

CORROSION OF MILD STEEL IN OPC / RHA MORTARS

By

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ABSTARCT

The effect of rice husk ash (RHA) additions on the corrosion of mild steel in the concrete in contaminated OPC mortars was studied. The corrosion potential of steel embedded in mortar mixes with different OPC / aggregate ratios with partial replacement of OPC with RHA containing different levels of chloride was monitored during the hydration period only. The chloride is taken as an admixture and added with the mix water. It is observed that RHA is beneficial in mitigation of corrosion when present with a reasonable amount of OPC. Low OPC mortars containing chloride ions show corrosion irrespective of the RHA content.

INTRODUCTION

The corrosion of steel in concrete is due to electrochemical processes in the presence of conductive medium, which in case of concrete, is supplied by the water present inside the porous network. Therefore, charge transfer reactions are possible at the interface between the ions in the electrolytic medium and the embedded steel.

The cement coating is a good barrier and it also furnishes hydroxyl ions¹⁻² in the pore environment that makes the steel passive. The passivity of steel is destroyed when the critical Cl^-/OH^- ratio exceeds a certain limit³. It has been observed that if the relative humidity is less than 40%, then corrosion risks, especially due to chlorides⁴ become negligible⁵.

The role of other materials as partial replacement in ordinary Portland cement (OPC) have been explored to reduce the costs and to mitigate corrosion. Pozzolans as fly ash⁶ have been found effective in reducing corrosion rates due to chloride in admixture. However, chloride as an admixture can be only fought against by reasonable amounts of ordinary OPC in the blend to initiate the pozzolanic activity and to furnish OH^- ions for the required passivity of steel.

Rice husk (RH) is also being investigated as a partial replacement material for OPC. RH occupies an important position among agro-industrial wastes, and its silica content is highest among all of them. It is widely available in rice producing countries. RH Pakistan produces about 4 million tons of paddy every year from which 0.8 million tons of RH are separated as by-product. Such huge amounts are not utilized properly and common practice is to burn out the RH which is a wasteful exercise⁷. Heap burning of RH causes pollution hazards for surrounding population and has disposal problems also.

Rice husk Ash (RHA) can be made from burning of rice husk under controlled conditions of temperature. The main constituent of RHA is SiO_2 , which constitutes about 80-90% of the material. It is present in the original rice husk in the form of hydrated silica and gets converted into amorphous silica at burning temperatures of 400-600 °C. The burning temperatures and time of burning are critically important as these affect the specific surface area and the reactivity of RHA⁸. The ash may also contain a few percent of K_2O and Na_2O and up to 20% of residual carbon.

OPC / RHA blends have been found to be successful in imparting compressive strength to concrete due to reduction in porosity⁹ and hence it is expected that it will also control ingress of

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chloride from outside to the embedded steel surface. Previous studies have likewise mainly focused on the diffusion of chloride ions into the cement matrix. In such cases RHA has been established as a good substitute for OPC in portion ^[10-11]. Also, when mixed with lime in certain ratio (commonly 1:2, lime : RHA), it finds wide applications to produce concrete blocks, well rings flooring and road sub-bases^[12].

The present investigations were conducted with an objective to study the behavior of OPC/sand mortars with different RHA replacements for OPC when chloride ion is already present in the mix. The free corrosion potential (E_{corr}) of the samples were measured during the entire hydration period to study the effect of RHA additions to the cement mortars.

EXPERIMENTAL

Rice husk (RH) was brought from the Anmol Rice Mills, Sehjoke (8 Km from Daska, Sialkot). Almost 2 kg RH was taken in a large tub. It was washed with tap water in order to remove the small particles and impurities from it. This process was performed repeatedly for almost fifteen days. To remove more impurities, almost 200 g of RH was taken separately in two different washing solutions. Washing of RH was done by two methods as follows:

- (a) Method 1: RH was washed using H₂SO₄/HNO₃ (1:1).
- (b) Method 2: RH was washed using H₂O/H₂SO₄/HNO₃ (2:1:1)

After several washings by both the methods, for over a month, RH was dried in air first and then in an oven for 10 minutes at 100°C and put in the desiccators for 28 hours. The dried RH was taken in a large pre-weighed ceramic crucible. It was placed in an electric furnace at 500°C for 5 hours. RHA was produced. The effect of time of burning was also studied on RHA by burning RHA for one hour before burning in the electric furnace for two hours at 500°C. The results are given in table 1.

