

Corrosion of reinforced steel in presence of mineral admixture with concrete in acid media

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Received: 27th February, 2008 ; Accepted: 3rd March, 2008

ABSTRACT

Rice Husk Ash (RHA) obtained from parboiling plants could be used to dramatically enhance the workability, strength and impermeability of concrete mixes. Research that has been carried out in this paper has proved efficiency that obtained by utilizing Rice husk ash even in small amounts (5% to 20% cement replacements), the properties of concrete can be significantly giving more inhibition for corrosion of reinforcement in 1 M of each HCl, H₂SO₄, HNO₃, CH₃COOH acid as aggressive media. The measurements carried out by three electrochemical techniques. The results showed that more efficiency of concrete blended with RHA, and the inhibition increased with increasing % of RHA than that without it toward corrosion prevention of reinforcing steel. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Rice husk ash;
Reinforced steel;
Corrosion;
Inhibition.

INTRODUCTION

Rice Husk Ash (RHA) has been used as a highly reactive pozzolanic material to improve the microstructure of the interfacial transition zone between the cement paste and the aggregate in high-performance concrete. The particle grading of cement and RHA mixtures also exerted significant influences on the blending efficiency. The relative strength increase is higher for coarser cement^[1].

When use with fresh concrete mixtures pozzolanic additions, such as RHA have the ability to reduce bleeding and segregation and thus cause significant improvement in workability and durability characteristics^[2].

Rice hull is an abundant material produced in many countries around the world containing approx. 20-25

of silica usually, Rice hull burned at the fields this lead to serious environmental damage. Since silica particles remain suspended in the air being a potential cause of respiratory diseases and environmental damage. So this waste agricultural product most used in cement industry. Recently, a method using Rice Husk Ash as raw material for synthesis β -Ca₂SiO₄ cement at temperature 700°C where Ca₂SiO₄ has five crystalline phases and in generally, the β - phase is predominant one also other phases are usually present^[3]. RHA has a highly micro-porous structure that is responsible for its very high surface area, which often exceeds that of silica fume. Such high surface area of RHA allows its pozzolanic activity to compete with that of the much finer silica fume^[4]. Ground RHA is finer than cement and should be expected to play not only a pozzolanic role but also

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TABLE 1 : Chemical composition and Blaine specific surface area of ordinary Portland cement

Composition	Loss in ignition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	L.O.I	Blaine Cm ₂ /g
%	1.88	21.50	5.18	2.3	63.31	1.84	2.77	119	3659

TABLE 2: Chemical analysis and mechanical properties for reinforcing steel

Chemical analysis %				Mechanical properties		
C	S	P	Mn	Yield stress MPa	Ultimate stress MPa	Elongation %
0.12	0.022	0.063	0.43	38.8	493	23

TABLE 3: Steady state potential values of reinforced steel embedded in cement pastes with different % of RHA in different acids solutions

Composition	Corrosion potential / V			
	In 1 M HCl	In 1 M H ₂ SO ₄	In 1 M HNO ₃	In 1 M CH ₃ COOH
OPC	-1.053	-0.852	-0.436	-0.787
5% RHA	-0.344	-0.2	-0.224	-0.746
10% RHA	0.3875	0.16	-0.12	-0.705
15% RHA	0.768	0.432	0.684	-0.34
20% RHA	0.905	0.96	0.85	-0.129

a micro-filler effect to enhance the particle packing density of concrete^[5].

Acids may uniformly corrode steel but they are capable of corroding steel under the most common conditions lead to localized corrosion. The aim of this work evaluate the improvement of reinforcement corrosion in presence of different types of acids as 1M of each HCl, H₂SO₄, HNO₃, CH₃COOH acids as aggressive media. When used Rice Husk Ash (RHA) as mineral admixture in concrete.

EXPERIMENTAL

Materials and preparation

The concrete was prepared containing Ordinary Portland Cement which contents are summarized in TABLE 1. The main materials of this study RHA which was burn at 750°C for 1 hour then sieved to 98%, then mixed with concrete according various proportion 5%, 10%, 15%, 20% of RHA. The cylinder rod of reinforcement steel was embedded in cube of concrete as working electrode.

Cylindrical specimens of reinforcement has 5Cm height, 1Cm diameter was cast in concrete its chemical analysis and mechanical properties are tabulated in TABLE 2, after molding specimen in concrete with and without additives were cured for 28 days at room temperature .

Test solution

After curing specimens were immersed in test solutions 1M of each HCl, H₂SO₄, HNO₃, CH₃COOH acids which prepared with bi-distilled water.

The electrochemical technique

1. Impressed current method

This method is reliable accelerated corrosion test for determining whether the given medium is corrosive or inhibitive. A constant current density was applied between the specimens and steel counter electrode . The electromotive force was measured against a reference electrode (SCE) with potentiometer (ORION SA520) at constant applied current density 10μA/Cm², the potential of working electrode in V was plotted against time in min.

2. Impressed voltage method

In which constant positive potential which is sufficient to cause a significant change in corrosion current value is applied to the steel bar in concrete and this current is measured periodically using the electronic potentiostat Amel model 549. The corrosion current-time plots presented were given with corrosion current mA/Cm² and time in hours. And the weight loss of the steel due to the corrosion process can be measured from the area under the curve.

