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Effect of rice husk ash (RHA) and phosphogypsum (PG) on the corrosion behavior of reinforcing steel in concrete

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ABSTRACT

Corrosion behavior of reinforced steel embedded in cement pastes has been studied with utilization of Rice Husk Ash and PG as mineral admixtures.These admixtures provides several advantages for cement such as improved strength, durability and reduced materials cost due to cement saving and environmental benefits related to the disposal of waste materials and to reduced carbon dioxide emissions. The results indicated that, steel passivity degree in aggressive media is low in OPC than its passivity when OPC mixed with variable proportion of RHA and phosphogypsum. Also, corrosion inhibition of reinforcing steel increased with increasing RHA and PG percentage until 20% RHA and 10% for PG, in different aggressive media such as sulphate and chloride.

KEYWORDS

Rice husk ash;
Phosphogypsum;
Corrosion;
Reinforced steel.

INTRODUCTION

Corrosion of reinforced steel is one of the main causes of degradation of reinforced concrete structures. The high coast of maintenance required preserving the structural integrity. During the last few years, some attention has been given to the use of the waste by-product, micrsilica as a possible partial replacement for Ordinary Portland Cement. Microsilica with its high silica content and ultra fine particles has a large potential for use in concrete as mineral admixture to improve the mechanical properties of concrete, as well as its chemical resistance, also it has been shown to provide the highest level of protection for reinforced steel against corrosion[1].

Rice Husk Ash is one of the promising pazzolanic materials that can be blended with Ordinary Portland Cement for the production of durable concrete, higher packing can be expected leading to improved behavior of blended system and at the same time it is a value added product[2].

Addition of RHA to OPC not only improves the early strength of concrete, but also forms a calcium silicate hydrate gel around the cement particles which is highly dense and less porous. This may increase the strength of concrete against cracking. So far a systematic and detailed investigation on the corrosion performance of rice husk ash blended concrete is very scarce[3].

RHA has a highly microporous structure that is responsible for its very high surface area which allows its pazzolanic activity to compete with that of the much finer silica fume. From this ground RHA is finer than cement and should be expected to play only a pazzolanic role but also a micro-filler effect to enhance the particle packing density of concrete[4].

When use with fresh concrete mixtures pazzolanic additions as RHA have the ability to reduce bleeding and segregation and thus cause significant improvement in workability and durability characteristics[5].

The possibility of recycling phosphogypsum for building material manufacture especially for Ordinary Portland Cement manufacture was considered such gypsum has been used during grinding of the clinker. There is an optimum gypsum content which impacts the cement maximum strength and minimum shrinkage without excessive expansion[6].

The potential of using a by product slag, produced by sulfur- recovery process from PG, as an aggregate in Ordinary Portland Cement concrete is studied. The phase composition and microstructure of two different samples of produced slag were studied. The study showed that although both slag have different microstructure, mineralogically both are suitable as aggregate in concrete as long as the amount of sulfate is not high <4.5[7].

PG is an important industrial by product derived from phosphoric acid and phosphate fertilizer manufactures by dehydrate process. It is separated from the medium of dissolved phosphate ore in sulphuric acid by filtration. It can cause serious environmental problems when it is dumped in sea or impounded on land. Phosphogypsum (PG) is a solid by product of the manufacture of phosphoric acid by the wet process. Its major constituent is hydrated calcium sulphate ($CaSO_4.2H_2O$) with some impurities such as P_2O_5, F^-, MgO, Fe_2O_3, and about 141×10^{-6} % rare earth elements derived from the used raw materials or during manufacture. It have been prepared using different percentages ranging from 5-10 wt pct. for adhesion strength[8].

The main source of reinforcement corrosion is identified as the presence of aggressive ions such as chlorides or sulfates. Concentrations of soluble sulfates greater than 0.1 percent in soil may have a deleterious effect on concrete, and more than 0.5 percent soluble sulfate in soil may have a serious effect. Most soils contain some sulfate in the form of gypsum (typically 0.01 to 0.05 percent expressed as SO_4), this amount is harmless to concrete. Higher concentrations of sulfate in ground waters are generally due to the presence of magnesium and alkali sulfates. While the chlorides mainly originate from external sources, destroy the protective oxide film, which develops on the steel surface, and in the presence of oxygen and moisture allow corrosion to occur. In this work the effect of two mineral admixtures as PG and RHA in various percentage of them when mixing with Portland cement on the physicochemical properties of cement past is studied. Also the corrosion protection efficiency occur in each case of these admixtures, when reinforced steel embedded in aggressive media such as 5%NaCl, 5%$MgSO_4$, 5%Na_2SO_4 have been evaluated by using potentiostatic polarization technique.

