

THE CORROSION OF MILD STEEL IN MAIZE JUICE, ACIDIFIED MAIZE JUICE AND ACETIC ACID ENVIRONMENTS

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ABSTRACT

The corrosion behaviour of mild steel in maize juice, acidified maize juice and acetic acid environments was studied in this investigation. The observed corrosion reaction of the steel's surface in these environments seems to be predominantly that of general corrosion. The acetic acid environment was found to be the most corrosive. The maize juice was the least aggressive environment and this might be due in part to the film formation that tends to passivate the steel's surface. The strength properties (load-to-failure and time-to-fracture) decreased with increase in exposure time in the three environments. The hydrogen atoms produced during the corrosion reaction could diffuse into the steel matrix to cause hydrogen embrittlement of the steel.

INTRODUCTION

Maize, which is of various species belongs to the botanical genus *zea*. Maize originated in America where it is termed corn. This continent is still producing half of the world's crop of this cereal, which provides the backbone of the diet of many millions of people. It is also largely grown in Nigeria particularly in the southern part of the country. Maize is now having increasingly large industrial application in Nigeria. Some of the uses include the production of animal feeds, soap, maize starch, corn flour (for custard, pap, corn-meal, baking powder and composite bread) and salad oil. Research into the utilization of maize (starch) as binder in tablet making and in breweries is also in progress in Nigeria.

However, corrosion of the construction materials have been observed in maize tower silos [1]. Equipment used for fermentation of maize are also known to be subject to corrosion. The present extensive industrial uses of maize and its other anticipated industrial utilization could also justify and investigation into the corrosion behaviour of alloys (representing the machineries, storage facilities and other processing equipments) in maize juice environment. The fermentation products of maize have been found to be lactic acid 2.0%, acetic acid 0.5%, and

butyric acid [2, 3]. Corrosion, such as mentioned above had been reported [1]. Some other works of corrosion in agriculture had also been done [4-7].

In this work, corrosion in silage and fermentation equipments have been simulated. Acetic acid is used as one of the corrosion media because it is one of the constituents of fermented maize products. Its higher concentration in this work is for accelerated corrosion result. This investigation is carried out on a mild carbon steel to know the nature and level of corrosion occurring and to be able to determine the most suitable methods for its mitigation and subsequent prevention. Research such as this might also establish criteria for design of more corrosion resistant tower silos through corrosion resistant materials and improved corrosion protection methods.

EXPERIMENTAL PROCEDURE

Specimen Preparation

Hot rolled steel rods (RST 37-2) with diameters 5mm and 15mm respectively from Oshogbo Steel Rolling Mill were cut into representative samples of 30mm and 20mm pieces. A hole of 5mm diameter was drilled at a distance of 5mm from one end side of each of the 20mm pieces. The other end of this same piece was machined through a length of 10mm to a diameter of 13mm. The average chemical composition of the steel used was 0.15%C, 0.23%Si, 0.50%Mn, 0.04%P, 0.04%S, 0.025%Cu, 0.1%Cr, 0.11%Ni, 0.5%Sn, and the rest Fe. The samples were ground using various grades of abrasive papers ranging from 200 to 600 grits and then polished using polishing powder of 1 micron and 0.05 micron on Selvyt cloth in a universal polisher. Some of the polished samples were etched with 2% Nital and the microstructure observed under the metallurgical (optical) microscope.

Preparation of Corrodent

Maize (white) obtained from Ile-Ife, Nigeria was steeped for two days in distilled water and then wet-milled. The wet-milled product was sieved. The fine

... was later allowed to settle for about two days after which the liquid on its surface (souring water) was removed. This souring water is the main corrodent.

Acetic acid (5%) was also prepared and used as another corrosive medium. Acidified maize juice of 2% acetic acid was also used as a corrodent.