3. Potentiostatic polarization method

In which a potential was applied ranging from -2000 mV to +2000 mV to reinforcing steel bar embedded in concrete, it is much more reflective of the corrosion behavior of the reinforcement. The potential- current plots give in mV against current in mA/Cm².

RESULTS

Impressed current method

Figures (1-4) show the potential-time curve at a constant impressed current of 15 μA/Cm² for reinforced steel embedded in cement pastes admixed with different % of RHA when immersed in 1M of each HCl, H₂SO₄, HNO₃, CH₃COOH acids in order, The steady state potential values of the samples with each acid and % of RHA are shown in TABLE 3. From these results

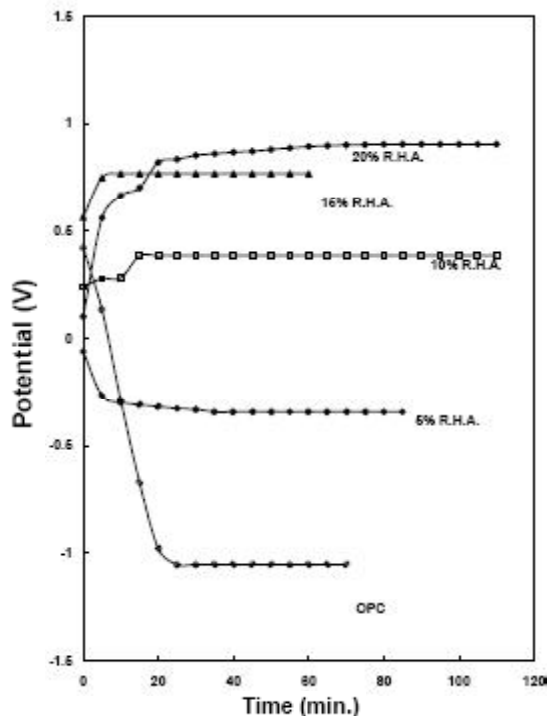


Figure 1 : Potential -time relationship of reinforced steel with different % of RHA immersed in 1M (HCl)

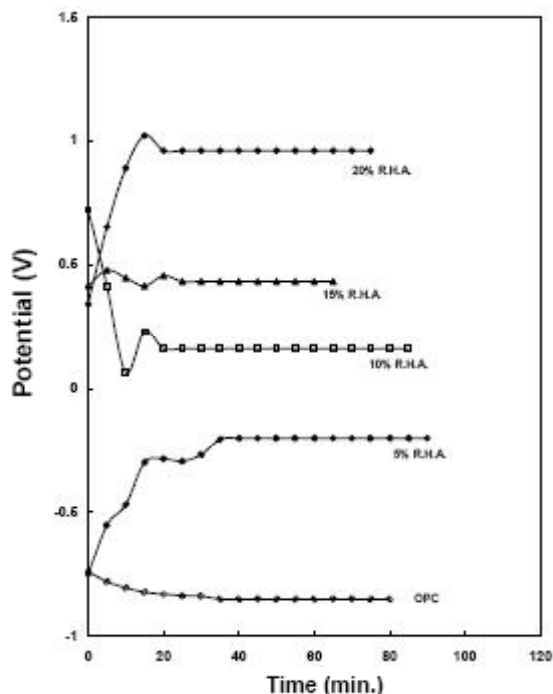


Figure 2 : Potential -time relationship of reinforced steel with different % of RHA immersed in 1M (H₂SO₄)

it can be noticed that while steel passivity degree is low in the OPC, it has increased with increasing % of RHA for all acids as the following order HCl>H₂SO₄>HNO₃

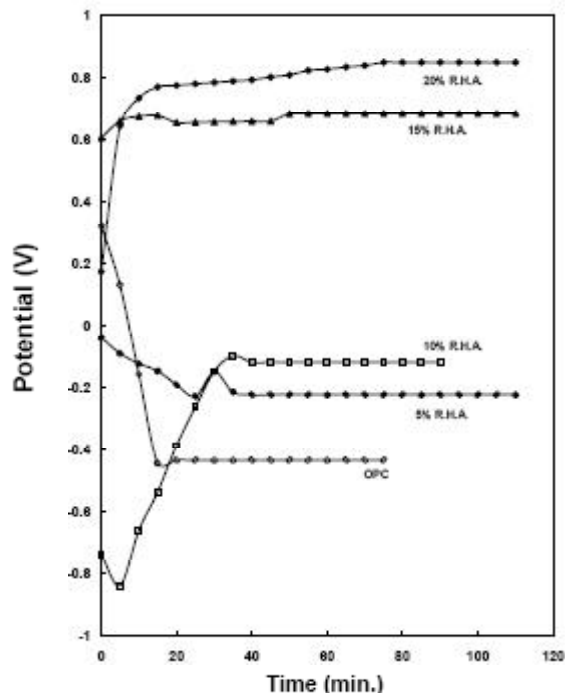


Figure 3 : Potential -time relationship of reinforced steel with different % of RHA immersed in 1M (HNO₃)

