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Corrosion Resistance Properties of Rice Husk Ash Blended Concrete

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Portland cement incorporating supplementary cementing material develops excellent mechanical properties and long term durability characteristics. India is a leading rice producing country and rice husk is considered as waste in the rice milling industries. In this present work, the rice husk ash (RHA) was added to concrete as cement replacement from 0 to 30%. Corrosion performance of reinforcing steel embedded in RHA blended concretes was studied using linear polarization, AC impedance and gravimetric methods. The corrosion rate of steel bars embedded in RHA concretes were compared with control concrete. The results clearly indicate that the corrosion rate of reinforcing steel embedded in concrete is significantly reduced with the incorporation of RHA. A good correlation among gravimetric method and electrochemical methods was observed. Electrochemical impedance study showed 98 percentage reduction in corrosion rate to the RHA blended concrete with 15% replacement than control concrete.

Keywords : *rice husk ash, cement replacement material, corrosion of reinforcing steel, electrochemical techniques*

1. Introduction

Carbon steel of large quantities is extensively used as reinforcement for concrete structures. Reinforcing steel in good quality concrete do not corrode even if sufficient mo1isture and oxygen are available. This is due to the spontaneous formation of a thin protective oxide film on the steel surface and in the highly alkaline pore solution of concrete. When sufficient chloride ions have penetrated to the reinforcing steel surface, the protective film is destroyed and corrosion in the form of rust formation occurs in the presence of water and oxygen.[1)] Concrete incorporating supplementary cementing materials such as fly ash, slag and silica fume develop excellent durability properties.[2),3)] Introduction of pozzolanic materials in blended cement generally improves concrete protection against chloride induced corrosion of steel reinforcement by reducing permeability / diffusivity.[3)] Several investigations have been carried out to utilize the rice husk ash (RHA) as a supplementary cementing material.[4)-8)] The chemistry of RHA cement involves the chemical reaction of the amorphous silica in the ash with the extra lime in the Portland cement during the hydration process to form additional calcium silicate hydrate.[8)] RHA in a highly reactive form has been used as suitable raw material for making hydraulic cement and as a good corrective admixture for reducing expansion due to alkali silica reaction.[9)] Studies have also been carried out to utilize the RHA as cement replacement material for making high performance concrete.[10)] The above studies have revealed that the RHA have attracted a great deal of attention for the research interest, because it has a good pozzolanic property due to the presence of amorphous silica.

India produces 18 million tons of rice husks annually and it is estimated that approximately 2.5 million tones of RHA is available as an excellent cement replacement material for producing highly durable blended Portland cement. The Bureau of Indian Standard for concrete IS456: 2000 included, for the first time, RHA as one of the pozzolanic admixtures that may be blended in concrete. The objective of the present study is to determine the influence of RHA as cement replacement material to minimize the corrosion rate of steel in concrete and identify the threshold level.

2. Experimental

2.1 Materials

Rice husk ash burnt at 650 ℃ for one hour under control

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Table 1. Physical properties and Chemical analysis of OPC and RHA

DETAILS	CEMENT	RHA
Physical properties:		
Specific gravity	3.1	2.06
Fineness passing 45μm sieve (%)	80	99
Specific surface area Blains (m^2/Kg)	326	-
Specific surface area BET (m^2/g)	-	36.47
Mean Grain size (μm)	19.8	3.8
Chemical analysis:		
Silicon dioxide (SiO_2)	20.25	87.32
Aluminium oxide (Al_2O_3)	5.04	0.22
Ferric oxide (Fe_2O_3)	3.16	0.28
Calcium oxide (CaO)	63.61	0.48
Magnesium oxide (MgO)	4.56	0.28
Sodium oxide (Na_2O)	0.08	1.02
Potassium oxide (K_2O)	0.51	3.41
Loss on Ignition (LOI)	3.12	2.1

condition and pulverized into fine powder was used as supplementary cementing material. Ordinary Portland cement (OPC) of 43 grade conforming to Indian standard IS 8112, graded river sand with fineness modulus of 2.85 and crushed granite aggregate with fineness modulus of 6.75 conforming to IS 383-1970 were used to prepare concrete specimens. Carbon steel conforming to IS 1786 -1979 (Fe415 grade) was used as reinforcing steel bars. The physical properties and chemical analysis of OPC and RHA are shown in Table 1.

