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Corrosion behavior of reinforced steel in presence of mineral and chemical admixtures in HCl, H_2SO_4 media

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ABSTRACT

The effect of 5% Rice Husk Ash (RHA) as a mineral admixture on the corrosion behavior of reinforced steel in presence of different concentrations of chemical admixtures as lignosulphonate and superplacticizer has been studied, in HCl, H_2SO_4 acid media using Impressed Current Method, Impressed Voltage Method and Potentiostatic Polarization Method. It was found that, the samples which contain 5 % RHA in presence of chemical admixtures are more resistant to the corrosive media than that containing chemical admixtures only. This is due to the large surface area of RHA which decrease the permeability of the samples.

KEYWORDS

Rice husk ash;
Chemical admixtures;
Reinforced steel;
Corrosion.

INTRODUCTION

Admixtures of concrete mortar or cement paste are organic or inorganic materials in solid state, added to concrete batch immediately before or during mixing. Chemical admixtures are often used to optimize the coast effectiveness of concrete mix and controlling the quality of the concrete[1].

The Rice hull is an abundant material produced in many countries around the world containing approx. 20-25 % of silica, which 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[2].

Corrosion behavior of reinforced steel embedded in cement paste incorporating with different amounts of silica fume as a partial replacement of Ordinary Portland Cement has been studied in chloride and sulphate solutions by using different electrochemical techniques. The results indicate that, while steel passivity degree is low in the control samples upon soaking in the corrosive media, it has been high in samples incorporating silica fume and increased with increasing silica fume content. The improvement effect of silica fume may be attributed to the pore solution structure of the cement paste, which limits the mobility of aggressive ions near the surface of the steel. The mechanism of steel corrosion due to chloride and sulphate attack, also passivation effect of silica fume are discussed[3].

Pazzolanic additions of RHA have the ability to re-

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 : Various proportion of the concrete mixtures

Mixture	Cement	Concrete mixtures		
		A	B	RHA
1	OPC	0.6	-	5%
2	OPC	1.2	-	5%
3	OPC	1.6	-	5%
4	OPC	2	-	5%
5	OPC	-	0.3	5%
6	OPC	-	0.45	5%
7	OPC	-	0.6	5%

Where: OPC is ordinary Portland cement, A is chemical admixture superplasticizing, B is chemical admixture lignosulphonate, RHA is natural Rice Husk Ash

duce bleeding and segregation and thus cause significant improvement in workability and durability characteristics. Hydration of 10 wt % Rice Husk Ash blended Ordinary Portland Cement has been studied in presence of 2 wt. % CaCl$_2$, 1 wt. % lignosulphonate and a mixture of the two admixtures by using different methods. The admixtures did not prevent the deterioration of the blended cement in corrosive atmosphere in N/60 H$_2$SO$_4$ because calcium chloride accelerates the corrosion of the cement[4].

The RHA blended Ordinary Portland Cement greatly improves the durability characteristics, and reduce the mass loss of concretes exposed to HCl acid solution and largely reduced the expansion due to sulfate attack and alkali-silica reaction[5].

Addition of RHA, superplactisizer and air-entraining admixture to cement paste at various ages of these concrete mixtures were evaluated and their resistance to chloride penetration was examined the results show that the chloride penetration was substantially decreased by RHA, a naphthalene sulfonated superplacticizer with a solid content of 42% was used to achieve the desired workability for all concrete admixtures, and a synthetic detergent air entraining (AEA) admixture was used to measure the AEA requirement versus the addition rate of SF and RHA[6].

The superplasticizer requirement for concrete mixtures incorporating SF was higher than that of concrete mixtures incorporating similar proportions of RHA. Comparable results were obtained by Bouzoubaa and Fournier[7].

The aim of the present work is to evaluate the corrosion inhibition value for reinforcing steel in presence of 5% RHA when blended with Ordinary Portland Cement as mineral admixture, with and without chemical admixtures such as lignosulphonate and superplacticizer, those lead to improve quality of concrete. The experiments occur in aggressive media of 1M HCl and 1M H$_2$SO$_4$ by using three different electrochemical techniques.

