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Effect of mineral and chemical admixtures on the corrosion behavior of reinforced steel in presence of nitric, acetic acids

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ABSTRACT

The effect of 10% Rice Husk ash (RHA) as mineral admixtures on the corrosion behavior of reinforced steel in presence of different concentrations chemical admixtures as lignosulphonate and superplacticizer has been studied, in acid mdia using different techniques. It was found that, the samples which contain 10% RHA in presence of chemical admixtures is more resistant to the corrosive media than that contain 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

Each year, more and more reinforced concrete structures undergo deterioration that is mainly due to attack from media generating uniform corrosion as acids. The high cost of maintenance required to preserve the structural integrity. Some structural designers now offer owners a tiered choice of protection systems with varying degrees of cost as corrosion inhibiting admixtures, that will prevent or minimize corrosion[1].

On the other hand, rice hull is an abundant material produced in many countries around the world containing approx. 20-25% of silica. Rice hull burned at the fields lead to serious environmental of damage. Since silica particles remain suspended in the air being a potential cause of respiratory diseases and environmental damage. Recently, a method using Rice Husk Ash as raw material for synthesis β-Ca_2SiO_4 cement at 700^{0}C where Ca_2SiO_4 has fine crystalline phases and β-phase is predominant one also other phases are usually present[2].

When use with fresh concrete mixtures pozzolanic additions as RHA have the ability to reduce bleeding and segregation and thus cause significant improvement in workability and durability characteristics[3].

Hydration of 10wt % Rice Husk Ash blended Portland cement has been studied in presence of 2wt.% $CaCl_2$, 1wt.% 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_2SO_4 due to calcium chloride accelerates the corrosion of the cement[4].

The RHA blended Portland cement greatly improves the durability characteristics. And helped substantially

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

Composition	Loss in ignition	SiO_2	Al_2O_3	Fe_2O_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		
		Admixture(A)	Admixture(B)	RHA
1	OPC	0.6	-	10%
2	OPC	1.2	-	10%
3	OPC	1.6	-	10%
4	OPC	2	-	10%
5	OPC	-	0.3	10%
6	OPC	-	0.45	10%
7	OPC	-	0.6	10%

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

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

to 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].

Investigation on the RHA include oxide analysis, X-ray differaction, carbon content, grindability, water demand, pazzolanic activity index, surface area, and particles size distribution measurements. The workability, superplactisizer and air- entraining admixture requirements, and compressive strength at various ages of these concrete admixtures were evaluated, and their resistance to chloride penetrability were examined. The results show the chloride penetrability was substantially decreased by RHA, a naphthalene sulfonated superplacticizer with a solid content of 42% was used to achieved the desired workability for all concrete mixture, 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].

Admixtures of concrete mortar or paste are in organic or inorganic materials in solid state, added to concrete batch immediately before or during mixing. The use of admixtures in many instances based more on art than on science This due to incomplete understanding of the principles governing their action in concrete. Chemical admixtures are often used to optimize the coast effectiveness of concrete mix and controlling the quality of the concrete[8].

The aim of this work is comparing and evaluate the corrosion inhibition value of corrosion for reinforcing steel in presence of 10 % RHA when blended with Ordinary Portland Cement as mineral admixture, with and without chemical admixtures as lignosulphonate and superplacticizer. Where these admixtures cause improve quality of concrete. The experiments occur in aggressive media of 1M of each acid HNO_3, CH_3COOH 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 750^0C for 1 hour then sieved to 98%, and mixed with concrete with certain percentage 10% with various proportions of chemical admixtures according to its type and its limiting value used as TABLE (2).
- The two types of chemical concrete admixtures used in this study are :

Admixture (A): Superplasticizer which is super water reducer derived from sulphonated naphthalene formaldehyde, its dosages used in range between 0.6 to 2 L / 100 K gm of cement.

Admixture (B): Retarding water reducing, it based on selected lignosulphonates its dosages 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 5Cm long with a small hole of 2mm diameter in center of upper side of electrode. The chemical analysis and mechanical properties of the reinforced steel bar are summarized in TABLE (3).