2.2 Preparation of concrete specimens

RHA was added to concrete by replacing an equal amount of OPC by percent mass (5, 10, 15, 20, 25 and 30 weight %). The burnt ash was initially blended with OPC thoroughly in dry condition, subsequently with sand and then coarse aggregate. Finally water was added and mixed evenly to obtain uniform mix. Six different RHA concrete mixes (5%-30%) and control mix were prepared with constant water-binder ratio of 0.53 for the designed cube compressive strength of 25 MPa. These mixes were designated as C for control and R1 to R6 for 5% to 30% replacement of RHA concretes. Reinforcing Steel specimens of 115 mm length (75 mm embedded) and 12 mm diameter were placed, one bar in each 100 mm x 100 mm x 100 mm size concrete cube with 20 mm cover, at one of the corners during the casting for electrochemical studies. Similar reinforcing steel specimens of size 50 mm length and 12 mm diameter were initially pickled in HCl solution, degreased, cleaned and weighed. The pre-weighed steel specimens were placed in RHA concrete cubes with 20 mm cover during casting for gravimetric method.

2.3 Methodology

The compressive strength of concrete cubes incorporating RHA at different cement replacement level (CRL) was determined at 7, 14, 28 and 90 days curing according to IS 10261-1982.

The corrosion of steel bars in concrete was induced by the alternate 7 days dry-wet exposure cycles in 3.0% NaCl solution for a period of 18 months. Gravimetric method and electrochemical techniques such as linear polarization and A.C. impedance were used to study the corrosion rate of reinforcing steel in RHA blended concrete cubes.

The corrosion rate of reinforcing steel bars embedded in RHA concretes was obtained using gravimetric method. After the exposure period, the concrete cubes were broken open. The pre weighed steel specimens were cleaned as per the procedure given in ASTM-G 1-90 and reweighed. From the loss of weight and the exposure period, the corrosion rate was estimated.

The electrochemical experiments were conducted using Advanced Corrosion Monitoring (ACM) field machine, England and related software package. This system includes potentiostat and personal computer. Three electrodes configuration, consisting of reinforcing steel bar embedded in concrete for a length of 7.5 cm with surface area of 28 cm^2 as working electrode, stainless steel plate of equal area as counter electrode, and saturated calomel electrode (SCE) as reference electrode was used. The counter electrode and the reference electrode were assembled in a wetted sponge of 100 mm x 50 mm x 30 mm in size. Linear polarization resistance and A.C. impedance measurements were carried out by placing the wetted sponge assembly on the surface of the concrete over the working electrode as shown in Fig. 1.

For linear polarization resistance studies, the measurements were carried out within the potential range of -20 mV to +20 mV with respect to open circuit potential and the current response was measured at a scan rate of 0.166 mV/sec. IR compensation was applied during the measurements. The polarization resistance (Rp) of the reinforcing steel in RHA concrete was obtained as the slope of the potential current plot. Also from the polarization studies, the corrosion potential (Ecorr), corrosion current (Icorr) and corrosion rate (C.R) were estimated using the following relationships

(1) Corrosion current (Icorr) = B/Rp (μA/cm^2)
where B= stern-Geary constant (B=26mV SCE) and Rp in kilo ohms-cm^2.