EXPERIMENTAL

Materials

- A Commercial fresh sample of OPC was used and its chemical composition and Blaine specific surface area are summarized in TABLE 1.
- The rice husk ash was burnt at 750^{0}C for 1 hour then sieved to 98%, and mixed with concrete with certain percentage 10% with various proportions of chemical admixtures according its type and its limiting value illustrated in TABLE 2.
- The two types of chemical concrete admixtures used in this study are:

Admixture (A): Superplasticizer which is super water reducer its advantages are produce concrete with high workability for easy placement, with a lower water content and also good durability characteristic. It was based on sulphonated naphthalene formaldehyde (SNF), its dosages used in range between 0.6 to 2 L /100 K gm of cement.

Admixture (B): Retarding water reducing, is based on selected lignosulphonate its advantages is retarding setting time with improving properties of hardened concrete, increase strength ,durability and decrease the heat of hydration. It is based on water soluble organic compound consists of Ca, Na, NH4 salts of lignosulfonic acid, its percentage used between 0.3 to 0.6 L/100 K gm of cement.

- The reinforced steel used was in the form of rods 1mm diameter and 5 Cm long with a small hole of 2 mm diameter in center of upper side of electrode. The chemical analysis and mechanical properties of the reinforced steel bar are summarized in TABLE 3.

TABLE 3: Chemical analysis and mechanical properties for reinforcing steel

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

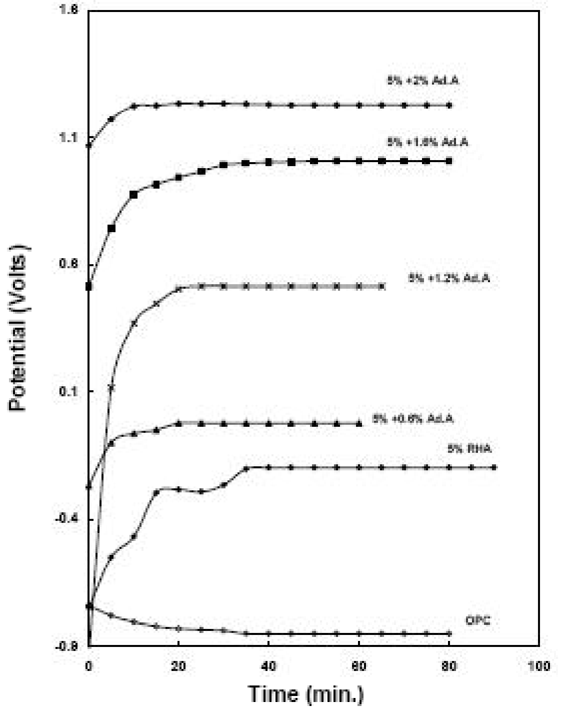

Figure 1 : Potential-time relationship of reinforced steel embedded in cement pastes with different amounts of adm. A and 5% RHA immersed in 1M H_2SO_4

Preparation of samples

- A weighed amount of OPC was placed on a smooth, non absorbent surface, and a crater was formed in the center. The required amount of mixing water with and without chemical admixtures was poured into the crater, tap water was used in mixing, and water-cement ratio was determined using vicat apparatus.
- The reinforced steel bars were mechanically polished and degreased with acetone, then covered with Teflon except an area of 1 cm^2. They were centrally placed in the cement paste in cubic 2.5×2.5×2.5 cm stainless steel moulds. After 24 hours the samples were molding with and without additives and cured in a humidity chamber at 100% relative humidity (R.H.) and at room temperature the samples were immersed in the tested solutions.
- 1 M of each acid HCl, H_2SO_4 was prepared from A.R grade and bi-distilled water and was checked to keep it at constant concentration values.