Weight Loss Experiment

The 30mm steel samples were used for the weight loss experiment. Some of these samples were weighed on a weighing chemical balance and the initial weights were recorded. The samples were each immersed in each of the three corrosion media. Each of the samples was removed after two days from their respective solutions, cleaned with distilled water and acetone, dried and weighed. The weight loss experiment was performed for a period of twenty days.

Potential Measurements

Each of the mounted 20mm steel specimen was partially immersed in each of the three corrodents separately. The potential (mv) between the steel specimen surface and the corrodent were recorded at regular intervals of 2 days using a digital voltmeter and saturated calomel electrode.

Constant-Strain-Rate Test

Tensile specimens, 120mm long, gauge length of 50mm and gauge diameter of 4.2mm were prepared from the mild steel. Five samples were immersed in 0.5 litre of each of the three corrodents and strained on a Monsanto tensile machine. These specimens were strained at a constant strain rate of 0.2mm/min after various periods of exposure to the three corrodents. Time to fracture and load-to-failure data were recorded.

RESULTS AND DISCUSSION

Effect of Exposure - Time on Corrosion

Generally, increase in exposure time tends to lead to an increase in susceptibility to corrosion of samples in many environments. But the extent of damage is known to depend on the aggressiveness of the environment (chemical reactivities), transport properties of environment, concentration of corrosive

species in the medium (pH), the metallurgy of the alloy specimen and temperature of the corrosive medium.

Effect of Exposure Time on Weight Loss of the Specimens

It was observed that the highest weight loss obtained was 0.081mg/mm² for steel samples immersed in acetic acid (for about 10 days). This shows (Fig. 1) that the acetic acid environment (pH 2.2) is the most aggressive of the three corrosion media used. This highest weight loss might be due to its lowest pH value of 2.2 which shows that it is most acidic and hence very reactive chemically. After the maximum weight loss, a gradual decrease in corrosion could be observed. This might be due to either repassivation or decrease in the strength of the corrosion reaction as a result of corrosion products deposited on the specimen's surface. It might, in addition, be due to contamination of the test solution by the dissolved corrosion products.

The curves obtained, Fig. 2, for the samples immersed in the acidified maize juice (pH 3.0) and maize juice (pH 3.3) also showed an increase of weight loss with increase of exposure time. This is an indication that the corrosion reactions remained active throughout the experimental period. However, the corrosion reactions in both appeared to be less than that of acetic acid. The phenomenal active corrosion might be due to insufficient corrosion deposits to stifle the chemical reactivities at the specimen/solution interface. It also probably means that the solution has not been contaminated enough with the dissolved corrosion products to reduce drastically its corrosive strength during the experimental period. The curves obtained for these two environments were similar with the maize juice showing a more reactive tendency during the first eight days of the experiment. After the eighth day, the acidified maize juice became more reactive (corrosive) as shown in Fig. 1. The observed whitish deposit on the specimen's surface in the maize juice around this time might contribute to its less corrosivity while the greater acetic acid content of the former could enhance its more chemical reactivities and hence more active corrosion.

Effect of Exposure Time on Potential

Fig. 2 shows the potential - time curves for the effect of acetic acid, maize juice and acidified maize juice on the corrosion behaviour of a mild steel. Generally, a more negative potential is indicative of

