. This is because during corrosion, the rate of oxidation is proportional to that of reduction. A small anodic area has to go into solution at a faster rate in order to meet up with the reduction rate at the cathode.

The microstructure of ST60 Mn has more carbide than that of RST37-2, since it contains more carbon. Pearlite corrodes in preference to ferrite when in galvanic contact since it is more anodic than ferrite; in addition,

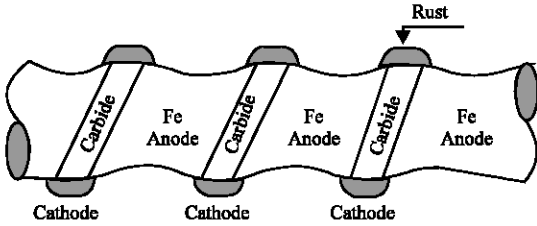


Fig. 9: The formation of galvanic microcells in steel due to the presence of carbide

small anode to cathode ratio causes more corrosion. This is because during corrosion, the rate of oxidation is proportional to that of reduction. A small anodic area has to go into solution at a faster rate in order to meet up with the reduction rate at the cathode. Thus, corrosion potentials are higher in RST37-2 due to small anode area effect. The small pearlite portion acting as the anode supplies electrons the large ferritic portion and hence, the dissolution of the pearlite is faster than in the ST60 Mn where the pearlite surface area supplying electrons to the ferritic is larger. Furthermore, ST60 Mn contains some alloying elements like chromium and manganese which may form passive layers on the steel, thus reducing the corrosion rate.

Steel is normally protected from corrosion when embedded in dense concrete owing to the formation of passive films. This film is established by the high concentration of hydroxyl ions associated with the concrete pore electrolyte and effectively stifles the anodic dissolution of ferrous ions so that the corrosion rate remains negligibly small. This passivity can also with reference to Poubaix Diagram shown here in Fig. 10.

As evident in Fig. 2-8, the early characteristic increase in potential/corrosion rate results from the breaking down of the passive films by the ingress of aggressive agents to the surface of the steel materials. Principally, the aggressive agents on getting to the steel surface bring down the pH to a level at which corrosion can occur (Fig. 10). Therefore the effect of the cassava juice is to introduce acidic cyanide ions which lower the pH of the environment and hence the breakdown of the passive film.

The next stage shows a decrease in potential/corrosion rate, which is probably due to the formation of iron oxide layer that temporarily prevents direct attack of the steel. The next stage, expectedly, characterizes an increase in potential/corrosion rate resulting from breakdown of passivity or the initiation of microcracks as a result of steel corrosion which is accompanied by volume increase leading to cracking and spalling and consequently more corrosion agents penetrate into the concrete thereby enhancing further corrosion.

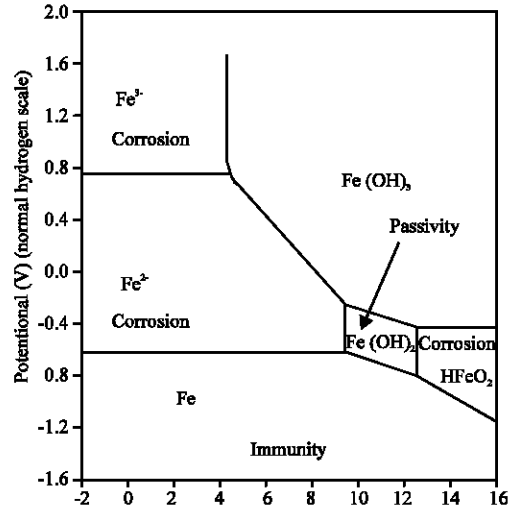


Fig. 10: The poubaix diagram for Fe-H<sub>2</sub>O system

The effect of curing on the corrosion characteristics of the steels can be seen in Fig. 4 and 5 which show the changes in potentials of the steels for the period of immersion in the environment for the curing times of three weeks and four weeks. It can be seen from the figures that corrosion potential/rate decreases with increasing curing time.

This is so because the percentage of the total space available for occupancy by either gases or liquids (porosity) decreases with increasing period of curing. The more porous a concrete, the more is the corrosion of the reinforcing steel. In addition, the capacity of the concrete to transmit fluid through interconnected pores (permeability) decrease with increasing period of curing. The more permeable a concrete, the less resistant to corrosion is the reinforcing steel. For the ST60 Mn steel, the progressive decrease in corrosion rate after the initial increase in the early days has to be investigated. The presence of alloying elements such as Cr and Mn might be playing some roles of slowing down corrosion rate.

**CONCLUSIONS**

From the results of this research, the following conclusions can be drawn:

- Cassava juice provides an acidic environment which leads increase in corrosion rate of steel embedded in concrete
- The rate of corrosion is dependent on the steel composition and the properties of the concrete which derive from its production. The RST37-2 with lower carbon content and lower anode area corrodes

more than the ST60 Mn with higher carbon content and higher anode area. Corrosion rate decreases with increasing curing time.

- Though cyanide content in cassava is low, long exposure of concrete structure to cassava processing effluent might result in catastrophic failure of structures especially in situations where attention are not paid to standards of construction. This work also can be extended to cassava processing equipment that is made of mild steel. Corrosion of this equipment will definitely be accelerated due to presence of cyanide unless the materials of construction are carefully chosen to mitigate its adverse effects.

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