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 bar considered as a counter electrode. The potential was measured against a reference electrode (SCE) with potentiometer (ORION S A 520) at constant applied current density 15 $\mu A/Cm^2$ 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 embedded in concrete and this current which flowing from the reinforced steel to counter electrode was measured periodically using the electronic potentiostat Amel model 549. The anode was the specimen to be tested and the cathode was a steel bar of the same dimensions as the anode. The corrosion current-time plots presented were given with corrosion current in mA/Cm^2 and time in hours. From this method, 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-2000V to +2000V to reinforcing steel bar embedded in concrete using a counter electrode of steel bar and a saturated reference electrode (SCE), it is much more reflective of the corrosion behavior of the bar in which the potential measured in mV and current in mA/Cm^2.

RESULTS AND DISCUSSION

Impressed current method

The potential-time curves at a constant current 15 $\mu A/Cm^2$ for reinforced steel embedded in cement paste admixed with admixture A and admixture B in presence 5 % of RHA with and without admixtures immersed in aggressive media 1M of each acid HCl, H_2SO_4 as test

TABLE 4 : Steady state potential values of reinforced steel embedded in cement pastes with and without chemical admixtures immersed in acid aggressive media

Composition	HCl	H_2SO_4
OPC	-1.053	-0.852
5% RHA	-0.344	-0.2
5%RHA + 0.6 adm. A	-0.058	-0.023
5%RHA + 1.2 adm. A	0.0917	0.515
5%RHA + 1.6 adm. A	0.1618	1.007
5%RHA + 2 adm. A	0.895	1.228
5%RHA + 0.3 adm. B	0.12	0.68
5%RHA + 0.45adm. B	0.3267	1.07
5%RHA + 0.6 adm. B	0.881	1.184

TABLE 5 : Corrosion parameters for reinforced steel embedded in cement pastes with and without chemical admixture A immersed in HCl

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.151	-400	0.16	200	1.856
5% RHA	0.035	-400	0.04	400	0.464
0.6% A	0.015	-500	0.02	500	0.232
1.2% A	0.009	-500	0.0112	300	0.12992
1.6% A	0.005	-500	0.0075	700	0.087
2% A	0.0015	0	0.0022	700	0.02552

TABLE 6 : Corrosion parameter for reinforced steel embedded in cement pastes with and without chemical admixture B immersed in acid aggressive media HCL

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.151	-400	0.16	200	1.856
5% RHA	0.035	-400	0.04	400	0.464
0.3% B	0.016	-800	0.0219	300	0.25404
0.45% B	0.003	-500	0.005	500	0.058
0.6% B	-0.064	-600	-0.058	700	-0.6728

TABLE 7 : Corrosion parameter for reinforced steel embedded in cement pastes with and without chemical admixture A immersed in acid aggressive media H_2SO_4

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.0538	400	0.055	1800	0.638
5% RHA	0.0244	100	0.025	1000	0.29
0.6% A	0.0106	700	0.0115	1800	0.1334
1.2% A	0.0047	-100	0.0055	1500	0.0638
1.6% A	0.0014	-300	0.002	600	0.0232
2% A	-0.0009	-300	0.0015	1300	0.0174

solutions are studied. Figure 1 is taken as representative curve. The steady state potential values of the samples are shown in TABLE 4.

From these results it was found that steady state potential of samples contain RHA and different ratios of the chemical admixtures have a values increase towards positive direction, this means that the samples have more resistance to corrosion than that with OPC only. This is due to improvement effect of RHA which is not restrict the effect of inhibition occurs due to presence of chemical admixtures A and B. But RHA can improve the effect of those admixtures and have more inhibition effect than their without RHA.