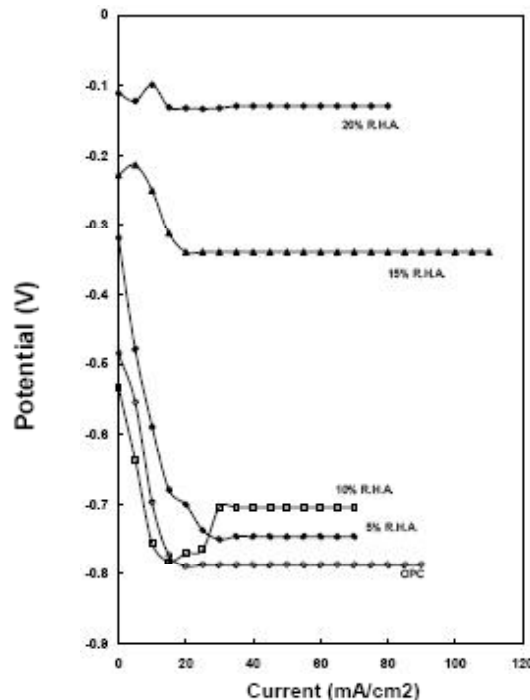


Figure 4 : Potential -time relationship of reinforced steel with different % of RHA immersed in 1M (CH₃COOH)

>CH₃COOH. The higher potential with higher % of RHA is due to improvement effect of RHA for corrosion of reinforcement when mixed with OPC.

Potentiostatic polarization method

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The potentiostatic polarization behavior are shown in figures (5-8) for reinforced steel embedded in cement pastes admixed with different % of RHA when

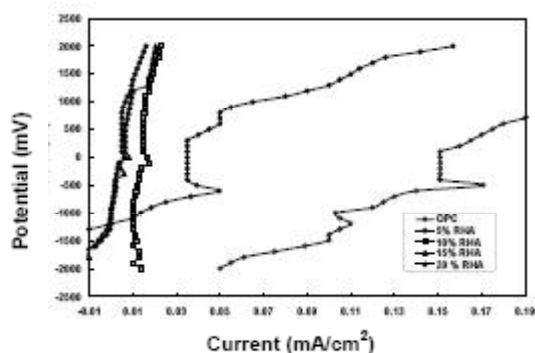


Figure 5: Potential-current relationship of reinforced steel embedded in cement pastes with different % RHA immersed in 1 M (HCl)

immersed in 1M of each acid HCl, H_2SO_4 , HNO_3 , CH_3COOH in order. It can be seen that increasing % of RHA content mixed with cement paste causing increase the ability of reinforced steel to be more passive against aggressive media of different acids. The different maxima shown on the potentiostatic polarization curves have been attributed to the formation of different types of iron oxide. The corrosion Parameter for reinforcement in concrete mixed with different % of RHA in different aggressive media of acids are summarized in TABLES (4-7) as in order of acids from more corrosive to less corrosive, we notice that I_{corr} , I_{pass} decreased with increasing % of RHA and corrosion rate decreased, this indicates presence RHA make reinforced steel more resist for corrosion and inhibition is occur.

The corrosion rates of the reinforced steel were

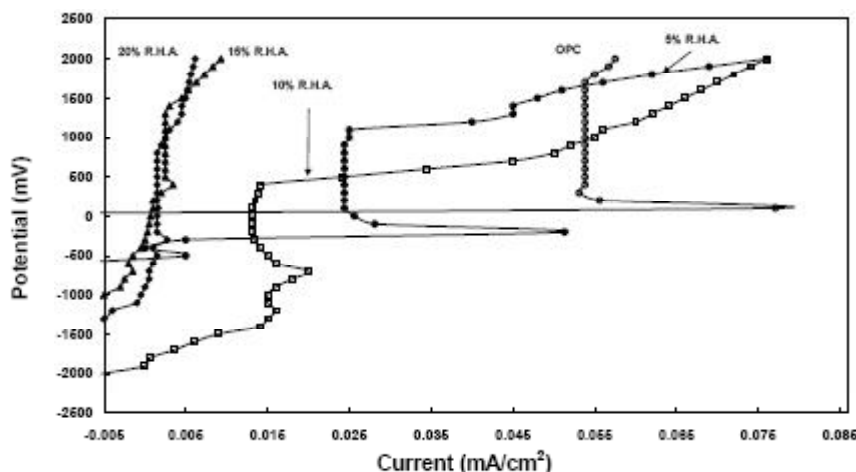


Figure 6: Potential-current relationship of reinforced steel embedded in cement pastes with different % RHA immersed in 1 M (H_2SO_4)