EXPERIMENTAL

Materials and preparation

The concrete was prepared containing Portland cement which its chemical composition contents are summarized in TABLE 1, while other main materials were detail as two series in TABLE 2. The main materials of this study phosphogypsum was obtained kindly from Abu- Zaabal fertilizers Co., cairo, Egypt as filter cake, it prepared after directly dried in the sun then burn for two hours in muffle furnace at 850⁰C then sieved through 90μm sieve. While RHA was burnt at

TABLE 1: Chemical composition of starting material as wt%

Composition % of	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.O.I	Blaine Cm^2/g
OPC	21.50	5.18	2.3	63.31	1.84	2.77	0.6	3659
PG	3.25	0.13	0.23	35.09	0.05	45.52	10.00	

TABLE 2 : Proportion of main material mixed with concrete in two series according various proportions of RHA and PG

Series 1	OPC %	PG %	RHA%	Series 2	OPC%	PG %	RHA%
Blank	100	0	0	Blank	100	0	0
I	95	5	0	I	95	0	5
II	90	5	5	II	90	5	5
III	85	5	10				
V	80	5	15	III	85	10	5
VI	75	5	20				

TABLE 3: Chemical analysis and mechanical properties

Chemical analysis %				Mechanical properties		
C	S	P	Mn	Yield stress MPa	Ultmiate stress MPa	Elongation %
0.12	0.022	0.063	0.43	388	493	23

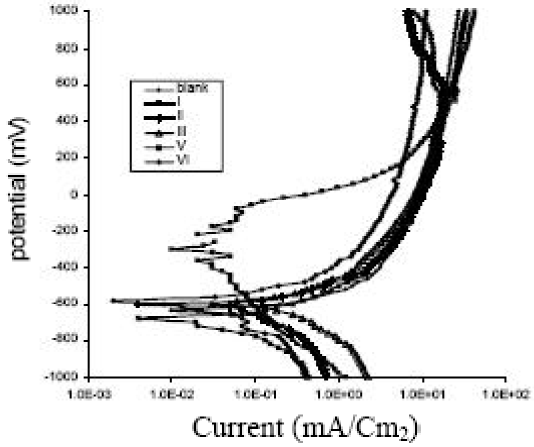

Figure 1: Effect of cement paste contain 5% PG and different % of RHA on corrosion of reinforced steel in 5% $MgSO_4$

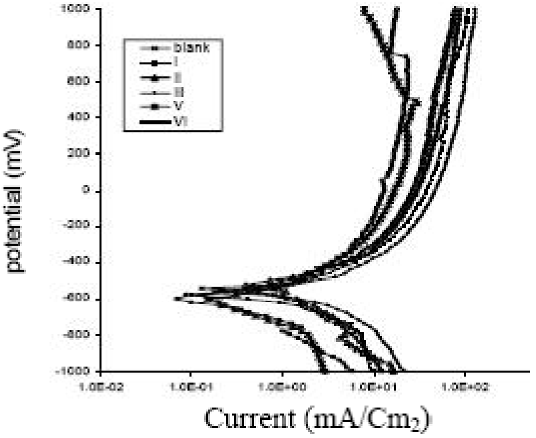

Figure 2: Effect of Cement paste contain 5% PG and different % of RHA on corrosion of reinforced steel in 5% Na_2SO_4

750°C also for 1 hour then sieved to 90%. After mixing each of them with concrete in the limited ratio would embedded sample of rod steel rebar in cube of cement mixture. This rod is cylindrical specimens of 5 Cm height, 1 Cm diameter was cast in concrete, its chemical analysis and mechanical properties are tabulated in TABLE 3, after molding specimen were cured for 28 days at room temperature

After curing specimens were immersed in test solutions 5%NaCl, 5%$MgSO_4$, 5%Na_2SO_4 which prepared with bi-distilled water.