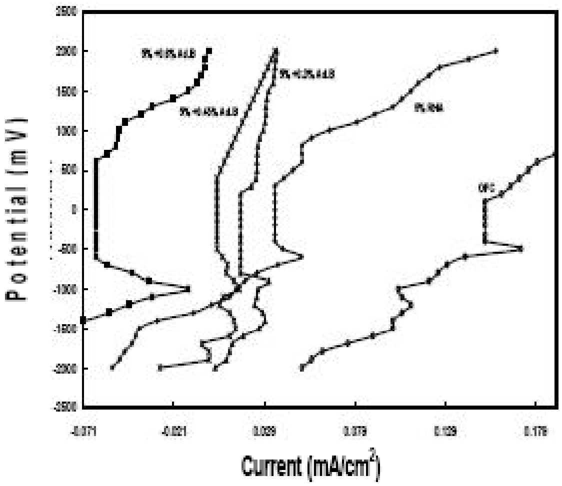

Figure 2 : Potential-current relationship of reinforced steel embeded in cement pastes with different amounts of adm. B and 5% RHA immersed in HCl

Potentiostatic polarization method

The potentiostatic polarization experiments for reinforced steel embedded in cement paste admixed with admixture A and admixture B in presence of 5 % RHA with and without admixtures immersed in 1M of each acid HCl, H_2SO_4 as test solutions are investigated. **Figure** 2 is taken as representative curve. It can be seen that, presence of RHA increases the ability of steel to be more passive against acids, while at ability increases with mixing chemical admixtures to OPC without any restricted of RHA. The different maxima attributed to the formation of different types of iron oxide. Corrosion rates of the test electrodes were calculated using the following equation[8]:

$$\text{Corrosion rate } (\mu m/yr.) = k\,(A\,i_{corr}/ND) \qquad (1)$$

Where: D density of the metal (g/cm^3), K constant depending on the penetration rate units desired for (μm/yr.) where K=3.27, A is atomic weight of the metal, N number of electrons and i_{corr} corrosion current density in μA/Cm^2. For iron or steel:

$$\text{Corrosion rate } (\mu m / yr.) = 11.6\, i_{corr}$$

and tabulated in TABLES (5-8) for admixture A and admixture B in test solutions of two acids, with other corrosion parameters of reinforcing steel that shown from the figures.

We notice that I_{corr} decreased in presence of RHA

TABLE 8 : Corrosion parameter for reinforced steel embedded in cement pastes with and without chemical admixture B immersed in acid aggressive media H_2SO_4

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.0538	400	0.055	1800	0.638
5% RHA	0.0244	100	0.025	1000	0.29
0.3% B	0.0045	-200	0.008	1300	0.0928
0.45% B	0.002	-400	0.0023	400	0.02668
0.6% B	0.0015	600	0.0017	1200	0.01972

TABLE 9 : Corrosion current values of reinforced steel embedded in cement pastes with and without chemical admixture immersed in both acid aggressive media at potential 2V

Composition	HCl	H_2SO_4
OPC	0.1664	0.1617
5% RHA	0.015	0.15
5%RHA + 0.6 adm. A	0.0115	0.0047
5%RHA + 1.2 adm. A	0.0107	0.004
5%RHA + 1.6 adm. A	0.0078	0.0016
5%RHA + 2 adm. A	0.0069	0.0005
5%RHA + 0.3 adm. B	0.01	0.125
5%RHA + 0.45 adm. B	0.009	0.077
5%RHA + 0.6 adm. B	0.005	0.023

and at decreases become more with chemical admixtures A and B in the aggressive media. Also corrosion rate (CR) of consuming steel per year decreased. another parameter as I_{pass} which is better indicator of corrosive behavior is decreased in presence of RHA without and with chemical admixtures A, B when samples immersed in aggressive media of acids illustrated in TABLES (5-8).

Impressed voltage method

In this method potentials of 2V and 4V were applied to the reinforced steel, the current flowing to the counter electrode in mA/Cm^{-2} being measured every 24 hours relating to a reference electrode (SCE). **Figure** 3 is taken as representative curve, show the current-time relationship for reinforcing steel embedded in cement pastes mixed with different values of both chemical admixtures with 5% RHA at potential of 2V as representative curve. While figure 4 represented as representative curve the current-time relationship for reinforcing steel embedded in cement pastes mixed with different percentage of both chemical admixtures with 5% RHA at potential 4V in 1M of each acid HCl, H_2SO_4. It can be seen that the values of corrosion current in experiments occurred at potential of 2V have same trend of behavior as experiments occurred at potential 4V, but different in the values of corrosion current according to the value of potential as in TABLES (9-10). The curves exhibit the same general trend where the corrosion current decreased sharply with time fol-