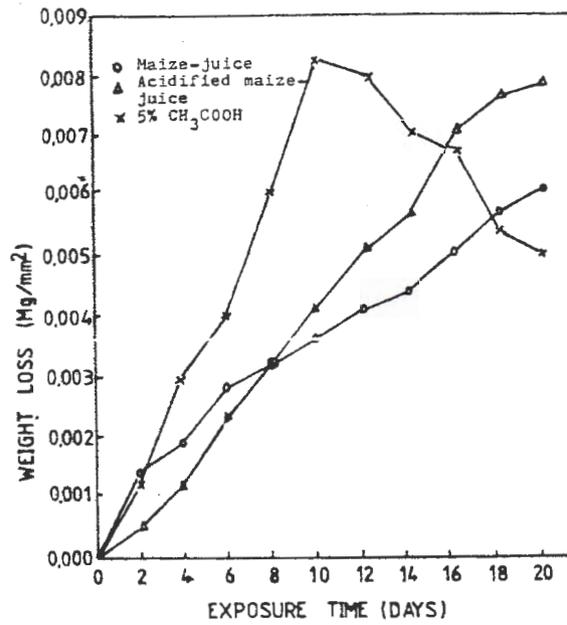


Fig. 1. Relationship between exposure time and weight loss

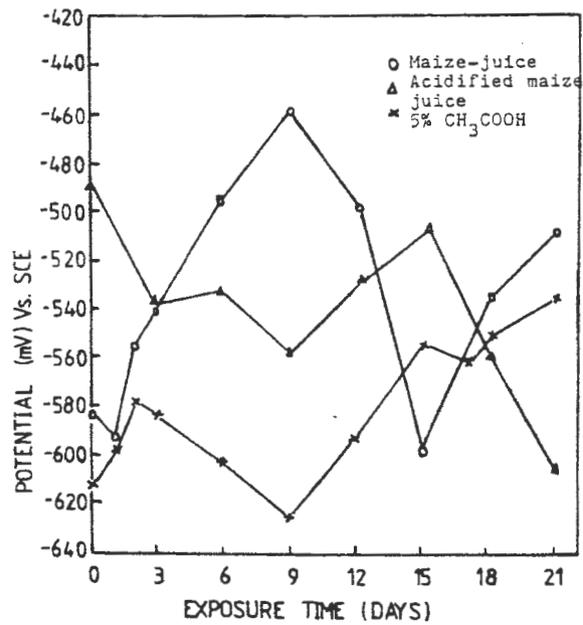


Fig. 2. Potential time curves for partially immersed steel samples

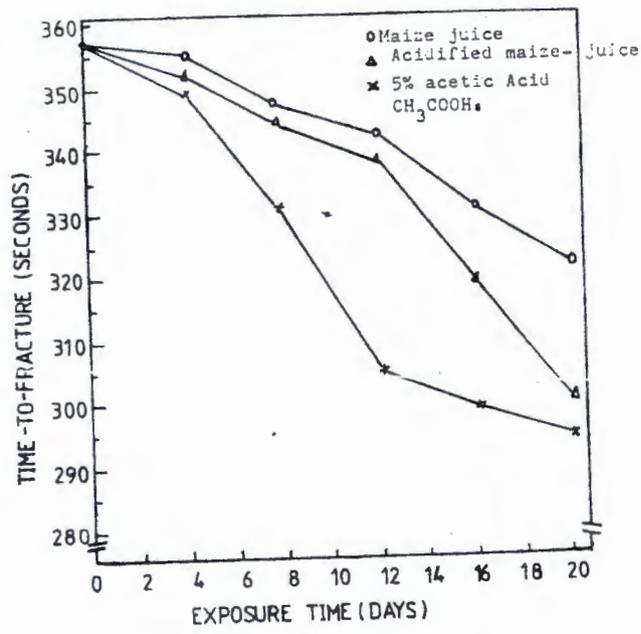


Fig. 3. Time to fracture as a function of exposure time

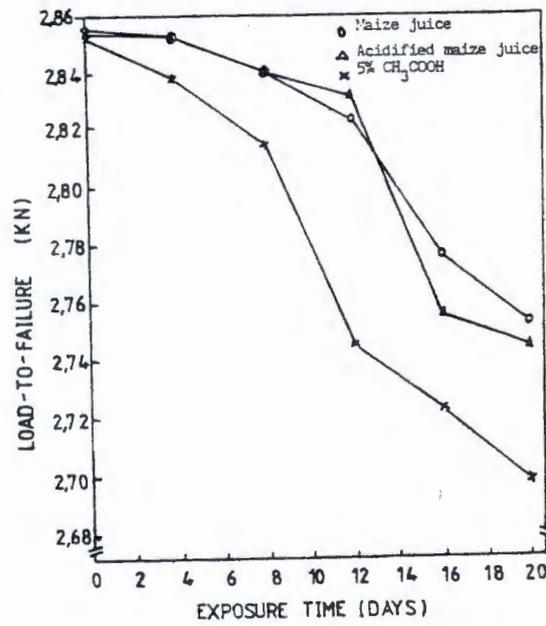


Fig. 4. Load to failure as a function of exposure time

susceptibility of specimen to active corrosion. The most negative potential recorded was 637 mV (against SCE) and this was obtained after 10 days of exposure to acetic acid solution.

Maize Juice Environment

In the maize juice environment, a decrease in potential indicating the occurrence of active corrosion was observed during the first day of the mild steel specimen's immersion into the corrosion medium. This might be due to the initial chemical reactivity of anodic dissolution at the specimen/solution interface within the first 24 hours (1 day) of the experiment. However, there was an increase in potential up to the 9th day when the cathodic peak was reached (Fig. 2) at -460 mV. This probably suggests that the mild steel was in a state of progressive passivation during this period. The occurrence of a film of 'whitish' substance which probably consists of maize constituents(s)/fermentation and corrosion products that was observed on the specimen's surface during this period might have hindered the access of the test solution to the specimen's surface and thereby stifling the corrosion reaction. This film was found extensively on the specimen's surface (Fig. 6).

The observed 'whitish' substance deposited on the steel specimen's surface might, in part, be due to the protein content of the extracted maize juice. Proteins are amphoteric, their behaviour as an anion or a cation depending on the pH of the solution [8]. At some definite pH, characteristic for each protein, the positive and negative charges are exactly balanced i.e., there is no net charge on the protein molecule, and the molecules will not migrate in an electric field (such as created by the electrochemical reactions