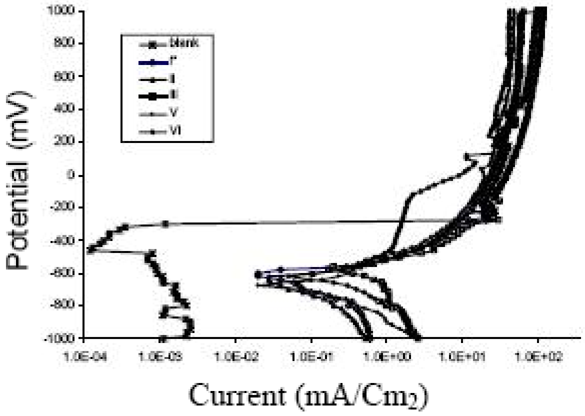

Figure 3: Effect of Cement paste contain 5% PG and different % of RHA on corrosion of reinforced steel in 5% NaCl

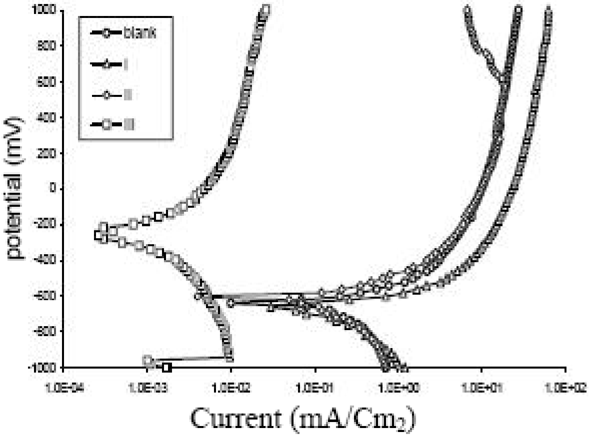

Figure 4: Effect of Cement paste contain 5% RHA and different % of PG on corrosion of reinforced steel in 5% $MgSO_4$

Measurement technique

In potentiostatic polarization method were examined by performing potential scan ranging from -1000mV vs SCE to 1000mV with scan rate was 1.34 mV/sec with using the electronic potentiostate model Amel 553 where working electrode is steel reinforced bar embedded in concrete against a reference electrode which is saturated calomel electrode (SCE) and platinum as counter electrode. The potential – current plots give potential in V against current in mA/cm^2. This technique is much more reflective of the corrosion behavior of the steel.

RESULTS

The figures (1-3) show the corrosion behavior of

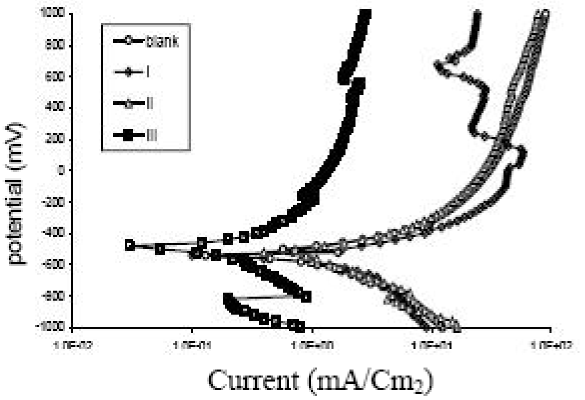

Figure 5: Effect of Cement paste contain 5% RHA and different % of PG on corrosion of reinforced steel in 5% Na_2SO_4

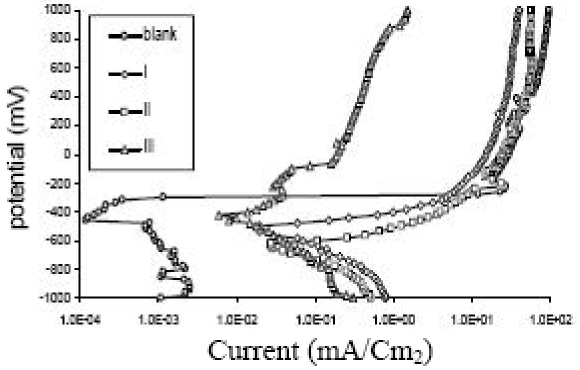

Figure 6: Effect of Cement paste contain 5% RHA and different % of PG on corrosion of reinforced steel in 5% NaCl