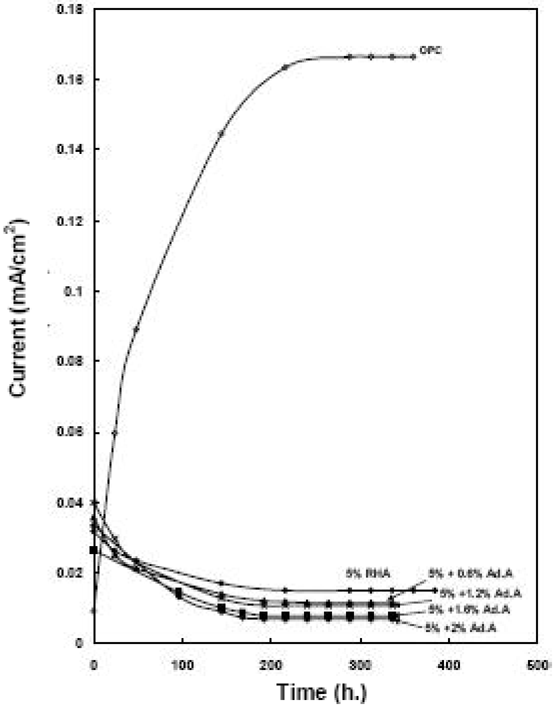

Figure 3 : Current-time relationship of reinforced steel embedded in cement pastes with different amounts of adm. A and 5% RHA immersed in 1M HCl at 2V

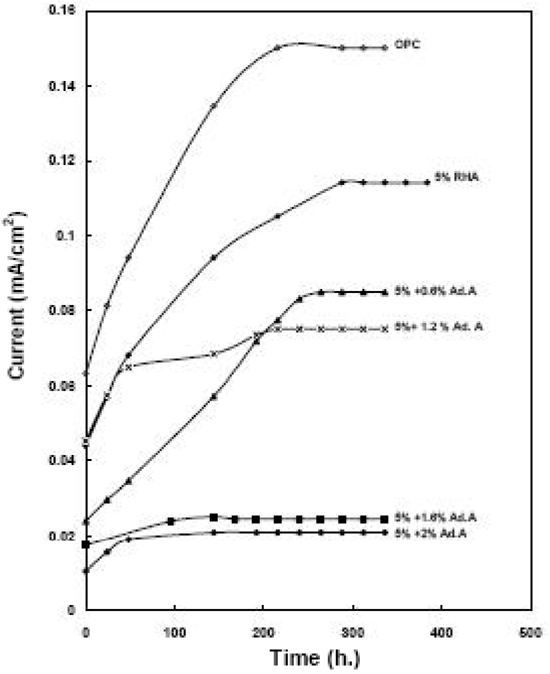

Figure 4 : Current-time relationship of reinforced steel embedded in cement pastes with different amounts of adm. A and 5% RHA immersed in 1M HCl at 4V

TABLE 10 : Corrosion current values of reinforced steel embedded in cement pastes with and without chemical admixture immersed in both acid aggressive media at potential 4V

Composition	HCl	H_2SO_4
OPC	0.15	0.1351
5% RHA	0.1142	0.0266
5%RHA + 0.6 adm. A	0.085	0.02
5%RHA + 1.2 adm. A	0.075	0.0168
5%RHA + 1.6 adm. A	0.0246	0.11
5%RHA + 2 adm. A	0.021	0.0087
5%RHA + 0.3 adm. B	0.029	0.0199
5%RHA + 0.45 adm. B	0.0279	0.014
5%RHA + 0.6 adm. B	0.009	0.0083