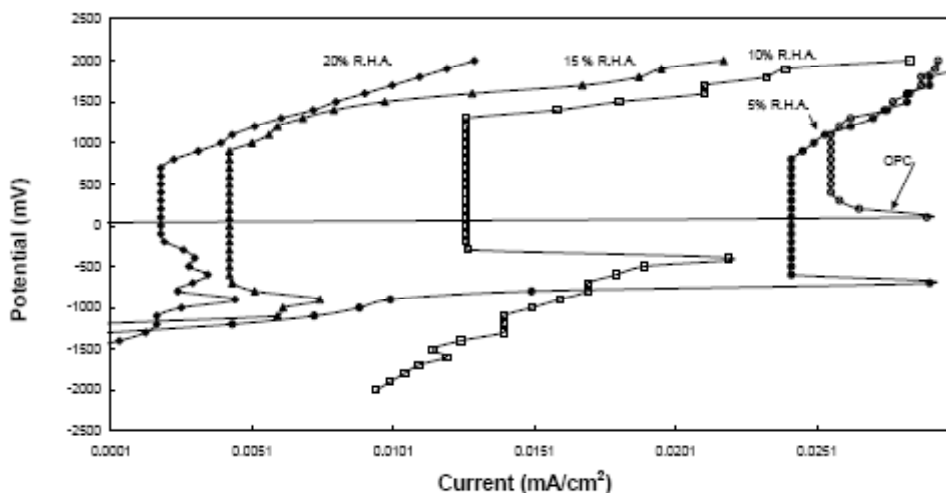


Figure 7: Potential-current relationship of reinforced steel embedded in cement pastes with different % RHA immersed in 1 M (HNO_3)

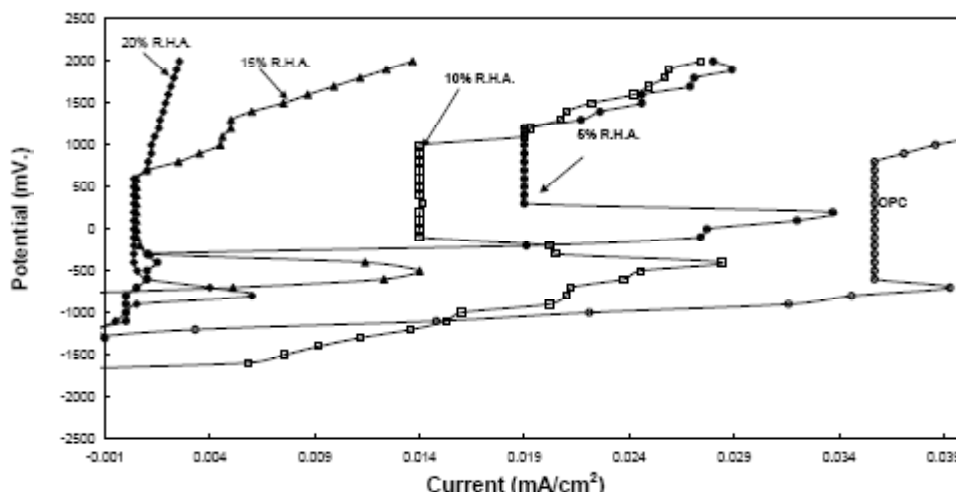


Figure 8: Potential-current relationship of reinforced steel embedded in cement pastes with different % RHA immersed in 1 M (CH₃COOH)

TABLE 4 : Corrosion parameter for rebar in concrete mixed with RHA in HCL

	I _{pass}	E _{pass}	I _{corr}	E _{corr}	CR
OPC	0.151	-400	0.16	200	1.856
5% RHA	0.035	-400	0.04	400	0.464
10% RHA	0.0148	100	0.0172	1200	0.19952
15% RHA	0.0065	100	0.0085	900	0.0986
20% RHA	0.005	100	0.0055	900	0.0638

TABLE 5 : Corrosion parameter for rebar in concrete mixed with RHA in H₂SO₄

	I _{pass}	E _{pass}	I _{corr}	E _{corr}	CR
OPC	0.0538	400	0.055	1800	0.638
5% RHA	0.0244	100	0.025	1000	0.29
10% RHA	0.0134	-300	0.0241	500	0.27956
15% RHA	0.0025	500	0.0045	1500	0.0522
20% RHA	0.0015	-200	0.002	900	0.0232

TABLE 6 : Corrosion parameter for rebar in concrete mixed RHA in HNO₃

	I _{pass}	E _{pass}	I _{corr}	E _{corr}	CR
OPC	0.0256	400	0.0263	1300	0.3051
5% RHA	0.0242	-600	0.025	1000	0.29
10% RHA	0.01276	-300	0.0159	1400	0.18444
15% RHA	0.0043	-600	0.006	1200	0.0696
20% RHA	0.00187	-100	0.00233	800	0.02703

TABLE 7 : Corrosion parameter for rebar in concrete mixed RHA in CH₃COOH

	I _{pass}	E _{pass}	I _{corr}	E _{corr}	CR
OPC	0.0357	-600	0.0371	900	0.43036
5% RHA	0.019	300	0.0217	1300	0.25172
10% RHA	0.014	-100	0.0193	1200	0.2239
15% RHA	0.00053	-100	0.0025	800	0.029
20% RHA	0.00038	-400	0.001	700	0.0116

calculated using the following equation^[6]:

$$\text{Corrosion rate } (\mu\text{m/yr.}) = k (A i_{\text{corr}} / ND)$$

Where: D density of the metal (g/Cm³); K constant depending

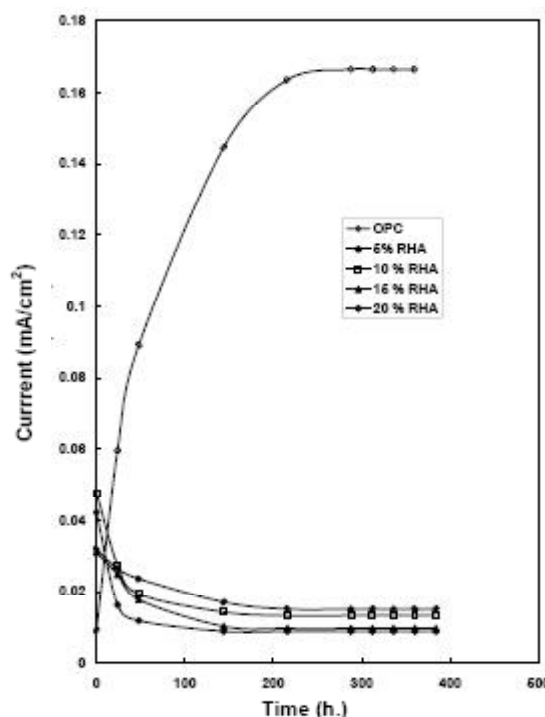


Figure 9 : Current-time relationship of reinforced steel embedded in cement paste with different % of RHA in 1M HCl at 2V

on the penetration rate units desired for (μm/yr.), K=3.27; A is An atomic weight of the metal, N number of electrons, i_{corr} corrosion current density in μA/Cm²

For iron or steel: corrosion rate μm/yr. = 11.6 i_{corr}

Impressed voltage method

In this method a potential of 2V and 4V was applied to the reinforced steel, the current flowing to the counter electrode in mA/Cm² being measured every 24

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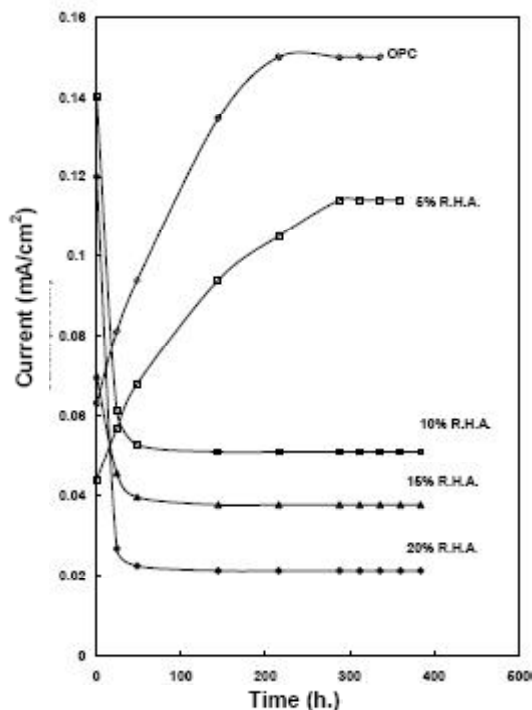


Figure 10 : current-time relationship of reinforcing steel embedded in cement paste with different % of RHA in 1M HCl at 4V

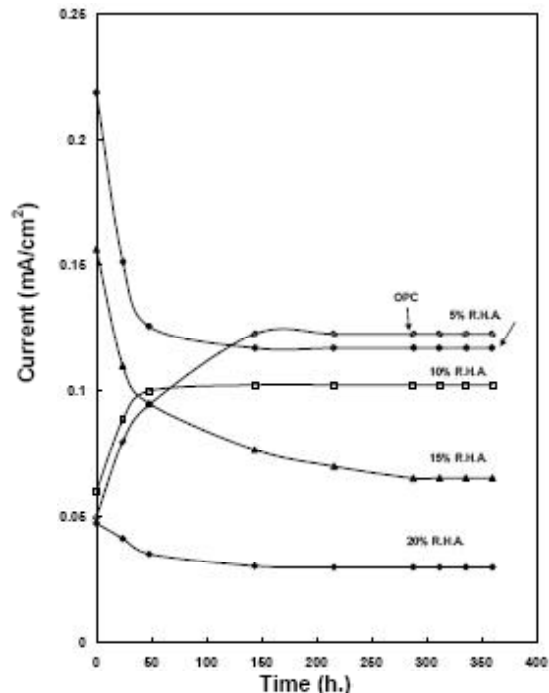


Figure 12 : Current -time relationship of reinforcing steel embedded in cement paste with different % of RHA in 1M (HNO₃) 4V

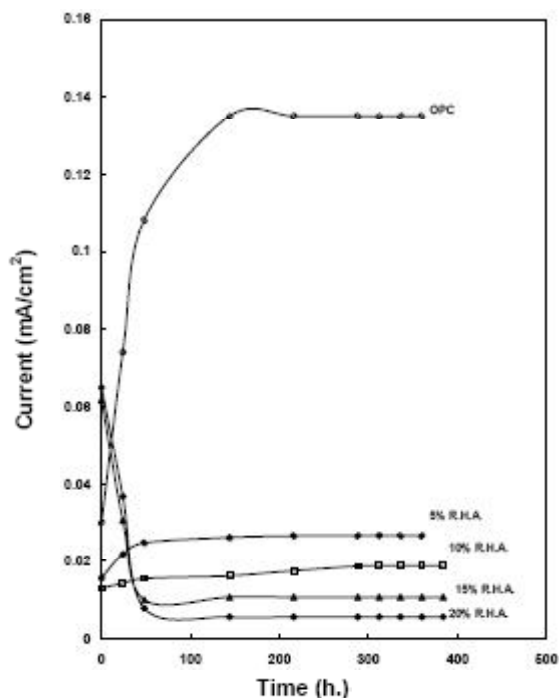


Figure 11 : Current-time relationship of reinforced steel embedded in cement paste with different % of RHA in 1M (H₂SO₄) at 4V