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, 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 HNO_3, CH_3COOH 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 counter electrode. The potential was measured against a reference electrode (SCE) with potentiometer (ORION SA520) 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 applying ranging from -2000V to +2000V to reinforcing steel bar embedded in concrete using a counter electrode of steel bar and a reference electrode, 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 DISSCUSSION

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, admixture B in presence of 10 % RHA with and without admixtures immersed in aggressive media 1M of each acids HNO_3, CH_3COOH as test solutions is 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 can be seen that while steel passivity degree is low in OPC in both acids, it has been high in sample with 10 % RHA and more high with all limiting percentage of the two chemical admixtures. The higher positive potential is due to improve-

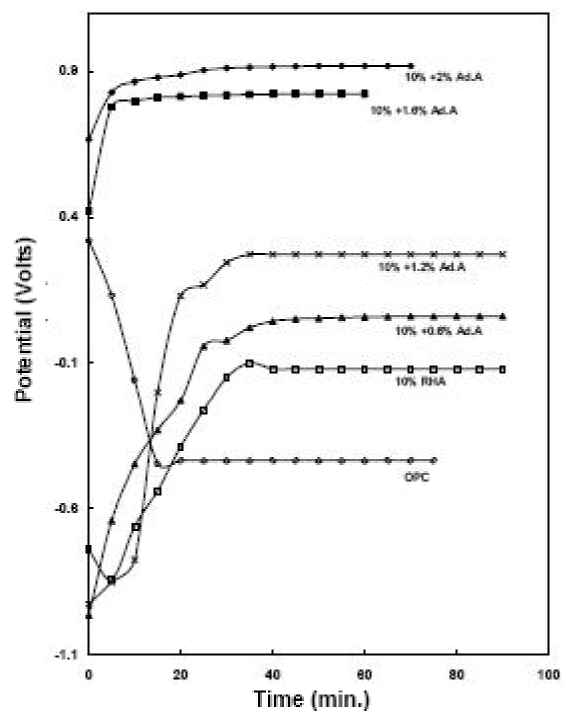

Figure 1 : Potential-time relationship of reinforced steel embedded in cement pastes with different amounts of adm. A and 10% RHA immersed in 1M HNO_3

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

Composition	HNO_3	CH_3COOH
OPC	-0.436	-0.787
10% RHA	-0.12	-0.705
10%RHA + 0.6 adm. A	-0.059	-0.625
10%RHA + 1.2 adm. A	0.271	-0.606
10%RHA + 1.6 adm. A	0.824	-0.535
10%RHA + 2 adm. A	0.918	0.097
10%RHA + 0.3 adm. B	0.545	0.803
10%RHA + 0.45 adm. B	0.757	0.891
10%RHA + 0.6 adm. B	0.969	0.903

TABLE 5 : Corrosion parameter for reinforcing steel embedded in concrete in presence 10% RHA with and without chemical admixture A immersed in HNO_3

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.0256	400	0.0278	1500	0.32248
10%RHA	0.01276	-300	0.0181	1500	0.20996
0.6% A	0.01	300	0.013	1500	0.1508
1.2% A	0.002	-600	0.005	900	0.058
1.6% A	0.0015	-600	0.0026	700	0.03016
2% A	-0.009	-200	0.002	1300	0.0232

TABLE 6 : Corrosion parameter for reinforcing steel embedded in concrete in presence 10% RHA with and without chemical admixture B immersed in HNO_3

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.0256	400	0.0276	1400	0.32016
10%RHA	0.01276	-300	0.0159	1400	0.18444
0.3% B	0.0045	-700	0.006	100	0.0696
0.45% B	0.004	-600	0.0045	400	0.0522
0.6% B	0.003	-600	0.0038	400	0.04408

TABLE 7 : Corrosion parameter for reinforcing steel embedded in concrete in presence 10% RHA with and without chemical admixture A immersed CH_3COOH

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.0357	-600	0.0386	1000	0.44776
10%RHA	0.014	-100	0.0190	1100	0.2204
0.6% A	0.012	-600	0.0145	700	0.1682
1.2% A	0.01	-700	0.0136	700	0.15776
1.6% A	0.005	-300	0.0055	700	0.0638
2% A	0.003	-500	0.0052	700	0.06032

TABLE 8 : Corrosion parameter for reinforcing steel embedded in concrete in presence 10% RHA with and without chemical admixture B immersed CH_3COOH