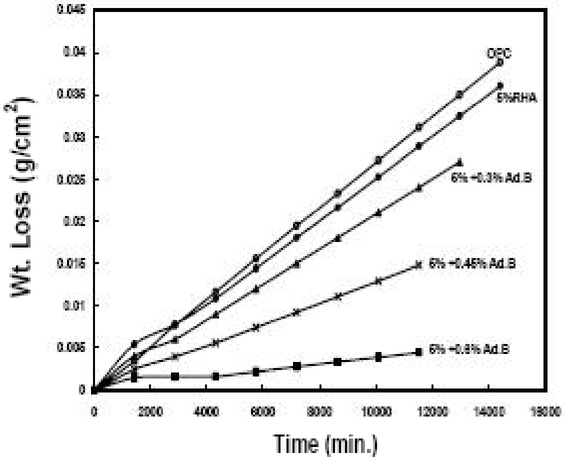

Figure 5 : Weight loss- time relationship of reinforced steel embeded in cement pastes with different amounts of adm. B and 5% RHA immersed in 1M H_2SO_4 at 2V

lowed by relatively small current variations reaching a steady state in most cases about 150 hours, and the corrosion current was decreased with increasing percentage of both chemical admixtures A and B in the following order HCl > H_2SO_4. The degree of the corrosion intensity which is related to the size of area under the corrosion current-time curves, can be estimated by using Faraday's law:

$$W = K (I . T) \qquad (2)$$

Where: W is the mass of substance liberated, I is the intensity of current, t is the prolonged time and K is a proportional constant = 0.0167g /A. min. for steel[9].

The weight loss of reinforcement steel can be determined quantitatively from the above equation and related to the time of the experiment. Figure 5 is taken as representative curve upon using potential 2V, where the weight loss increases linearly with time. While figures (6-9) shows the weight loss of reinforcement steel upon using potential 4V in 1M of each HCl, H_2SO_4 acid as test solution with admixtures A and B. It can be seen that the curves exhibit the same general trend where

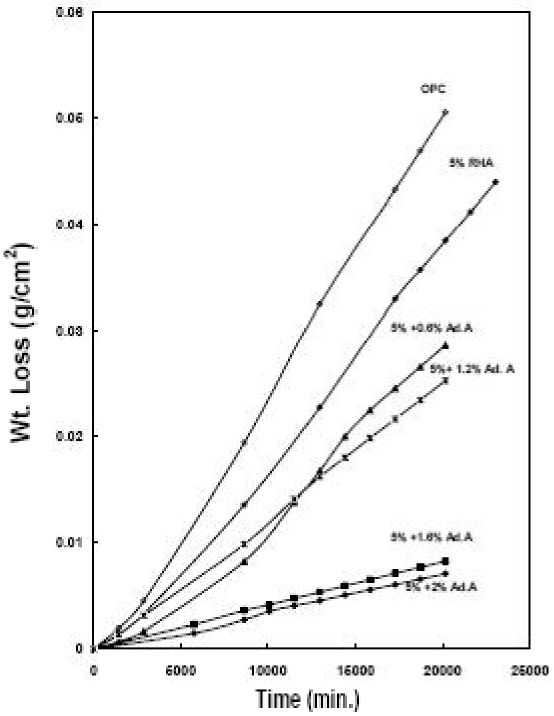

Figure 6 : weight loss-time relationship of reinforced steel embeded in cement pastes with different amounts of adm. A and 5% RHA immersed in 1M HCl 4V