in this experiment). In this condition, protein is said to be at its isoelectric point and at this pH the protein has its least solubility, i.e., it is most readily precipitated. It is also known [8] that on application of a potential difference across the cell containing the protein solution, the molecules move to the anode, the rate of travel depending on the value of the net charge and the size of the molecule. Though, the protein content of maize juice is low, its electrochemical effect might not be ignored. The above process could probably stifle the anodic dissolution reaction at the anodic sites. However, since the pH of a corrosion reaction such as in this work is dynamic depending upon the corrosion rate, the isoelectric point might not be maintained permanently as can be inferred from the results obtained in this work (Fig. 2). In addition, the movement of the protein molecules to the anode due to the potential difference across the cell might not be sustained for

for too long a time since the protein content of the solution is low and all might be precipitated within a short period of time. Further anodic dissolution of the specimen's surface from the decreasing potential to a low level of -600 mV. This phenomenal active corrosion might be due to the solubility of the deposited corrosion product on the specimen's surface face which creates a fresh bare metal surface to the solution for further anodic and cathodic processes that result from the chemical reactivity at the steel's/solution interface (Fig. 7).

Further increase of potential from the 15th day to the 21st day (Fig. 2) is probably indicative of a repassivation process — the stifling of the corrosion reactions. This phenomenon might have resulted from the weakness and deterioration of the test solution's strength due to the corrosion products contamination, which might have hindered the anodic dissolution process of active corrosion. In addition, the gradual accumulation of corrosion deposits on the specimen's surface at this time might disturb the corrosion reaction and hence enhance a repassivation process.