| Washing Solutions | Wt. of RH taken in washing soln. | Wt. of RH after washing and drying | Wt. of fully dried RH | Wt. of RH taken in the crucible | Temperature (°C) | Time (hours) | Wt. of RHA formed |
|-------------------|----------------------------------|------------------------------------|-----------------------|---------------------------------|------------------|--------------|-------------------|
| 1 | 200g | 72.2987g | 70.2016g | 43.3706g | 500 | 5 | 4.48g |
| 2 | 200g | 74.3350g | 70.5039g | 44.5675g | 500 | 5 | 4.73g |
| 1 | 100g | 50.9217g | 49.6923g | 49.6923g | 500 | 3* | 6.90g |
| 2 | 100g | 52.5609g | 51.0302g | 51.0302g | 500 | 3* | 6.89g |

* one hour burning of RH in gas furnace + 2 hours in the electric furnace = 3 hours burning time

Table 1. Amount of RHA obtained with washing solutions 1 and 2

The results show that the washing solution composition does not affect the amount of RHA obtained. However, the time of burning influences the weight of RHA gained i.e., less RHA is obtained when the RH is burnt for longer time period i.e., 5 hours as compared to 3 hours.

The specimens were made from ordinary mild steel, courtesy Black Gold industry, Bund Road link, Bogiwal Road, Lahore. The steel was Model steel grade-40.

The steel bars was made to size on lathe machine and then cut in cylindrical shape of about half an inch in size. The steel samples were roughly grinded to have a uniform and clean surface. These were threaded on one side to tightly attach an iron rod for a sound connection. The density, surface area and diameter of each sample was measured and recorded.

The bottom of the sample (the area to be exposed for test) was polished by emery paper of various numbers, starting from 100 till 600. A PVC pipe was cut in pieces larger than the size of

steel sample. The steel sample was placed inside it and then mounted using cold mounting technique. The epoxy used for this purpose was Magic Depoxy Steel (filler made in Pakistan stock no. DS 400) and mixed with hardner. The epoxy completely covered the gap between the pipe and the steel specimen. These samples were then left undisturbed for about 24 hours so that the epoxy hardens and bonds well with the sample and the covering pipe.

The exposed area of the specimen for the corrosion studies fell in the range 0.78 – 0.85 cm². The polished bottom end was then washed with alcohol and dried with a tissue paper and covered with paper tape till the time of test. This is a safety precaution to ensure the removal of any unnecessary epoxy that gets on to the surface of the specimen. Furthermore, it has been proved that polished samples show more resistance to corrosion^[13].

The prepared steel specimen were cast into OPC mortars by placing the specimen inside a larger PVC pipe and filling the gap between the specimen and the PVC pipe inner boundary with epoxy so that half an inch space is left. It is hardened and then filled with OPC mortars with different OPC/sand ratios, RHA and different admixtures. The mortar samples were allowed to set for 24 hours. The samples were then stored in polythene bags to avoid further contact with atmospheric moisture to preserve the polished bottom surface.

Concrete mortars were prepared with different admixtures such as RHA, sand, and NaCl. The sand was taken from River Ravi near Bakkarmandi, and washed several times to remove the impurities. It was dried well before using in the concrete mortars. The chemical composition of the cement used, courtesy CRI, Tusdec, Lahore, is given below in table 2.

| SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | MgO | SO ₃ | LOI | Insoluble Residue |
|------------------|--------------------------------|--------------------------------|-------|------|-----------------|------|-------------------|
| 20.34 | 4.9 | 4.14 | 62.05 | 1.59 | 2.65 | 2.72 | 0.36 |

Table 2. Chemical analysis (wt. %) of OPC cement Sample

Mortar samples were prepared of different composition of OPC : sand : RHA : NaCl. The water: cement ratio was fixed at 0.5 and NaCl was added in the mix water. Different sets of mortars prepared are as follows:

Set 1: OPC : Sand + RHA (% by wt. of OPC) + NaCl (% by wt. of OPC)

a) 1:1 + 10 + 0

b) 1:3+ 10 + 0

Set 2: OPC : Sand + RHA (% by wt. of OPC) + NaCl (% by wt. of OPC)

a) 1:1+ 10 + 1

b) 1:1+ 20 + 1

c) 1:1+ 30 + 1

Set 3: OPC : Sand + RHA(% by wt. of OPC) + NaCl (% by wt. of OPC)

a) 1:1+ 20 + 1

1:3+ 20 + 1

These mortar samples were placed in 30 ml distilled water for hydration in individual beakers after 24 hours of casting. After 1 day their E_{corr} values were measured against standard calomel electrode with the help of multimeter (DT-830B).

RESULTS AND DISCUSSION

The present investigations were conducted to study the effect of addition of RHA upon the corrosion performance of embedded steel in OPC sand mortars with different levels of chloride both in good and poor mixes. The RHA, which is a waste material (obtained from burning of the RH) that can be used as a replacement material in place of OPC. It is reported that RHA aids in OPC hydration^[14] and thus provides low porosity and more strength^[15].

