ELECTROCHEMICAL BEHAVIOR OF PHOSPHATIZED REINFORCING STEEL IN CONCRETE IN PRESENCE OF SUGAR CAN ASH

Aprael S. Yaro, Baha'a G. Ikzair*, and May A. Ibrahim
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq
* Building and Glass Research Center – Ministry of Industry - Iraq

ABSTRACT

The chemical analysis of the sugarcane (begasse) which is a by product from sugar industry shows a high concentration of SiO_2 *and* Al_2O_3, *which reduce the heat of hydration that resulting from cement-water reaction. Additionally this material is considered as a filler material, which increases concrete durability, and reduces its permeability besides it prevents the corroding species from reaching the steel surface.*

Accordingly an attempt was made in this paper, using electrochemical measurements to watch the behavior of phosphatized reinforced steel embedded in concrete samples containing different concentrations of bagasse and immersed totally in a corrosive environment. The results of tests are summarized as follows:

Compared with concrete samples without bagasse contained, a shift in free corrosion potential to the negative direction, an increase in corrosion current and a decrease in electrical resistance were recovered.

Keywords: corrosion of steel, concrete structures, environment resistance, sugarcane ash, micro-cell corrosion, phosphatizing.

INTRODUCTION

For a wide range of structures in different corrosive environments, reinforced concrete can be used efficiently. When steel rusts, the corrosion products generally occupy considerably more volume than that of the original steel. This expansion causes cracking and spilling of the concrete, which accelerate the rate of corrosion.

An electrochemical process accompanied by anodic and cathodic reaction lead to the corrosion of reinforcing steel concrete. In the anodic reaction, hydrated ions of iron are transferred into solution with two electrons left in the reinforcing steel as shown by equation (1) and figure(1), these two electrons are transferred to the cathode to assimilate in cathodic reduction reaction, (equation (2)).

$$Fe \longrightarrow Fe^{+2} + 2e^- \qquad (1)$$

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (2)$$

Equation (2) is an active reaction in alkaline solution and it's the rate-determining step in diffusion of oxygen[1].

In concrete, macro-cell corrosion frequently proceeds first(i.e., both the anodic and cathodic reactions frequently take place in different places some distance a part on reinforced steel besides the potential difference between the anode and cathode of macro-cell is larger than that of micro-cell). The mechanism of macro-cell is shown schematically in figure (1)[2].

When corrosion occurs on the reinforcing steel in concrete, the electrochemical reactions involved are dependent on the environments at the steel-concrete interface:

In Presence of Oxygen

1. At the anode, oxidizing of iron to the ferrous state, releasing electrons as shown in equation (1)
2. At the cathode, the combination of these electrons with O_2 and moisture to form OH ions takes place as shown in equation (2).
3. The ferrous ions of equation (1), and hydroxyl ions of equation (2) combined together to produce ferrous hydroxide. Further oxidizing of latter in presence of moisture lead to ferric oxide formation:

$$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2 \qquad (3)$$

$$4Fe(OH)_2 + 2H_2O + O_2 \longrightarrow 4Fe(OH)_3 \qquad (4)$$

$$2Fe(OH)_3 \longrightarrow Fe_2O_3 + 3H_2O \qquad (5)$$

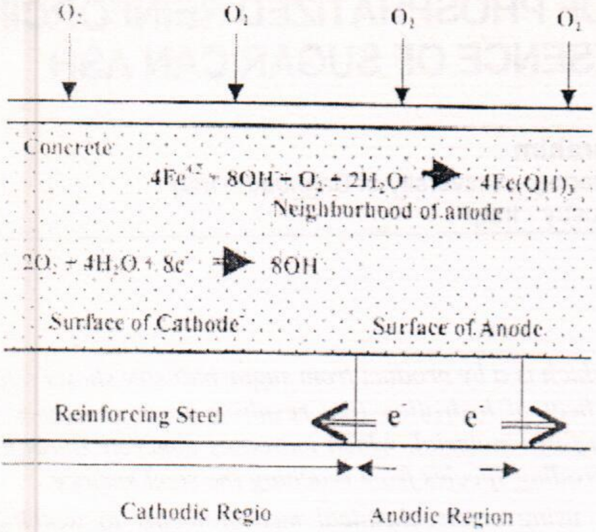

Fig. (1) Macro-cell corrosion

In Absence of Oxygen

1. At the anode, the oxidized iron reacts with Cl ion to form an intermediate iron complex.

$$Fe^{+2} + 4Cl^- \longrightarrow (FeCl_4)^{-2} + 2e^- \qquad (6)$$

2. The complex then reacts with moisture to form ferrous hydroxide.

$$(FeCl_4)^{-2} + 2H_2O \longrightarrow Fe(OH)_2 + 2H^+ + 4Cl^- \qquad (7)$$

3. At the cathode, the hydrogen ions are reduced or combined with electrons to form hydrogen gas.

$$2H^+ + 2e^- \longrightarrow H_2 \qquad (8)$$

It is obvious from the above reactions that high concentrations of chloride and oxygen would favor the corrosion of steel, whereas a high concentration of (OH) would retard it[3].