	Ipass	Epass	Icorr	Ecorr	CR
OPC	0.0357	-600	0.0429	1300	0.49764
10%RHA	0.0205	-300	0.0193	1200	0.22388
0.3% B	0.0089	-200	0.00116	1100	0.13456
0.45% B	0.0025	200	0.004	1000	0.0464
0.6% B	0.0012	-500	0.0015	900	0.0174

ment effect of RHA which is not restricted the effect of inhibition occurs due to chemical admixtures A and B. But RHA can be improve the effect of these admixtures

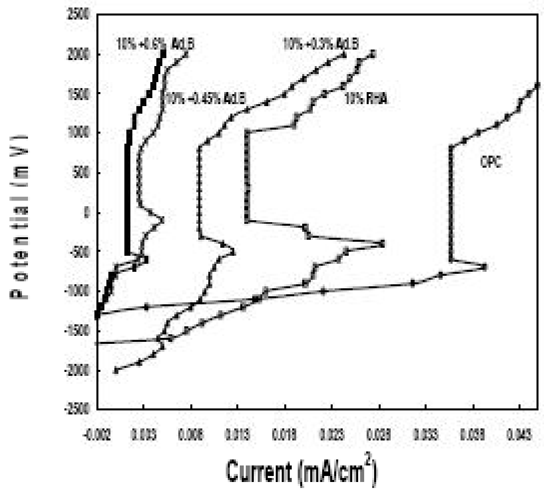

Figure 2 : Potential-current relationship of reinforced steel embeded in cement pastes with different amounts of adm. B and 10% RHA immersed in CH_3COOH

and have more inhibition than its presence without RHA.

Potentiostatic polarization method

The potentiostatic polarization experiments for reinforced steel embedded in cement paste admixed with admixture A and admixture B in presence of 10 % RHA with and without admixtures immersed in 1M of each acids HNO_3, CH_3COOH as test solutions are investigated. Figure (2) is taken as representative curve. It can be seen that, presence of RHA increased the ability of steel to be more passive against acids, while these ability increase 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[9].

Corrosion rate (um/yr.) = k (A i_{corr} / ND)

Where : D density of the metal (g/cm^3) , K constant depending on the penetration rate units desired for (um/yr.) where K=3.27, A is atomic weight of the metal, N number of electrons and i_{corr} corrosion current density in uA/Cm^2. For iron or steel: corrosion rate um/yr. = 11.6 i_{corr}

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

We noticed that I_{corr} decreased in presence of RHA and this decreasing becoming more with chemical admixtures A and B in the aggressive media. Also corrosion rate (CR) of consuming steel per year decreased.

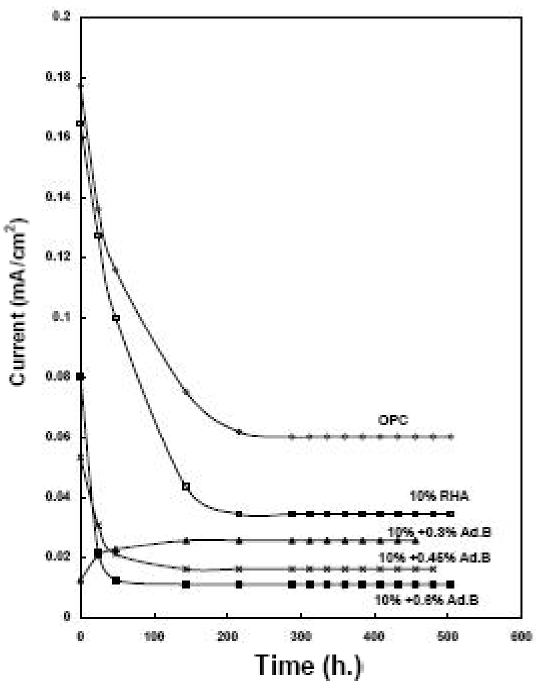

Figure 3 : Current-time relationship of reinforced steel embeded in cement pastes with different amounts of adm. B and 10% RHA immersed in 1M CH_3COOH at 2V