hours relating to reference electrode. Figure (9) as representative curve of the current- time relationship for

reinforcing steel embedded in cement pastes mixed with different % of RHA at potential 2V in HCl, while figures (10-13) represents the current- time relationship for reinforcing steel embedded in cement pastes mixed with different % of RHA at potential 4 V in different acids. It can be seen that the values of corrosion current in experiments at potential 2V would be the same trend at potential 4V with difference in values according potential which used. The curves exhibit the same general trend where the corrosion current decreased sharply with time followed by relatively small current variations reaching a steady state in most cases after about 150 h also, the corrosion current was decreased by increasing % of RHA and with the following order of different acids HCl > H₂SO₄ > HNO₃ > CH₃COOH.

The corrosion current values of the different % of RHA in different acids are shown in TABLE 8 when used potential 2V and TABLE 9 when used potential 4V.

The degree of the corrosion intensity which related to the size of area under the corrosion current-time curves, can be estimated by using Faraday's law:

$$W = K(I.T),$$

Where W is the mass of substance liberated, I is the intensity of current, t is the prolonged time and K is a proportional

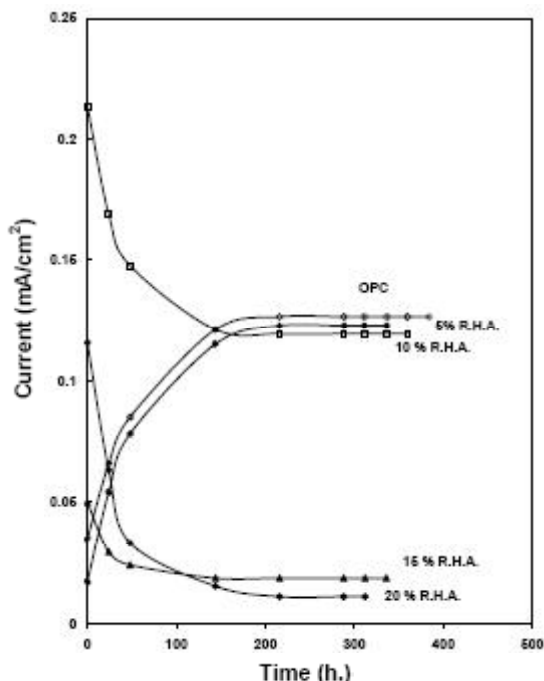


Figure 13 : Current -time relationship of reinforcing steel embedded in cement paste with different % of RHA in 1M (CH₃COOH) at 4V

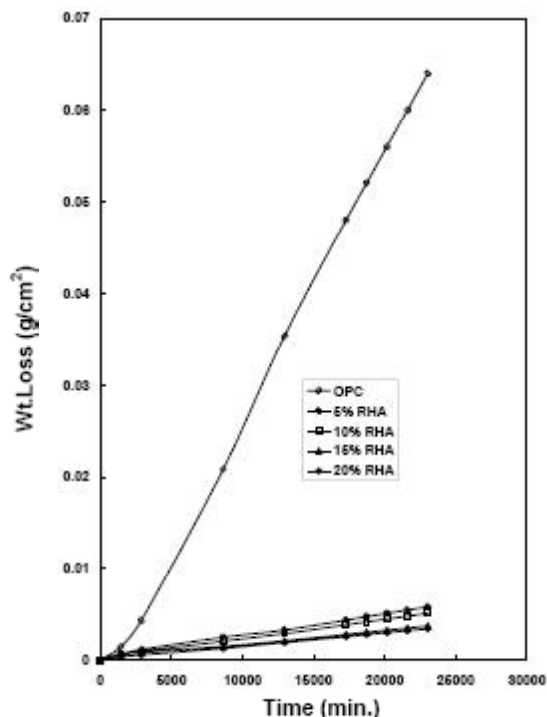


Figure 14 : Weight loss-time relationship of reinforced steel embedded in cement paste with different % of RHA in 1MHCL at 2V

constant equaling to 0.0167g/A.min for steel^[7].