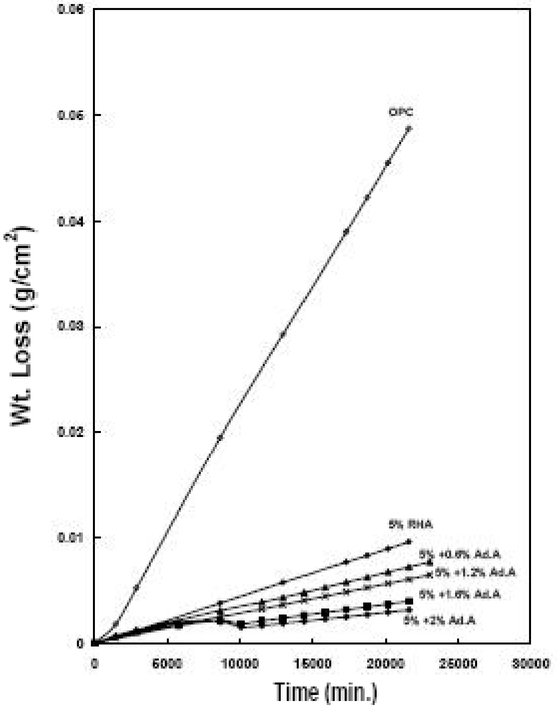

Figure 7 : Weight lossl-time relationship of reinforced steel embedded in cement pastes with different amounts of adm. A and 5% RHA immersed in 1M H_2SO_4 at 4V

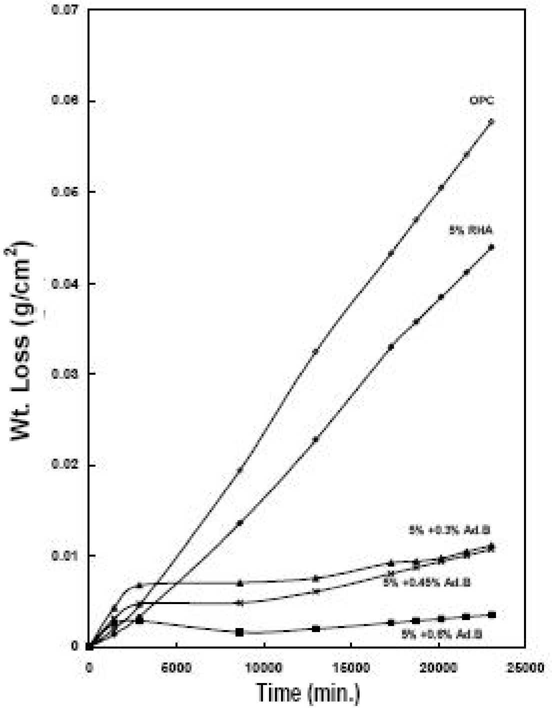

Figure 8 : Weight loss-time relationship of reinforcd steel embeded in cement pastes with different amounts of adm. B and 5% RHA immersed HCl at 4V

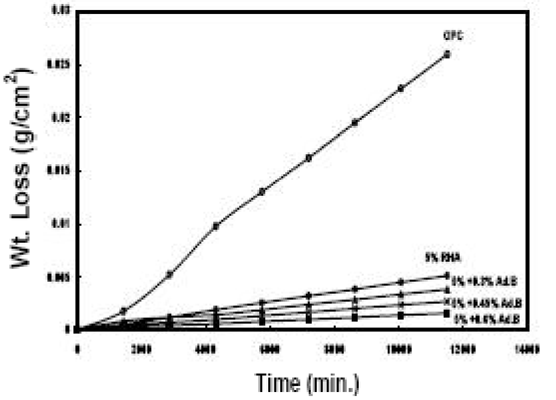

Figure 9 : Weight loss- time relationship of reinforced steel embeded in cement pastes with different amounts of adm. B and 5% RHA immersed in 1M H_2SO_4 at 4V

the weight loss (g/Cm^2) increases linearly with along whole experiments. It can be noticed that while the weight loss of reinforced steel bars is high in the OPC sample in the acids media, it has been low in samples mixed with chemical admixtures and RHA. Also the amount of steel dissolved due to corrosion decreased in presence RHA with chemical admixtures depending on % of chemical admixtures and types of acid as aggressive media.

The results can be explained on the bases that, the increase of inhibition in OPC paste sample blended with RHA attributed to the higher specific area of RHA compared to Ordinary Portland Cement. Thus the corrosion inhibition was enhanced considerably in presence of RHA which is pazzolanic material that reduced the pore structure and improved the particle packing density of the blended cement, leading to a reduced volume of larger pores. Also, RHA has a highly micro porous structure that is responsible for its very high surface area which allows its pazzolanic activity to compete with that of the much finer OPC. From this ground RHA is finer than cement and should be expected to play not only a pazzolanic role but also a micro-filler effect to enhance the particle packing density of concrete.