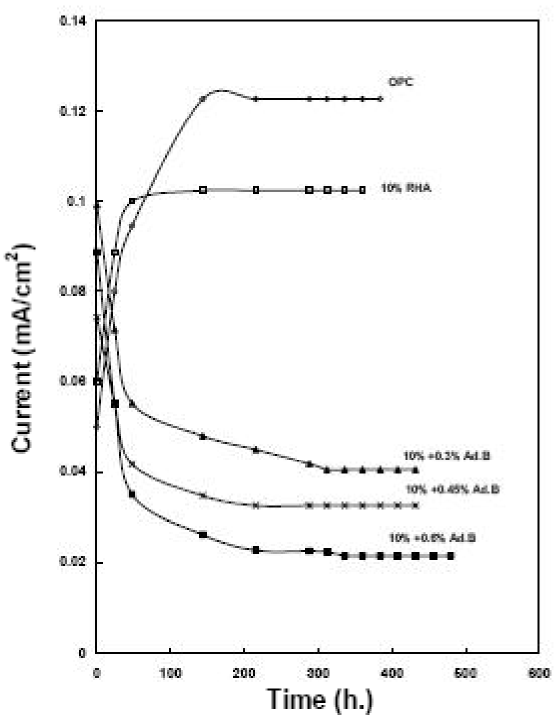

Figure 4 : Current- time relationship of reinforced steel embedded in cement paste with different amounts of adm. B and 10% RHA immersed in HNO_3 at 4V

And other parameter as I_{pass} which is better indicator of corrosive behavior is decreased in presence of RHA

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

Composition	HNO_3	CH_3COOH
OPC	0.0404	0.06
10% RHA	0.0315	0.0343
10%RHA + 0.6 adm. A	0.0291	0.0273
10%RHA + 1.2 adm. A	0.02	0.017
10%RHA + 1.6 adm. A	0.0074	0.0129
10%RHA + 2 adm. A	0.005	0.003
10%RHA + 0.3 adm. B	0.0283	0.0255
10%RHA + 0.45 adm. B	0.0265	0.0158
10%RHA + 0.6 adm. B	0.0236	0.0107

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

Composition	HNO_3	CH_3COOH
OPC	0.1227	0.1268
10% RHA	0.1024	0.1195
10%RHA + 0.6 adm. A	0.0746	0.11
10%RHA + 1.2 adm. A	0.03	0.028
10%RHA + 1.6 adm. A	0.025	0.02
10%RHA + 2 adm. A	0.01	0.011
10%RHA + 0.3 adm. B	0.0405	0.067
10%RHA + 0.45 adm. B	0.0325	0.029
10%RHA + 0.6 adm. B	0.0215	0.0149

without and with chemical admixtures A, B when samples immersed in aggressive media of acids as shown from TABLES.

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 reference electrode. Figure (3) is taken as representative curve, shows the current–time relationship for reinforcing steel embedded in cement pastes mixed with different values of both chemical admixtures with 10% RHA at potential 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 % of both chemical admixtures with 10% RHA at potential 4V in 1M of each acid HNO_3, CH_3COOH. It can be seen that the values of corrosion current in experiments occurred at potential 2V has 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 corro-

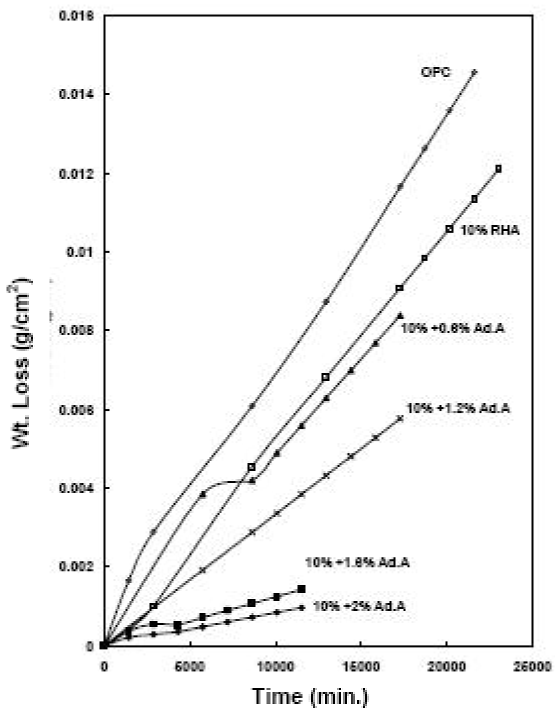

Figure 5 : Weight loss-time relatioship of reinforced steel embeded in cement pastes with different amounts of adm. A and 10% RHA immersed in 1M HNO_3 at potential 2V