Acidified Maize Juice Environment

A sharp drop in potential (i.e., becoming increasingly negative) was observed during the first three days of exposure Fig. 2. This might be an indication of active corrosion occurring on the surface of the freshly polished specimen when immersed into the solution. Because of the additional acetic acid content and lower pH 3.0 value, the solution would be expected to be more reactive than the maize juice discussed above, since more hydrogen ions would be made available for reduction during cathodic reaction than that of the maize juice. The dissolution reaction can be maintained only by the removal of electrons from the corrosive environment. In this case, the removal of electrons is enhanced by the production of hydrogen ions. A slight negative decrease of potential was maintained for about three days after which an increasingly negative potential of -560 mV (against SCE) was observed on the 9th day of specimen's immersion in the solution. The beginning of this sharp decline from the cathodic peak provides a reasonably reliable indication of the onset of anodic dissolution and hence active corrosion [9-11]. Fig. 8 shows the photomicrograph of the specimen's surface as at the 10th day of immersion into the test medium. The corrosive action of the environment could be clearly observed. The decrease in potential was immediately followed by an increase of potential rising to -509 mV on the 15th day of specimen's immersion. After the 15th day and to the end of the experiment

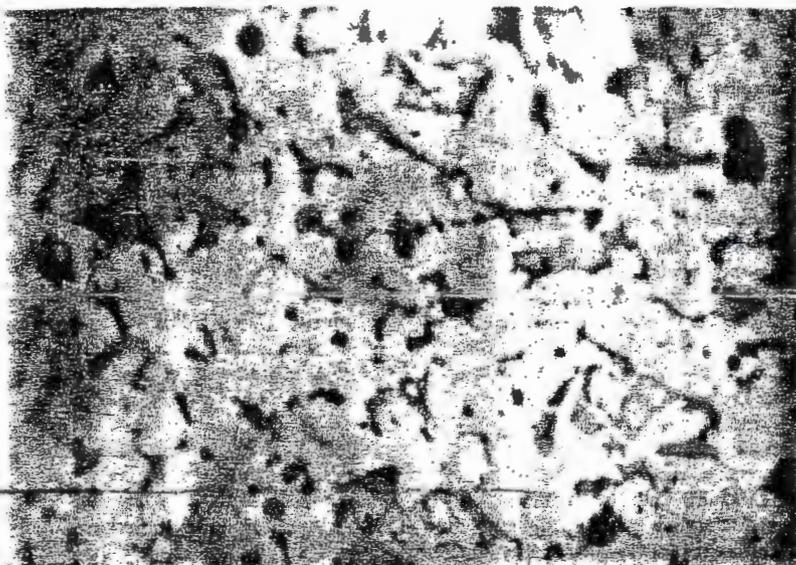


Fig.5. Microstructure of as-received steel sample. Etched in 2% Nital. Magnification X200 (Optical Metallurgical microscope)

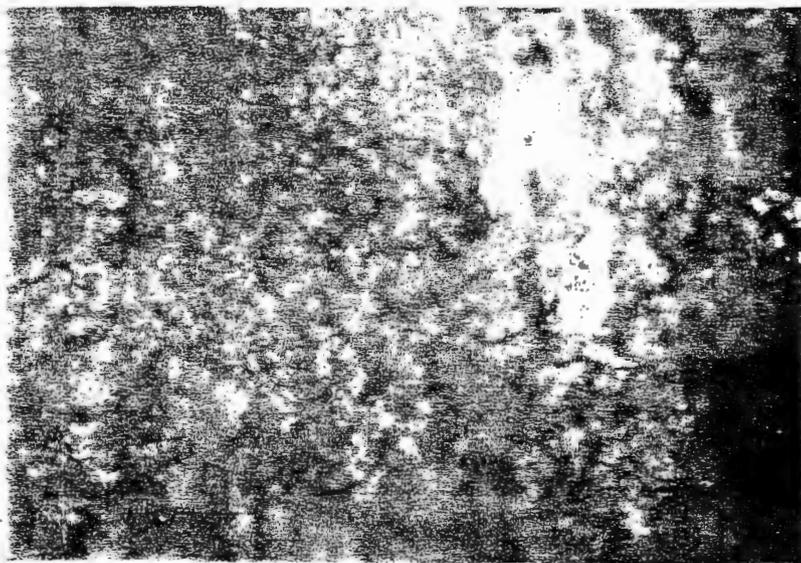


Fig.6. Surface of the steel sample after 7 days of immersion in maize juice. (The whole surface is covered with dense corrosion deposits and probable fermentation products). X 200