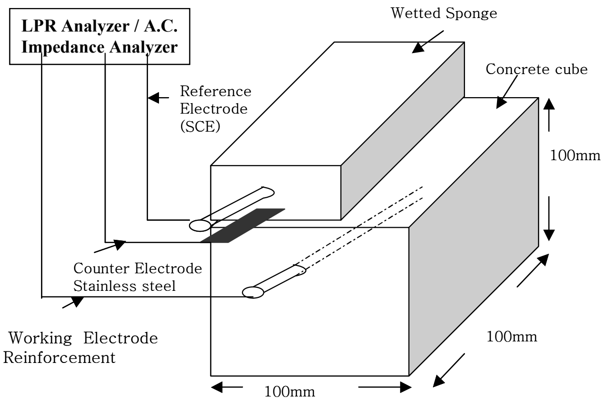

Fig. 1. Electrochemical Experiment

(2) Corrosion rate (C.R) = $301 \times 10^{-3}/Rp$ (mmpy)

For A.C impedance studies, the measurements were carried out at corrosion potential with A.C amplitude of 15 mV for the frequency range of 30 KHz to 10 mHz. The real and imaginary part of the impedance values were plotted in Nyquist plot. From the Nyquist plot, the charge transfer resistance (Rct) was obtained. Icorr and C.R were also estimated using the above expressions with Rct values instead of Rp values.

For the quantitative assessment of corrosion inhibitive performance of reinforcing steel in RHA blended concretes, the percentage reduction in corrosion rate of steel in RHA concrete systems are estimated using following equations.

(3) $$\text{Percentage Reduction in C.R} = \frac{1/Rp - 1/Rp_{(R)}}{1/Rp} \times 100$$

(4) $$\text{Percentage Reduction in C.R} = \frac{1/Rct - 1/Rct_{(R)}}{1/Rct} \times 100$$

(5) $$\text{Percentage Reduction in C.R} = \frac{C.R - C.R_{(R)}}{C.R} \times 100$$

where Rp and $Rp_{(R)}$ are the linear polarization resistance values in the absence and presence of RHA, Rct and $Rct_{(R)}$ are charge transfer resistance values in the absence and presence of RHA and C.R and $C.R_{(R)}$ are the corrosion rate values in the absence and presence of RHA respectively.

3. Results and discussion

Compressive strength of concretes with different percentage of RHA as cement replacement is shown in Table 2. As anticipated the compressive strength of control concrete and RHA concretes increased with curing times (7, 14, 28 and 90 days). In the presence of 20% replacement of RHA, the maximum compressive strength value of 45.98 MPa was obtained and it is 1.2 times higher than control concrete. RHA concretes up to 30% CRL showed compressive strength, higher than control concrete at all curing periods. Even at 30% CRL the increase in compressive strength value is found to be 1.11 times of control concrete at 90 days.

The corrosion rate values obtained from gravimetric method for the reinforcing steel embedded in concrete containing RHA at different CRL are shown in Table. 3. For control concrete, the C.R of embedded steel is found to be 21.63×10^{-3} mmpy and the C.R of steel in RHA concretes ranged from 4.23×10^{-3} to 13.75×10^{-3} mmpy. The C.R values are considerably reduced in RHA blended concretes up to 30% CRL. Steel embedded in 15% CRL concrete showed 5 times decrease in C.R than control concrete. The percentage reduction in C.R data reported for RHA concretes also revealed a maximum value of 80.44% at 15% CRL and even at 30% CRL the percentage reduction in C.R is found to be 36.43%. These results

Table 2. Compressive strength of Concrete containing RHA

Specimen	Cement replacement level %	Compressive strength (MPa)			
		7 days	14 days	28 days	90 days
Control	0	27.22	32.30	36.05	38.30
R1	5	27.62	34.30	40.06	43.33
R2	10	28.00	35.33	41.26	44.83
R3	15	29.33	36.00	41.83	45.65
R4	20	32.00	39.33	42.50	45.98
R5	25	28.67	36.10	38.83	43.00
R6	30	28.83	33.67	36.58	42.67

Table 3. Gravimetric method of corrosion rate values of RHA concretes

Specimen	Cement replacement level %	Corrosion rate x 10^{-3} mm py	Percentage reduction in C.R = $\frac{C.R-C.R_{(R)}}{C.R}$ x 100
Control	0	21.63	-
R1	5	13.25	38.74
R2	10	8.17	62.23
R3	15	4.23	80.44
R4	20	10.45	51.69
R5	25	11.19	48.27
R6	30	13.75	36.43

showed that the introduction of pozzolanic material (RHA) in blended concrete improves protection against chloride induced corrosion of steel.