The weight loss of reinforcement steel can be de-

TABLE 8 : Corrosion current values of reinforced steel embedded in cement pastes with different % of RHA in different acids solutions at potential 2V

Composition	Corrosion current (mA/Cm ²)			
	In 1 M HCl	In 1 M H ₂ SO ₄	In 1M HNO ₃	In 1 M CH ₃ COOH
OPC	0.1664	0.1617	0.0404	0.06
5% RHA	0.015	0.15	0.0381	0.036
10% RHA	0.0132	0.082	0.0315	0.0343
15% RHA	0.0096	0.0492	0.0145	0.0186
20% RHA	0.0088	0.015	0.0063	0.0085

TABLE 9 : Corrosion current values of reinforced steel embedded in cement pastes with different % of RHA in different acids solutions at potential 4V

Composition	Corrosion current (mA/Cm ²)			
	In 1 M HCl	In 1 M H ₂ SO ₄	In 1M HNO ₃	In 1 M CH ₃ COOH
OPC	0.15	0.1351	0.1227	0.1268
5% RHA	0.1142	0.0266	0.117	0.123
10% RHA	0.0511	0.01867	0.1024	0.1195
15% RHA	0.0377	0.0107	0.0654	0.0186
20% RHA	0.0213	0.0056	0.03	0.011

termined quantitatively from the above equation and related to the time of the experiment. Figure (14) as representative curve when used potential 2V and figures (15-18) show, the weight loss of reinforcement steel when used potential 4V in 1M HCl, H₂SO₄, HNO₃, CH₃COOH acids as test solutions. It can be seen that the curves exhibit the same general trend where the weight loss (g/Cm²) increases linearly with time along time of experiments. It can be noticed that while the weight loss is high in the OPC in the acids media, it has been low in samples mixed with RHA. Also the amount of steel dissolved due to corrosion decreased in presence of RHA depending on % of RHA and types of acid as aggressive media.

DISCUSSION

The previous results can be explained on the basis that, the reinforced steel embedded in concrete is well protected against corrosion by a passivating film of ferrous oxide which developed on the steel surface. The protective action of the passivating film and high alkalinity of concrete is the basis of concrete ability to chemically protect steel from corrosion process. Steel exhibit passive behavior over an extended range of potential, pH and oxidizing power, for which a very thin film adherent and of low ionic permeability develops on the surface of the steel (passive state) this reduces the ki-

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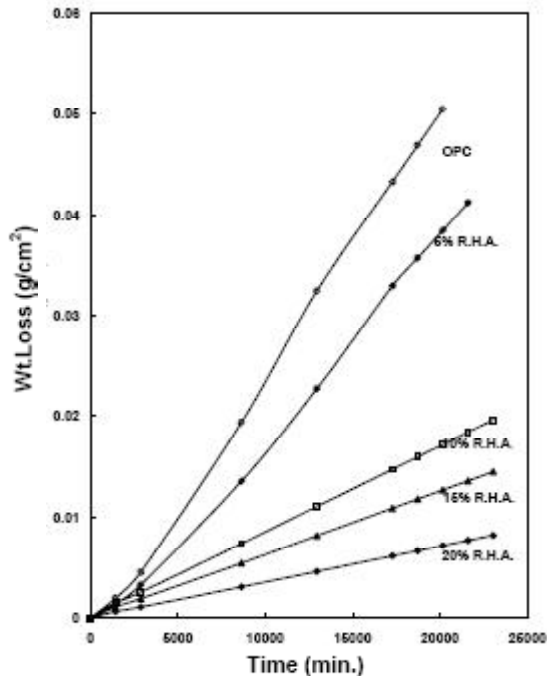


Figure 15 : Weight loss-time relationship of reinforced steel embedded in cement paste with different % of RHA in 1M HCl at 4V

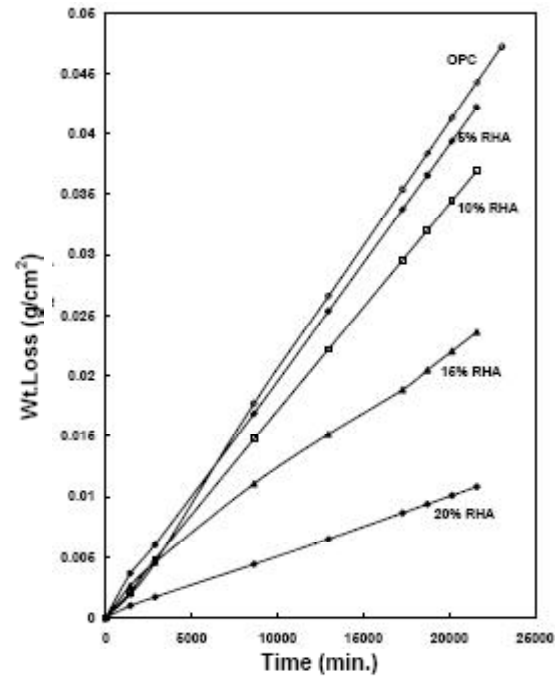


Figure 17: Weight loss-time relationship of reinforced steel embedded in cement paste with different % of RHA in 1M HNO₃ at 4V

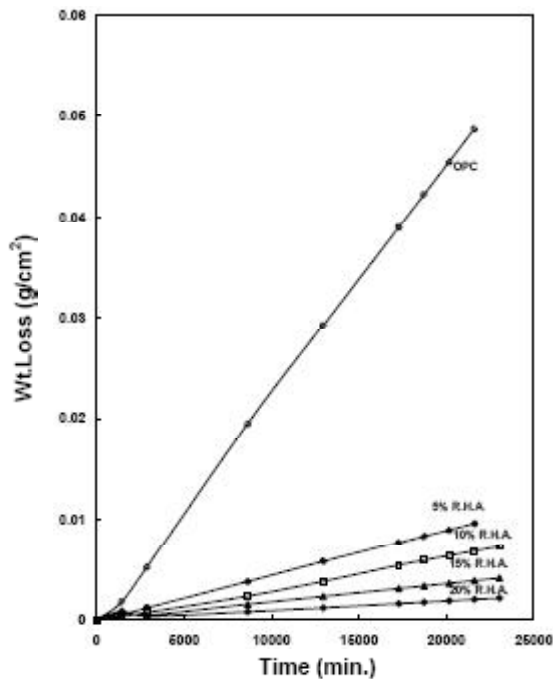


Figure 16: Weight loss-time relationship of reinforced steel embedded in cement paste with different % of RHA immersed in H₂SO₄ at 4V