The objectives of this investigation were two fold:

1. Study the effect of various sugarcane ash (bagasse) concentrations added to the concrete on the corrosion resistance steel reinforcement totally immersed in the corrosive media.
2. Evaluate the corrosion protection of reinforcing in the concrete due to phosphatization process.

EXPERIMENTAL WORK

Specimen Preparation

A batch of 5 concrete specimen of cylindrical geometry (mix design is given in table (1) of dimensions illustrated in figure (2) and contained a single length of reinforcing steel were used in present study. A saturated standard calomel electrode as reference electrode[4] was placed adjacent to the cylindrical concrete exactly in midway opposite to steel the steel rod for the purpose of the potential measurements (i.e., A computerized program(5) was used in analysis of data obtained from polarization measurement taking in consideration the IR drop in potential measurements). The steel rods used in this study were chemically coated named as phosphatizing steel using 5 % mole H_3PO_4. The chemical analysis of the steel specimens is given in table (2).

In the case mentioned above, was to keep it totally immersed into water. The water used as a corrosive environment was taken actually from River pumping station in south of Nasiriya (Dhekar Governorate). The chemical analysis of the water is given in table (3).

All the batches of the 5 concrete specimens were made of type V Portland concrete cement. The chemical composition of this type is given in table (4).

Sugarcane ash obtained from burning the natural "bagasse" which is a waste from sugar industry to about 550 °C was mixed with the mix design concrete cylinders. The bagasse concentration was in the range of 0 to 17% by weight of cement. The chemical analysis of the bagasse is given in table (5).

After the 28 days curing in tap water, the concrete samples were exposed to the desired environment.

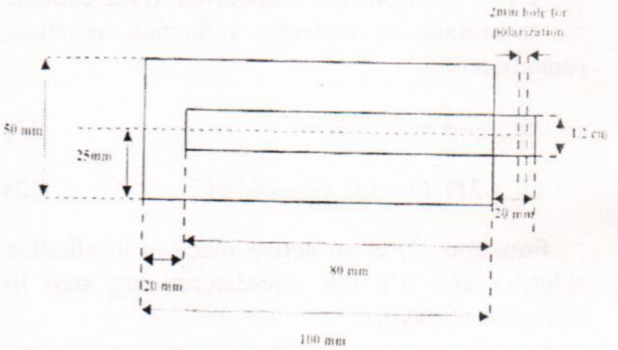

Fig. (2) Geometry of specimens employed in present study

Table (1) Mix design for one cube meter used in the study

1	Kg cement
1.503	Kg dry sand
3	Kg dry gravel,5 mm max diameter
W/C	0.5

Table (2) Chemical analysis of the steel used in the study

Component	*Weight percent (%)*
C	0.1
Si	1.5
Mn	0.83
PO_4	3.7
Cr	0.06
Ni	0.1
Al	0.01
Cu	0.34
Fe	The remainder

Table (3) Chemical analysis of the corrosive water

pH	8.25
Calcium(PPM)	312
Magnesium(PPM)	382
Sodium (PPM)	1392
Potassium (PPm)	8.2
Chloride (PPM)	2068
Sulphate (PPM)	2100
Bicarbonate (PPM)	237
CO_3 (PPM)	26.4
Nitrate (PPM)	4.2

Table (4) Composition of type V Portland cement concrete used in this study

Composition	*Weight percent (%)*
CaO	63.51
SiO_2	19.99
SO_3	1.95
MgO	3.61
R_2O_3	9.55
L.O.I	1.29

Table (5) Chemical analysis of bagasse ash after burning to 505°C

Composition	*Weight percent (%)*
SiO_2	43.7
Fe_2O_3	2.65
Al_2O_3	6.14
FeO	0.95
CaO	9.82
MgO	4.9
SO_3	3.9
N_2O	4.45
K_2O	9.5
Cl	1.45
P_2O	1.82

Electrochemical Procedure

The anodic and cathodic potentiostatic polarization curves were obtained weekly after 28 days curing, for all of the concrete specimens and for a period of six months (24 weeks). The potential of steel rod was measured with a saturated calomel electrode (SCE). A potentiostatic anodic and cathodic polarization tests were also carried out weekly for these samples. For these tests, the potential of steel was kept at many hundreds of mV in comparison to the SCE for few minutes. Then the potential was scanned towards the more positive direction up to many hundreds of mV from E_{corr}. A sweep rate of about 0.3 mV/s was used.