The electro chemical parameters (Ecorr, Rp, Icorr and C.R) obtained from the linear polarization resistance measurements are presented in Table. 4. For control concrete, the C.R of embedded steel is found to be 20.28 x 10^{-3} mmpy. In the case of RHA blended concrete, the C.R is considerably reduced (C.R values of RHA concretes varies from 0.464 x 10^{-3} mmpy to 7.51 x 10^{-3} mmpy). For example, the C.R value is 10 times reduced at 15% CRL. The percentage reduction in C.R of the specimens calculated using Rp and $Rp_{(R)}$ values are presented in Table 4. The percentage reduction in C.R data reported also revealed a maximum value of 97.71% at 10% CRL. Even at 30% CRL, the percentage reduction in C.R is found to be 62.94%. These data also clearly showed that the finer RHA particles considerably refined the pore structure and reduced the corrosion rate of embedded steel.

The C.R values obtained from ACM machine for A.C.impedance studies are given in Table. 5. The C.R of control concrete is found to be 24.56 x 10^{-3} mmpy and the C.R values of embedded steel in RHA concretes varies from 0.773 x 10^{-3} mmpy to 16.94 x 10^{-3} mmpy. C.R values for steel embedded in RHA concrete up to 30% CRL are found to be again less than control concrete. A maximum reduction of 32 times in C.R value is found in concrete with 15% CRL. The percentage reduction in C.R values estimated using Rct are also given in Table. 5. The percentage reduction in C.R data reported also revealed that a maximum value of 96.86% at 15% CRL. At 30% CRL, the C.R value is found to be 31.03%. These data again showed that the formation of additional calcium silicate Hydrate (C-S-H gel) during the hydration of RHA concrete is responsible for transformation of large permeable pores to small impermeable pores and improvement in corrosion resistance of steel in RHA concretes.

The results obtained from A.C impedance studies on concrete containing RHA at 0,15 and 30% replacement levels are presented in Bode plot, and Nyquist plot as shown in the Figs. 2a and 2b. Nyquist diagrams show typically more or less perfect semicircles, from which associated Rct values were calculated. From the Nyquist plot (Fig. 2b), it is shown that the concrete with 15 %

Table 4. Linear polarization resistance measurement values of RHA concretes

Specimen	Cement replacement level %	Corrosion potential Ecorr mV vs SCE	Rp k.ohms-cm^2	Icorr µA/cm^2	Corrosion Rate x 10^{-3} mmpy	Percentage reduction in C.R $\frac{1/Rp-1/Rp_{(R)}}{1/Rp} \times 100$
Control	0	-495	14.94	1.740	20.28	-
R1	5	-353	114.70	0.226	2.64	86.97
R2	10	-300	653.06	0.039	0.464	97.71
R3	15	-365	151.88	0.171	1.99	90.16
R4	20	-385	91.83	0.283	3.29	83.73
R5	25	-404	44.01	0.590	6.88	66.05
R6	30	-461	40.31	0.645	7.51	62.94

Table 5. A.C. Impedance measurement values of RHA concretes

Specimen	Cement replacement level %	Corrosion potential Ecorr mV vs SCE	Rp k.ohms-cm^2	Icorr µA/cm^2	Corrosion Rate x 10^{-3} mmpy	Percentage reduction in C.R $\frac{1/Rp-1/Rp_{(R)}}{1/Rp} \times 100$
Control	0	-448	12.31	2.119	24.56	-
R1	5	-387	40.13	0.650	7.532	69.32
R2	10	-331	97.14	0.269	3.122	87.32
R3	15	-301	392.0	0.066	0.773	96.86
R4	20	-385	37.52	0.695	8.056	67.19
R5	25	-420	25.37	1.028	11.91	51.48
R6	30	-443	17.85	1.468	16.94	31.03