TABLE 4 : Corrosion parameter for rebar in concrete mixed with RHA in $MgSO_4$ in series 1

	E(I=0)	Ipass	Epass	Icorr	Ecorr	CR
Blank	-630	2.2	-460	16.4	380	190.24
0%RHA	-240	3.38	120	13.4	360	155.44
5%RHA	-590	1.3	-460	11.2	60	129.92
10%RHA	-590	1.7	-380	6.4	-80	74.24
15%RHA	-690	2	-420	5.5	-180	63.8
20%RHA	-590	0.93	-380	2.3	-220	26.68

TABLE 5 : Corrosion parameter for rebar in concrete mixed with RHA in Na_2SO_4 in series 1

	E(I=0)	Ipass	Epass	Icorr	Ecorr	CR
Blank	-530	8.3	-360	54.8	420	635.68
0%RHA	-590	6.5	-280	15.8	140	183.28
5%RHA	-530	6.9	-360	40.2	280	466.32
10%RHA	-590	3.9	-440	63.6	160	737.72
15%RHA	-610	2.92	-420	21.8	140	252.88
20%RHA	-570	4.9	-420	49.7	160	576.52

TABLE 6: Corrosion parameter for rebar in concrete mixed with RHA in NaCl in series 1

	E(I=0)	Ipass	Epass	Icorr	Ecorr	CR
Blank	-990	23	-260	50.8	320	589.28
0%RHA	-610	12.9	-220	42.1	340	488.36
5%RHA	-630	11	-240	37.9	220	439.64
10%RHA	-570	9	-360	25.7	120	298.12
15%RHA	-670	8	-280	27.6	60	320.16
20%RHA	-610	2.8	-100	3.6	-80	41.76

TABLE 7: Corrosion parameter for rebar in concrete mixed with RHA in $MgSO_4$ in series 2

	E(I=0)	Ipass	Epass	Icorr	Ecorr	CR
Blank	-630	2.2	-460	16.4	380	190.24
0%PG	-650	3.8	-500	28.8	140	334.08
5%PG	-590	1.3	-460	12.9	120	149.64
10%PG	-230	0.0038	-60	0.006	80	0.696

TABLE 8: Corrosion parameter for rebar in concrete mixed with RHA in Na_2SO_4 in series 2

	E(I=0)	Ipass	Epass	Icorr	Ecorr	CR
Blank	-530	8.3	-360	54.8	420	635.68
0%PG	-550	9.7	-380	22.4	300	259.84
5%PG	-530	6.9	-360	34.7	160	402.52
10%PG	-490	0.46	-360	0.98	-120	11.368

TABLE 9 : Corrosion parameter for rebar in concrete mixed with RHA in NaCl in series 2

	E(I=0)	Ipass	Epass	Icorr	Ecorr	CR
Blank	-990	23	-260	50.8	320	589.28
0%PG	-520	3.21	-340	25.8	340	299.28
5%PG	-630	3.59	-420	37.9	220	439.64
10%PG	-430	0.026	-340	0.25	140	2.9

reinforcing steel in presence of various percentage of RHA from 0% to 20% mixed with concrete and the constant ratio 5% of PG in all cases of series (1). It can be seen that increasing content of RHA in cement pastes generally increases the ability of reinforced steel to be more passive against aggressive ions than in case of blank without any additives. Also, the results show that the more corrosion inhibition in case of 5%$MgSO_4$ than 5%Na_2SO_4.

While figures (4-6) show the corrosion behavior of reinforcing steel in presence various proportions of PG from 0% to 10% mixed with concrete and the constant ratio 5% of RHA in all cases of series (2). It can be seen that, as in series 1 increasing percentage of phosphogypsum giving more passive corrosion behavior against aggressive media generally than blank without any additives. And also more passive corrosion behavior in case of 5%$MgSO_4$ resulted than 5%Na_2SO_4 in all percentages.