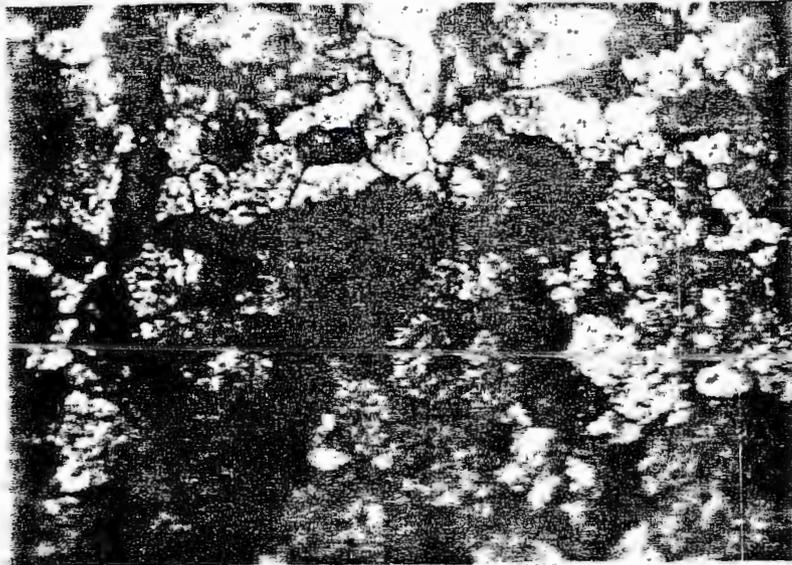


Fig. 7. Surface of the steel sample after 21 days of immersion in maize juice. (Dissolution of corrosion deposits earlier formed occurred here). X200

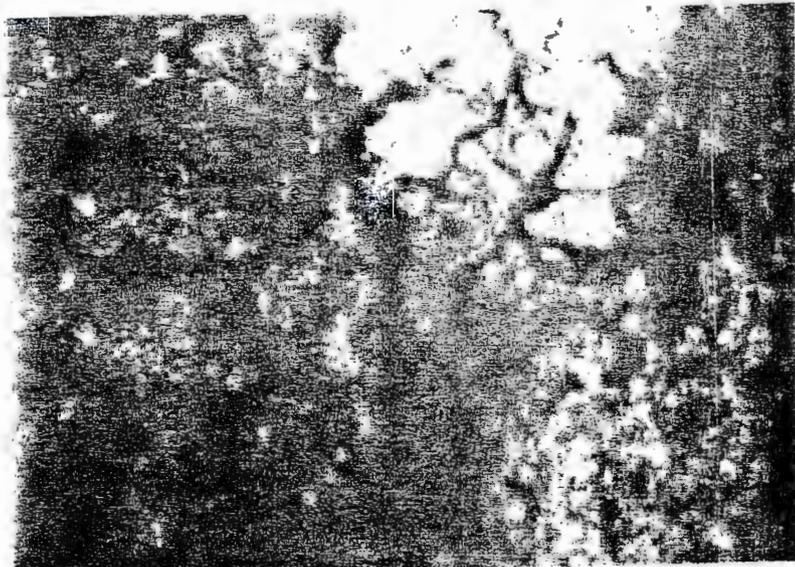


Fig.8. Surface of the steel sample after 7 days of immersion in acidified maize juice. (Part of the surface was covered by film formed from corrosion products). X200

on the 21st day, an increasingly negative potential indicating active corrosion was observed and a potential of -610 mV was recorded on the 21st day. This behaviour is in agreement with the weight loss curve where the highest corrosion was observed during the 20th day (0.0078 mg/mm²). This period (from the 15th day) also showed the highest weight loss as observed in Fig. 1.