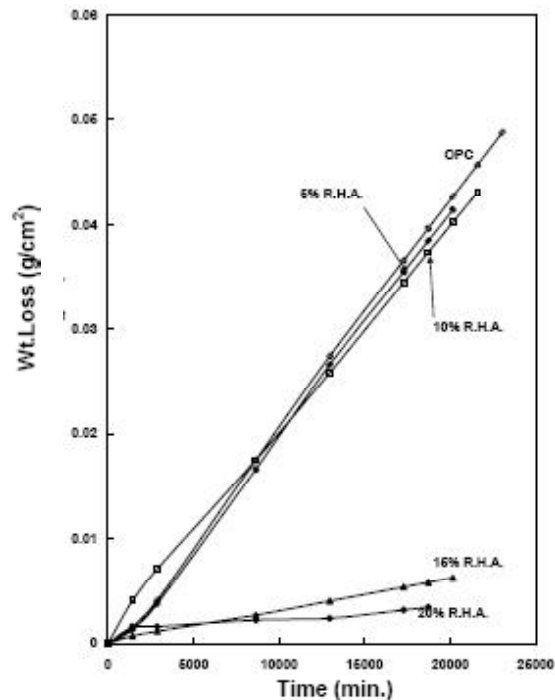


Figure 18: Weight loss-time relationship of reinforced steel embedded in cement paste with different % of RHA in 1M CH₃COOH at 4V

netics of dissolution (corrosion) to a level acceptable to the user. When service conditions become more aggressive the loss of the nature passivity of concrete struc-

tures will be lost. The degree of attack depend on many factors which accelerating the corrosion process. Acids are examples of media generating uniform corro-

sion, In this work we used different types of acids according to their nature.

Hydrochloric acid as reducing type mineral acids which causing general corrosion from high activity of it and due to the fact that this reducing medium is very unfavorable to the passivation of steel. It follow from this that the presence of oxidants, which leads to an increase in the kinetics of the cathodic reaction, increases the exchange current and therefore the dissolution rate of the steel.

Such behavior is thus fundamentally different from that observed, in sulfuric acid for which the presence of oxidants can lead in many cases to passivation of steel. Where sulfuric acid is considered Non-oxidizing mineral acid but it has less activity than hydrochloric acid and significantly increases the corrosion rate in the active state of the steel and in a moderately concentrated sulfuric medium. Nitric acid is strongly oxidizing mineral acids, it is obtained by catalytic oxidation of ammonia NH_3 , which forms gases NO_2 or N_2O_4 which are then absorbed by water. These compounds are not particularly corrosive for steel, the only significant problem encountered, is the risk of intergranular corrosion on welded structures. as well as moderately concentrated solutions containing highly oxidizing cations are very aggressive and induce a particular form of localized intergranular corrosion, independent of the microstructure of the reinforcement^[8].

Acetic acid is example of an organic acid which is generally less aggressive media than mineral acids for they are weakly dissociated in solution. So, the results show the effective of test solutions according the following order of acids $\text{HCl} > \text{H}_2\text{SO}_4 > \text{HNO}_3 > \text{CH}_3\text{COOH}$. Although acetic acid has a very low ionization constant ($K_a = 1.8 \times 10^{-5}$) compared to other acids, the effective acidity in aqueous solution increases rapidly with the concentration, making this product relatively less aggressive than mineral acid.

The consistency of OPC paste blended with RHA increased with increase in the amount of RHA. This attributed to the higher specific surface area of RHA so, it is not only has a pozzolanic role, but also a micro-filler effect to enhance the particle packing density of concrete compare to cement. Addition of rice husk ash to Portland cement forms a calcium silicate hydrate (CSH) gel around the cement particles which is highly dense and less porous. This may increase the strength

of concrete against cracking. And due to its affect both the chemical composition of cement paste and the chemical properties of concrete. This may increase the strength of concrete against corrosion of reinforcing steel embedded in it. This indicate that the replacement of rice husk ash refined the pores and thereby the permeability and corrosion gets reduced. The percentage of RHA was optimizing by measuring the initial and final setting times^[9].

CONCLUSION

Using RHA as a mineral admixture with OPC is very useful not only for improving the concrete properties but also from the results giving lower corrosion current values of the samples incorporating with OPC when mixing with RHA and this inhibition increase with increasing % of RHA than that of OPC in absence RHA, this means corrosion inhibition due to improvement effect of adding RHA. Where RHA act as micro-filler reducing permeability of ions increases the resistivity of the paste and thus reduces the corrosion rate of the reinforcing steel.

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