The parameters obtained are shown in tables from (4-9). Including corrosion current (I_{corr}), (I_{pass}) which decreased with increasing % of RHA as series (1) and increasing % of PG as series (2) than blank in both aggressive media sulphate and chloride, also (E_{Corr}) which is a better indicator of corrosive behavior than the time of exposure. While it is true that for many samples, the longer the exposure time, the greater the probability of corrosion-product buildup, the corrosive behavior of individual samples selected on the basis of exposure time may give misleading results insofar as the mechanism by which steel goes from the passive to active state is concerned. Therefore the values of (E_{Corr}) show decreases with increasing % of RHA as series (1) and increasing % of PG as series (2) than blank in both aggressive media sulphate and chloride this indication for the importance of study additives when mixed with cement paste. Generally in two series the current of passivity was decreased with increasing ratio of mineral admixtures in two series and potential also decreased. This indication to the degree of passivation of reinforcing steel depends on percentage of additives of rice husk ash or phosphogypsum. It can be calculate from the corrosion current in the curves the corrosion rate per year as consuming in environment as (um/yr.). and show in TABLES (4-9) for two admixtures.

From 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.) (K=3.27), A is atomic weight of the metal and N is number of electrons.

And from (i_{corr}) corrosion current density in uA/Cm^2 For iron or steel:

Corrosion rate (um/yr.) = 11.6 i_{corr}

DISCUSSION

When the control sample immersed in test solutions, chloride or sulphate ions penetrate into the near surface regions by diffusion in the pore solution. Sulfate attack causes serious structural problems, where Sulphate ions react with crystalline $Ca(OH)_2$ present in the hydrated cement to yield crystalline gypsum $CaSO_4.2H_2O$ for $MgSO_4$ as in Eq.(1), formation of relatively insoluble magnesium hydroxide. In the absence of hydroxyl ions in the solution the calcium of hydrated silicates (C-S-H) is no longer stable and is also attacked by the sulfate solution. So the magnesium sulfate attack is more severe on concrete. While for Na_2SO_4 as in Eq.(2). the formation of sodium hydroxide as a by product of the reaction ensures the continuation of high alkalinity in the system, which is essential for the stability of the cementitious material C-S-H.

Sulphate ions react also with hydrated aluminates to form ettringite $C_3A.3CS.H_{32}$ as Eq. (4), the presence of gypsum, ettringite can cause a progressive loss of strength and loss of mass due to loss of cohesiveness in the cement hydration products and lead to expansion deterioration and cracking of hardened Portland cement paste and eventually the transformation of concrete into a mushy or non-cohesive mass.

$$MgSO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + Mg(OH)_2 \quad (1)$$

$$Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow CaSO_4.2H_2O + 2NaOH \quad (2)$$

$$3\,MgSO_4 + 3CaO.2SiO_2.3H_2O + 8\,H_2O \rightarrow 3CaSO_4.2H_2O + 3Mg(OH)_2 + 2SiO_2.H_2O \quad (3)$$

$$C_3A + 3CSH_2 + 26H \rightarrow C_3A.3CS.H_{32} \quad (4)$$

(Ettringite)

Magnesium sulphate reacts with the $Ca(OH)_2$ in concrete and through the substitution of Mg for Ca, secondary gypsum in flat prisms and brucite $Mg(OH)_2$ in superimposed platelets are formed. $MgSO_4$ also displaces the calcium of the hydrates silicates, CSH, transforming it into a hydrated calcium magnisum silicate, CMSH, which has no binding properties at the beginning reaction. Moreover, the action of $MgSO_4$ on the aluminates is manifested in the formation of ettringiteither nearly amorphous, or in a thick fan-shaped mass that limit the transport of water and ions[10].