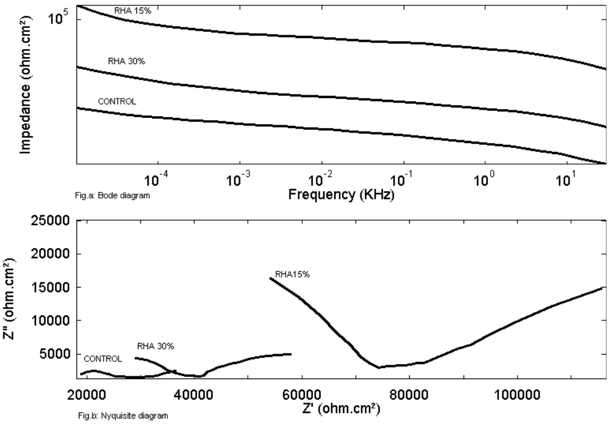

Fig. 2. Impedance study on steel embedded in RHA concrete

Fig. 3. Icorr values obtained by LPR and A.C. Impedance Techniques

RHA has greatest semicircular arc (maximum Rct value), followed by concrete with 30 % RHA and control concrete has the smallest semicircular arc representing minimum Rct value. Bode diagram also shows the same higher Rct+Rc values for 15 % RHA concrete.

Icorr values obtained from both Linear Polarization and AC Impedance techniques clearly demonstrate that the control concrete after 18 months exposure was in very active state[11)] (Icorr > 1.5 μA/cm^2) and RHA concretes are in passive states (Icorr < 1.5 μA/cm^2). Also the RHA concrete containing 10 to 15 % replacement levels showed the lowest Icorr value and passive state in both electrochemical techniques.[11)]

Further the corrosion rates obtained by gravimetric, polarization resistance and A.C. impedance methods agree very well by showing the same trend of corrosion rates for different CRLs. More negative half cell potential reading was associated with large corrosion current determined. Linear relationship between corrosion potential and Icorr has been established, theoretically in chloride induced corrosion.[12)] A comparison of Icorr values obtained from linear polarization and A.C. Impedance techniques using a plot is shown in Fig. 3. A solid reference line was applied to indicate the linear trend between the measurements. It appears that both techniques are in a relatively good agreement (correlation coefficient, R = 0.931 close to the unity) with respect to Icorr values of the reinforcing steel bar in RHA concretes.

The above corrosion studies indicate that concrete containing RHA from 5 to 30 % replacement level has higher corrosion resistance property than control concrete. The presence of reactive silica in RHA, formation of additional calcium silicate hydrate during the hydration of RHA cement, pore refinement and excellent resistance against chloride ion penetration make RHA concrete a very good durable/corrosion protection material. Generally compressive strength and water- cementitious materials ratio are employed to describe the quality of concrete and these properties have been used so far as guideline for formulating specifications and design. With the advent of high performance concrete incorporating cement replacement materials, it is now feasible to design and build more durable long lasting concrete structures.

4. Conclusion

(1) The compressive strength increased by 20% for RHA blended concrete (20% of CRL) than control concrete. RHA blended concretes from 5 to 30% CRL showed higher compressive strength than control concrete at all curing periods.

(2) Corrosion rate of steel observed using gravimetric method showed 5 times decrease for RHA concrete with 15 % CRL than control concrete. The percentage reduction in corrosion rate data also revealed a maximum value of 80% for RHA concrete with 15% CRL.

(3) Corrosion rate of steel measured using linear polarization technique observed 10 times decrease for RHA concrete with 15% CRL than control concrete. The maximum percentage reduction in corrosion rate was 98% in RHA blended concrete (10% CRL).

(4) Corrosion rate of steel studied using A.C.impedance technique showed 32 times decrease for RHA concrete with 15% CRL than control concrete. The percentage reduction in corrosion rate data also revealed a maximum value of 97% in RHA blended concrete (15% CRL).

(5) Corrosion current values obtained from the linear polarization and A.C. impedance techniques showed a good correlation (R=0.931) among the Icorr values for RHA blended concretes.

(6) The results obtained from this study indicated increase in compressive strength and decrease in corrosion

rate with the addition of RHA in concrete from 5 to 30% CRL compared to control concrete. The concrete incorporating RHA (10 to 15% CRL) showed proven track record for improving corrosion resisting characteristic of concrete. Hence RHA blended concrete may be considered as better substitute for durable concrete.

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