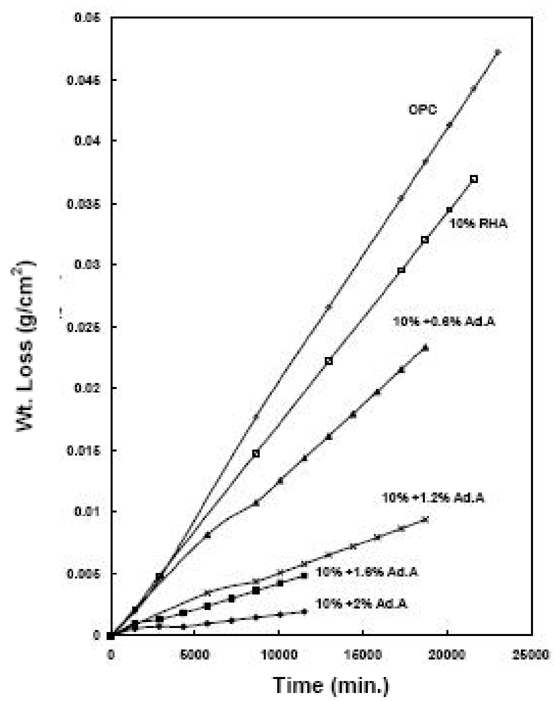

Figure 6 : Weight loss-time relatioship of reinforced steel embeded in cement pastes with different amounts of adm. A and 10% RHA immersed in 1M HNO_3 at potential 4V

sion current decreased sharply with time followed by relatively small current variations reaching a steady state

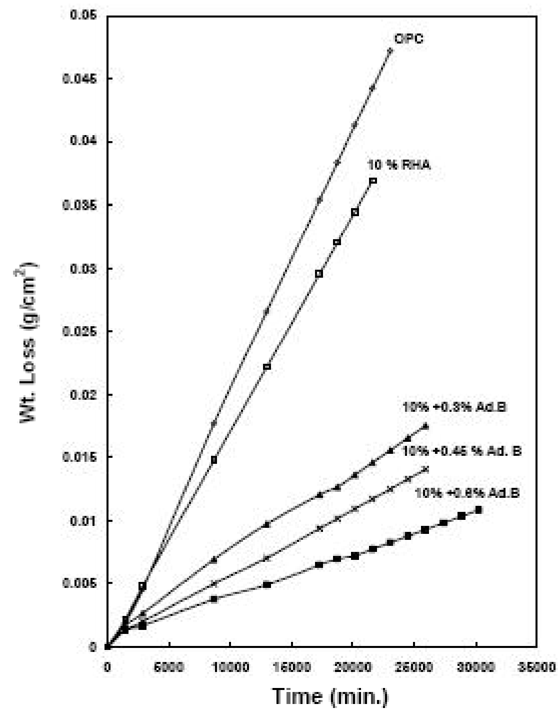

Figure 7 : Weight lossl-time relationship of reinforced steel embeded in cement pastes with different amounts of adm. B and 10% RHA immersed in HNO_3 at 4V

in most cases about 150 hours, and the corrosion current was decreased by increasing percentage of both chemical admixtures A and B with the following order HNO_3>CH_3COOH. 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 constant = 0.0167g /A. min. for steel[10].

The weight loss of reinforced steel can be determined quantitatively from the above equation and related to the time of the experiment. Figure (5) is taken as representative curve when used potential 2V. Which shows that, the weight loss increases linearly with time, while figures (6-9) shows the weight loss of reinforced steel when used potential 4V in 1M of each HNO_3, CH_3COOH acids as test solution in both admixtures A and B. It can be seen that the curves exhibit the same general trend where the weight loss (g/Cm^2) 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