In presence of chloride ions interact with the hydrous oxide layer to replace OH^- ions inside the oxide film, destroying the protective layer which develops on the steel surface and in presence of oxygen and moisture allows corrosion to occur. The corrosion steps involve both chemical and electrochemical reactions resulting in further dissolution of iron as indicated by the increase of anodic current density in the passive region then Cl^- ions interact with hydrous oxide layer to replace OH^- inside the oxide film, The reactions may be written as:

$$Fe^{+2} + 2\,OH^- \rightarrow Fe(OH)_2 \quad (5)$$

$$Fe(OH)_2 + 3Cl^- \rightarrow FeCl_3 + 2OH^- + e \quad (6)$$

$$FeCl_3 + 3OH^- \rightarrow Fe(OH)_3 + 3\,Cl^- \quad (7)$$

It should be noted that although the consumption of chloride ions is balanced by the release of chloride ions, the ions presence promotes the disruption of the oxide layer through the looping reaction process. The product of $FeCl_3$ a soluble corrosion product forms and react with OH^- to produce a very porous precipitate $Fe(OH)_3$ accelerates the disruption due to its high solubility, also higher chloride concentration results in faster dissolution of the oxide layer. The diffusion of chloride ions in hardened concrete is widely recognize as being of importance in relation to the corrosion of reinforcing steel. When ever chloride ions are present in concrete their influence on the passivity and anodic dissolution of embedded steel must depend on their mobility in the vicinity of the metal/concrete interface, ionic mobility being linked to diffusivity[11].

Transportation of ions, both anions and cations through cement based materials is one of the important processes in their durability. The diffusivity of ions increases with increasing porosity, the penetration of ions depends on the permeability[12].

The previous results may be explained on the bases that, rice hull is an agricultural by-product containing about 20% of silica. It is a raw material to prepare Ca_2SiO_4 related element which is a component of commercial Portland cement, consistency of OPC paste blended with RHA increased with increase in the amount of RHA. This may be attributed to the higher specific surface area of RHA so it is not only has a pazzolanic 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 decrease permeability of aggressive ions through it. The dose of RHA was optimizing by measuring the initial and final setting times.

Phosphogypsum is a fine powder with high calcium sulfate content and when heated at elevated temperature, produced an stable anhydrite and due to the close proximity of P_2O_5 and F content and the impurities become inert. And exist on the surface of gypsum crystals and in the interstices of agglomerated crystals as H_3PO_4 and ($CaHPO_4$-$2H_2O$) which gets converted into calcium pyrophosphate (CaP_2O_7) which is water insoluble and thus harmless[13].

The total porosity decreases and the bulk density increases with curing time when mixing PG with OPC this may be due to the increase of relative amounts of the denser products as the hydration proceeds. Also total porosity decreases and the bulk density[14]. PG act as a filler. It has more adhesion strength so, it adhere to the surface of gypsum crystals that substitute in the crystal lattice of gypsum and it filling the porous surface with fine particles as a result it restrict the corrosion rate in aggressive media . The inherent surface passivation due to the use of complex gypsum causing a denser microstructure and finally a lower porosity and permeability the aggressive ions. However, chemical-mineralogical investigations have shown that ettringite or thaumasite as shown from the following Eq.(8) formed by the reaction of carbonate, sulphate and silicate in combination with calcium and water.

$$\textbf{CSH + gypsum + calcite + water} \rightarrow \textbf{thaumasite + portlandite} \quad (8)$$

On the other hand, it can be formed from ettringite. After formation ettringite, The alumina content will be substituted by carbonate and silicate ions and the solid solution . Summarizing, it can be said that thaumasite is a complex reaction product of a sulphate attack can formed in small amounts without cause an evident decrease in durability while the formation of ettringite accelerate the disruption of the gel layer formed on the surface of cement grains with low porosity and also permeability[15].

So, Phosphogypsum give good inhibition for reinforcing steel embedded in concrete against corrosion when mixing with OPC with a limiting value.