RESULTS AND DISCUSSION

The corrosion potential measurements relative to saturated reference electrode (SCE) is shown in Figure (3). The results indicate that the free corrosion potential of phosphatized steel embedded in concrete containing different concentrations of bagasse was shifted to more active value after subjecting all samples to the corrosive medium. In such cases the high negative potential are not indicative of high corrosion activity. This behavior is probably due to the higher moisture content of concrete samples after 28 days of curing in a tap water. From the curves, a trend of decreasing, through fluctuation, positive potentials could be observed through out the experimental period.

Figure (4) represents the anodic and cathodic curves for phosphatized steel embedded in concrete with various bagasse concentrations, under totally immersed conditions. The results indicate that the cathodic current requirements decrease as bagasse concentrations increase, while the situation is exactly opposite for anodic current requirement. It can be concluded accordingly that the Cl and O_2 ions in the corrosive media play a very important role in the current requirement and its relation with break down in the passive film. Table (6) shows the results obtained using a mathematical model as derived [5] to determine numerically the unknowns i_{corr} and R_cA by deriving linear equations and solving them by the method of averages [6,7]. The program was written in basic language and the exposure time was six months. The results showed that:

1. Generally, as the bagasse concentrations increase the corrosion rate increase.
2. Compared with 0% bagasse, the presence of the different concentrations of bagasse led to enhance the corrosion rate.
3. The values of concrete electrical resistance obtained in presence of bagasse were generally less than that of 0% bagasse and is good agreement with the increase in corrosion rate.

Figure (5) represent the relation ship between i_{corr} and exposure time for phosphatized steel, it is clear that:

(i) In absence of bagasse (i.e. 0 % bagasse), the results indicate that generally the steel is in passive region except in the range of time limited by (14 to 20 weeks), the steel shows low to moderate corrosion rate values.

(ii) In presence of different bagasse concentrations (8, 11, 14, and 17%), generally the data shoes moderate to high corrosion rate value.

The results indicate that, generally, corrosion currents show a significant reduce and increase with exposure time. This can be attributed to the development and break down passive with time.

Rodrigez et al(8),reports that corrosion rates less than 0.2 $\mu A/cm^2$ indicate low to moderate rates, while values in the range of 0.5 $\mu A/cm^2$ to 1.0 $\mu A/cm^2$ indicate moderate to high corrosion rates, and values greater than these are indicative high corrosion rate.

Figure (6) presents the relationship of electric resistance of the electrolyte containing different concentrations of bagasse for phosphatized steel totally immersed in corrosive media, it is clear that:

(i) The presence of bagasse in the concrete reduces the resistance of the electrolyte regardless its concentrations compared with its absence.

(ii)The addition of different concentrations of bagasse to the concrete was not pronounced during the period studied (i.e., the resistance obtained was generally and for all concentrations less than 500 Ω.

Finally, it can be stated that although the bagasse which is a waste by product from sugar industry shows in its chemical analysis and nature is pozzolanic (i.e., these materials usually slow up the hardening and reduce the heat of hydration, increase the resistance to chemical attach or effect economics by reducing the amount of cement required). But the results of this study confirms that it can not be recommended to be an additive to the cement from corrosion point of view, because samples of higher bagasse contents retain more water than samples with no bagasse or lower bagasse content. This can be attributed to the deliquescent property of bagasse which absorbs moisture, leading to create moisture gradient along the steel rod, resulting a local action current flow between the anodic and cathodic regions.

Table (6) Corrosion current density and concrete resistance of embedded steel totally immersed in water obtained iteratively in resisting Portland cement after twenty four weeks of exposure time to the corrosive media.