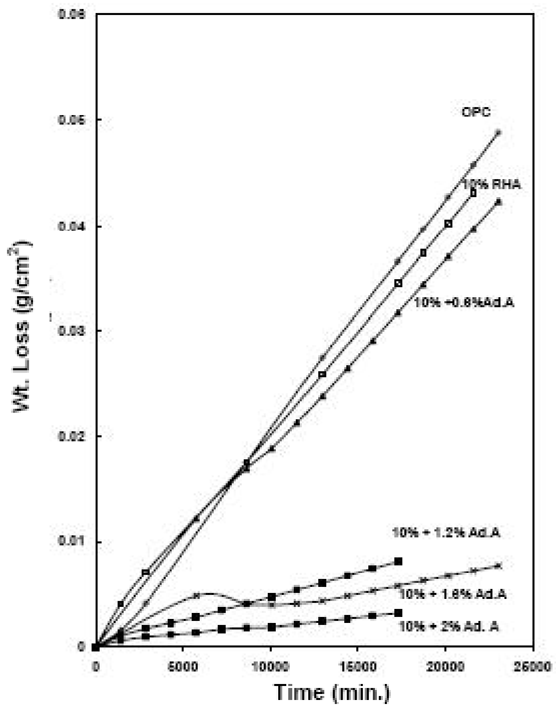

Figure 8 : Weight loss-time relationship of reinforced steel embeded in cement pastes with different amounts of adm. A and 10% RHA immersed in CH_3COOH at potential 4V

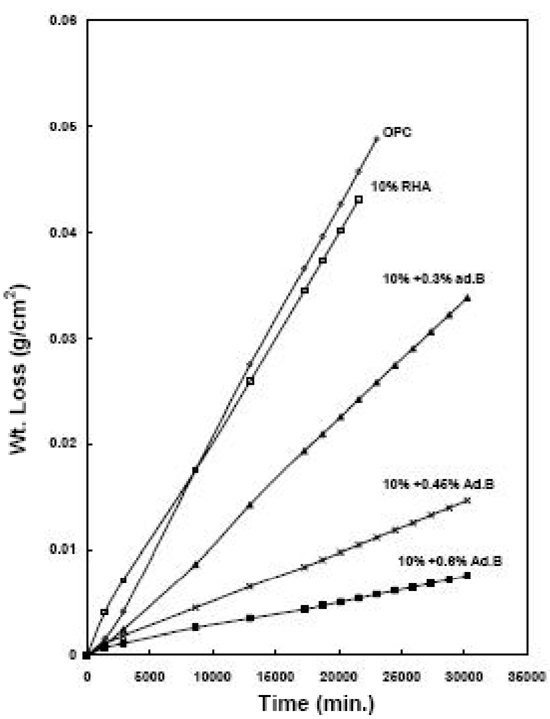

Figure 9 : weight loss-time relationship of reinforced steelembeded in cement pastes with different amounts of adm. B and 10% RHA immersed in CH_3COOH at 4V

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 sample of OPC paste blended with RHA attributed to the higher specific area of RHA compared to Portland cement. Thus the corrosion inhibition was enhanced considerably in presence of RHA which is pazzolanic material that increased the porosity and 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.

The admixture may remain in a free state as a solid or in solution, may interact at the surface, or chemically combine with the constituents of the cement in cement paste. The extent of interaction may influence the physicochemical properties of concrete such as water demand, viscosity, hydration kinetics, composition of the products, setting, microstructure, strength and durability. The mechanism of hydration of the constituents of cement involves the physical or chemical adsorption and chemical reaction with certain cement constituents.

The action of additive (A) involves adsorption and dispersion in cement-water system where this action depends on its concentration in the concrete and various constituents of the concrete. Also the action of additive (B) involves their effect on hydration of cement similar to (A) is related to their adsorption and dispersing effects in the cement water system.

Presence of lignosulphonate or superplacticizer increased degree of inhibition which increase as percentage of these chemical admixtures increased in its limited value which used. Lignosulphonate acts as a retarder due to its effect on the water requirement is reduced. The effect of aggressive media 1M acetic acid or nitric acid will 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 decreased the permeability of ions which attack steel from acids.

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 which increase the compressive strength of concrete. This indicated that 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.

CONCLUSION

Corrosion of reinforcing bars in the electrolytic concrete pore solution involves electron or charge transfer through the chemical reactions at the interface. Samples blended with 10 percentage RHA only or in presence chemical admixtures is more resistant to the corrosive media of acids than that blended with Ordinary Portland Cement only and also there was more inhibition to corrosion in presence of chemical admixtures with RHA than their effect only, due to the effect of Rice Husk Ash which decrease permeability of ions through concrete.

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