To understand the mechanisms and the parameters controlling the reactivity of tricalcium aluminate in the presence of gypsum and the role of C_3A source and its fineness were also that it reacts immediately upon contact with water and the hydration rate reaches a maximum after about 10 min. Then the hydration rate decreases probably because of a lack of the water at the retarding surface due to the formation of hexagonal hydro-aluminates coating C_3A grains, so that water molecules must reach the reacting surface either by surface migration or diffusion, also ions of aggressive media[16]. It is well known that C_3A hydration is substantially responsible for the flash setting of Portland cement, in presence of aggressive ions as sulphate the mechanism of retardation of C_3A hydration is generally accepted to be caused by the formation of ettringite crystals coating the clinker grains. Where Gupta et al proposed that very small and thin crystals of C_4AH_x form a nearly imperious coating around C_3A grains which retards water diffusion to the anhydrous surface and therefore the hydration rate. When the presence gypsum, C_4AH_x is obtained which subsequently is transformed into ettringite by releasing fresh $Ca(OH)_2$ near the reacting surfaces. This keeps the impervious coating of C_4AH_x operative. When the ettringite layer is sufficiently thick C_4AH_x is converted to monosulfate because mobility of $CaSO_4$ is limited, and this process flakes off the retarding layer, because expansion caused by transformation of C_4AH_x into monosulfate. So that the movement of ions or dislocations on the crystal surfaces is inhibted[17].

The results show improvement for samples with gypsum than with OPC only due to the smaller size of ettringite crystals, which they able to fit to the irregular shape of C_3A particles better than the larger crystals of ettringite formed in absence of gypsum. In case of Na_2SO_4 substitutes $CaSO_4.2H_2O$ practically no retardation is observed during the initial period of C_3A hydration. At the same time, ettringite is not formed in the presence Na_2SO_4 as it is the presence $Ca\ SO_4.2H_2O$[18]. So, from the results it will show that quality of concrete, specifically a low permeability, is the best protection against sulfate or chloride attack. The sulphate effect on the corrosion of reinforcing steel can be arranged in a decreasing order as follows : $Na_2SO_4 > MgSO_4$ in two series it was found that Na_2SO_4 more harmful than $MgSO_4$ for corrosion of reinforcing steel.

CONCLUSIONS

This work indicates the important role of RHA and PG waste materials when mixed with concrete is more useful to increase efficiency of rebar against corrosion with time in different aggressive media as sulphate or chloride which presence in most environment. Where Ettringite crystals are formed by a through solution mechanism but they are assumed prefentially to form the surface of C_3A because of the catalytic action of the C_3A surface on the nucleation of ettringite.

REFERENCES

[1] V.G.Papadakis; Cement and concrete research, **29**, 79 **(1999)**.
[2] D.Buid; 'Rice husk ash as a mineral admixture for high performance concrete thesis', Delft University press, Delft, **(2001)**.
[3] V. Saraswathy, Ha-Won Song; 'Construction and Building materials', **21**, 1779 **(2007)**.
[4] Moncef Nehdi; Cement Conc.Res., **34**, 1271-1272 **(2004)**.
[5] N.B.Singh, V.D.Singh, Sarita Rai, Shivani Chaturvedi; Cement Concrete research, **32**, 387 **(2002)**.
[6] E.T.Atakuziev; Uzk, Klim Zh: Fan, **3**, 46 **(1997)**.
[7] A.Roy, G.P.Byerly, R.K.Seal; Journal of Materials in Civil Engineering, ASCE, **6**, 439 **(1994)**.
[8] A.A.Hanna, A.I.M.Akarish, S.M.Ahmed; J.Mater. Sci.Technol., **15**, 431 **(1999)**.
[9] 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 **(1993)**.
[10] M.Collepardi, G.Baldini, M.Panri, M.Corradi; Cement Concrete Research, **8**, 571 **(1987)**.
[11] H.G.Midgely, J.M.Illston; Cement and Concrete Research, **14**, 546 **(1984)**.
[12] S.Chatteri; il cemento., **3**, 139 **(1995)**.
[13] M.Singh, M.Grag; Cem.Concr.Res., **30**, 571 **(2000)**.
[14] S.H.Tantawi, S.S.Ibrahim; 22nd international conference on J.Solid waste technology and management, March 18-21, **(2007)**.
[15] V.Tesch, B.Middendorf; Cement and Concrete Research, **36**, 1516 **(2006)**.
[16] Mario Collepardi, Giorgio Baldini, Marco Pauri; Cem.Conc.Res., **8**, 571-580 **(1978)**.
[17] P.Gupta, S.Chatteri, J.W.Jeffery; Cement Technology, **4**, 1 **(1973)**.
[18] Mario Collepardi, Giorgio Baldini, Marco Pauri, Mario Coradi; Cement Concrete Research, **8**, 571 **(1978)**.