Mixtures with high workability and very high early strengths are called high performance concrete (HPC) by some researchers. The incorporation of fine particles of RHA dramatically enhances the workability and impermeability thus making the concrete durable(10). However, the contribution of RHA to strength is relatively small in low water-cementitious ratio in HPC mixtures. The high strength of these HPC mixtures are attributable to extremely low water-cement ratios resulting from the application of a large percentage of superplasticizer, which is added to the concrete mix for properly dispersing the fine particles of the pazzolanic admixture.

The physical effect, followed by the chemical effect involving the pozzolanic reaction (in which the calcium hydroxide formed during hydration of cement in concrete reacts with the silica present in the admixture to form calcium hydride silicate), fills up the empty spaces and results in the densification (pore refinement) and strengthening of the microstructure.

Studies have shown that RHA can reduce large pores in hydrated cement pastes to much smaller pores. It has also been observed that such transformation of an open-pore system into a closed-pore system through the process of pore refinement has a much greater effect on the permeability than on the strength of the materials.

Presence of lignosulphonate or superplacticizer increased degree of inhibition upon increasing as percentage of these chemical admixtures increase in its limited value, Lignosulphonate acts as a retarder, due to its effect the water requirement is reduced. The effect of aggressive media 1M HCl, H_2SO_4 will be reduced due to addition of Rice Husk Ash to Ordinary Portland Cement forms a Calcium Silicate Hydrate (CSH) gel around the cement particles which is highly dense and less porous, this decrease the permeability of aggressive ions which attack steel.

This may increase the strength of concrete against cracking due to its positive effect towards 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 with effect of chemical admixtures used.

CONCLUSION

Corrosion of reinforcing bars in the electrolytic concrete pore solution involves electron or charge transfer through of chemical reactions at the interface. Samples blended with 5% RHA only or in presence chemical admixtures are more resistant to the corrosive media of acids than that blended with Portland cement only and also there were more inhibition to corrosion in presence of chemical admixtures with RHA than its effect only. This is due to the replacement of Rice Husk Ash refined the pores, improves the particle packing density of the blended cement, leading to a reduced volume of larger pores and thereby the permeability and corrosion gets reduced.

REFRENCES

[1] V.S.Ramachandran; il cemento, **1**, 13 **(1986)**.

[2] Moncf Nehdi; Cement Concrete research, **34**, 1271-1272 **(2004)**.

[3] Z.A.El- Hadi, N.S.Tantawi, I.Z.Selim; J.Mater.Sci.Technol., **18**, 83-88 **(2002)**.

[4] N.B.Sing, V.D.Sing, Sartita Rai, Shivani Chaturevedi; Cement Concrete Research, **32**, 387-392 **(2002)**.

[5] P.K.Mehta; 'Rice Husk Ash as Mineral Admixture in Concrete', in: L.Berntsson, S.Chandra, L.Nilson (Eds.); Proc.Intl.Conf.Durability concr., Chalmers university of Technology, 131-137 **(1989)**.

[6] M.Nehdi, J.Duquette, A.El Damatty; Cement and concrete research, **33**, 1203-1210 **(2003)**.

[7] N.Bouzoubaa, B.Fournier, Concrete incorporating rice husk ash: Report MTL2001-5(TR), CANMET, 17PP **(2001)**.

[8] M.I.Jafar, J.L.Dawson, D.G.John; 'Electrochemical Impedance and Harmonic Analysis Measurements on Steel in Concrete', Electrochemical Impedance: Analysis and Interpretation, ASTM STP 1188, J.R.Scully, D.C.Silverman, M.W.Kending, (Eds.); American Society for Testing and Materials, Philadelphia, 384-403 **(1993)**.

[9] L.R.Yuan, W.F.Chen; Performance of Concrete marine Environment, American Concrete institute, SP-65, 291 **(1980)**.

[10] Al Hilal; Group: Gulf construction on line.com, **26(3)**, March, **(2005)**.