In the acidified maize juice environment, the anodic and cathodic reaction processes that occurred was as described and explained previously, for the maize juice environment. The acetic acid content of this corrosion medium, however, might not have favoured a prolonged repassivation process. The corrosion deposits appeared as they might have probably undergone dissolution at a shorter period at that concentration when compared with the maize juice environment alone.

Acetic Acid (CH₃COOH) Environment

During the first two days of the specimen's immersion a rise in potential to -580 mV was observed (Fig. 2). This passivating phenomenon seems difficult to explain. However, an explanation based on probable initial film formation on the specimen's surface around this time might be given as the cause of the passivation. The passivation did not last more than two days before the potential started to decrease, that is, becoming increasingly negative until the 10th day when a potential of -637 mV was obtained. This trend indicates active corrosion after the dissolution of the passive film. The reacting species of the solution might have penetrated the film and thereby setting up a process of anodic and cathodic reactions resulting in the anodic dissolution of the specimen. This probably resulted in general corrosion of the specimen surface as could be seen in Fig. 9. The interface reaction might have been aided by the heterogeneous nature of the metallurgical composition of the steel which show a lot of inclusions (Fig. 5).

The active general corrosion of the specimen did not last more than the 11th day when the potential started to rise again to -550 mV. A slightly fluctuating, (though near steady state-like) curve was observed from the 15th to the 18th day after which the potential continued to increase until the 21st day. This rise in potential indicates a re-passivation reaction. The increasing passivation might be due to the precipitation of the corrosion deposits on to the specimen's surface and thereby stifling the active corrosion reaction. In addition, the chemical reactivities of the test solution might have been weakened by the probable dissolved corrosion

products and thereby rendering it inactive against the deposited corrosion products on the specimen.

Effect of Exposure Time on the Time to Fracture and Load-to-Failure

The time-to-fracture and load-to-failure, Figs. 3 and 4 respectively, decrease with increase in the time of specimens' exposure (immersion) to the environment. In Fig. 3, the acetic acid curve has the sharpest drop and the maize juice curve the least. These phenomena seem to be in agreement with the weight loss/time and the potential/time curves in which the acetic acid solution was the most corrosive and the maize juice the least corrosive. The same trend was observed in Fig. 4, but with the difference of load-to-failure/time of exposure of the specimen not so well pronounced for the maize juice and acidified maize juice until after the 13th day. The more susceptibility to failure of the specimen in the acetic acid solution might be due to the low pH of 2.2 of the acid (at the time of specimen's immersion). This low pH may enhance more hydrogen ion production which might result into atomic hydrogen being absorbed into the steel specimen. This could probably result in loss of ductility and tensile strength [12] thus indicating the mechanistic hydrogen embrittlement of the steel specimen. The above could be observed in the lowest time-to-fracture and load-to-failure of the specimen at a specific exposure time in the acetic acid solution when compared with the other test media. It then probably implies that the lower the pH, the more the amount of hydrogen atom that is likely to diffuse into the steel matrix and the greater the reduction in both the tensile strength and time-to-fracture that will be obtained. The reduction in specimen thickness caused by corrosion could have also resulted in reduction of ductility and hence failure of the specimen in the corrosive test media relative to the exposure time.

CONCLUSIONS

The following conclusions are made:

1. Mild carbon steel is corroded by the maize juice, acidified maize juice and 5% acetic acid solution.
2. The corrosion characteristic is predominantly general corrosion caused by the metal's anodic dissolution. The active-passive corrosion behaviour exhibited by corroding steel could be attributed to the unstable corrosion products deposited on the specimen.



Fig.9. Surface of the steel sample after 21 days of immersion in 5% CH_3COOH .

3. The acetic acid solution was found to be the most corrosive while the maize juice was the least corrosive.
4. The hydrogen atoms produced during the reactions could have diffused into the steel matrix to cause loss in ductility and tensile strength and thereby resulting into hydrogen embrittlement.
5. The time to fracture and load-to-failure of the steel specimen decreased with the increase in exposure time in the test media.

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