Totally immersed in water		
Bagasse Concentration (%wt.)	*Phosphatized steel*	
	i_{corr} ($\mu A/cm^2$)	R_c (Ω)
0	0.14	771.970
8	0.9	169.376
11	0.61	309.755
14	0.79	234.317
17	0.93	213.074

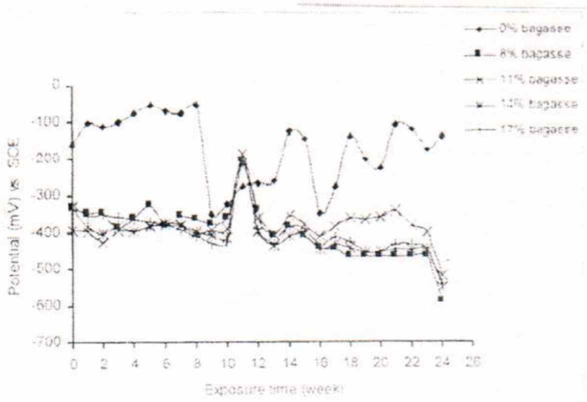

Fig. (3) Corrosion potential/exposure time plot for phosphatized steel totally immersed in water.

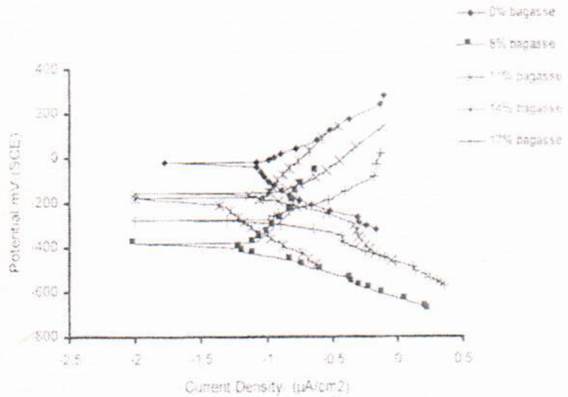

Fig. (4) Polarization curves of phosphatized steel embedded in concrete containing different concentrations of gagasse, after twenty four weeks of totally immersed in water.

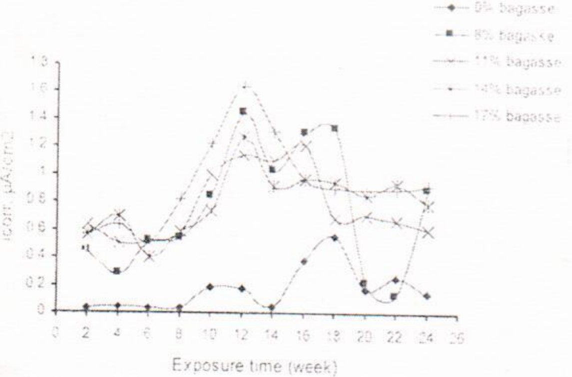

Fig. (5) Relationship between corrosion rate and exposure time for phosphatized steel embedded in concrete containing different concentrations of bagasse totally immersed in water.

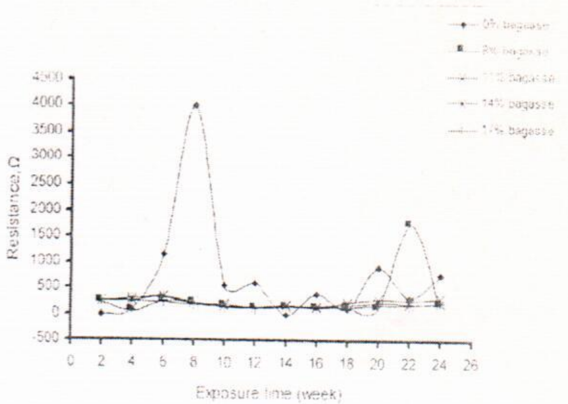

Fig. (6) Electrical resistance of phosphatized steel embedded in concrete containing different concentrations of bagasse totally immersed in water.

REFERENCES

1. Tomashov, N.D., "Theory of corrosion and protection of metals", Macmillan, New York, 1966.
2. Kiyoshi, O., and Toyoaki, M., "International Conference a Performance of Concrete in Marine Environment", Canada, 1980.
3. Mehta, P.K., "Effect of Cement Composition on Corrosion of Steel in Concrete", proceeding of symposium on corrosion of steel in concrete, ASTM Philadelphia, 1975.
4. Locke, C.E., and Dehghanian C., "An Embeddable Reference Electrodes for Salt ContaminantConcrete",Material Performance, Vol. 18, No.2, February 1979.
5. Yaro, A.S., "Optimization of an Adsorption Type Corrosion Inhibitor" ph. D. thesis, University of Baghdad, 1996.
6. Scarborough, J.B. "Numerical Mathematical Analysis", John Hopkins press, Baltimeir, 6th edition, pp.(545-551), 1981.
7. Swinbourin, E.S., " Analysis of Kinetic Data", pp. (24-30), New York 1985.
8. Mark G. Richardson, "Fundamental of Durable Reinforced Concrete" Spoon press, London and New York, 2002(cited).