RHA was prepared by washing, followed by drying and burning the RH at fixed temperatures. It is observed that RHA formed is not affected by the composition of the washing solution used (see table 1). Similar procedure is adopted by James et. al. for RHA preparation^[16]. The time of burning affects the RHA obtained i.e., lower amounts of RHA are produced when heated for 5 hours as compared to a time of 3 hours. This shows that heating for longer time helps to burn out more organic matter i.e., carbonaceous mass is lost^[17] with SiO_2 undergoing structural changes i.e., amorphous silica formation.

Free corrosion potential measurements are widely accepted for the identification of passive and active areas of rebar embedded in concrete. ASTM specification 876-87 (1987) states that the potential values more noble than -0.20 CSE signify a 90% probability that steel is passive in this area. Potentials below -0.35 V CSE indicate that a 90% probability exists for corrosion. The values between -0.20 V to -0.35 V CSE show that corrosion of steel in this area is uncertain.

The free corrosion experiments conducted on the steel specimens embedded in various mixed mortars, showed very interesting features. The E_{corr} of a clean mix with cement / sand ratio of 1:3, show that the specimen is passive, see Figure 1.

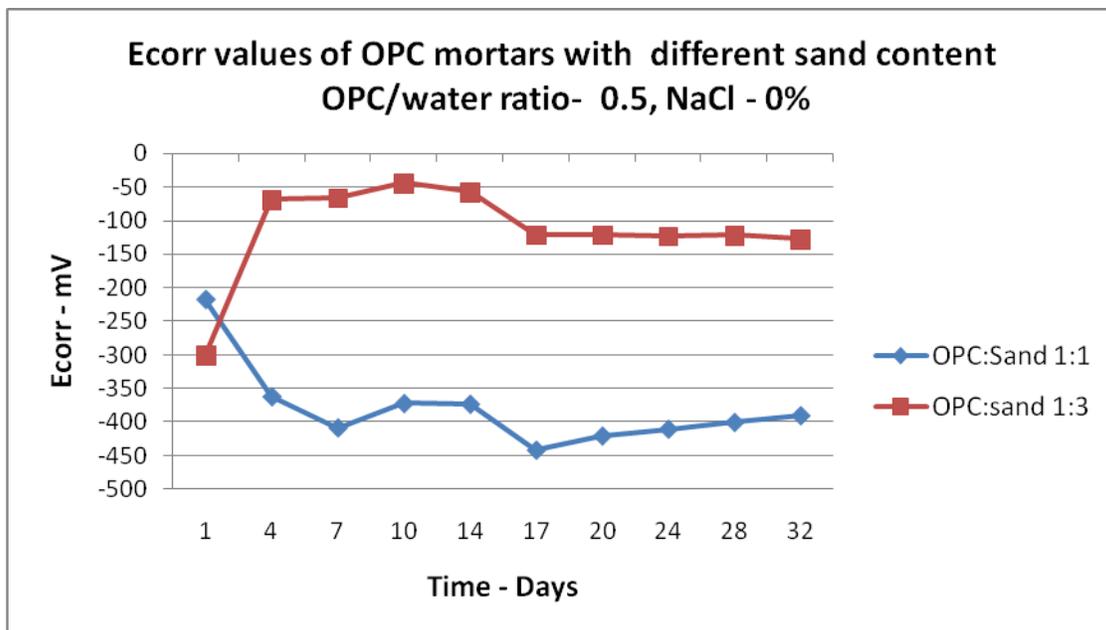


Fig. 1. Comparison of mortars with different OPC: sand ratios and no RHA

In comparison to 1:3 mortars, the 1:1 cement/sand ratio shows lower potential values. This shows that the specimen in 1:3 mix is having plentiful supply of O_2 to support passivity of steel. The potential slowly moves down after 17 days of hydration as the pores close and the oxygen at the surface of steel starts to diminish. As the OPC is hydrating in 1:1 mortar, the porosity is decreasing. Higher OPC content and therefore, more hydration of cementitious compounds and hence, more compaction till 7 days limited the O_2 access to the embedded steel forcing towards

a limiting cathodic reaction. Plausibly a crevice developed that forced the potential to drop down. No pits were observed on visual inspection of the specimen. After 17 days when hydration reactions are stabilizing, the steel starts to passivate. May be the crevice healed and the potential did not fall further.

Fig.2 shows the effect of different percentages of RHA by weight of OPC containing 1% NaCl. The results show that an increase in the percentage of RHA i.e. 10-20% by weight of OPC increases the E_{corr} values, improving the condition of steel by pushing the E_{corr} in the passive direction. The specimen containing 10% replacement of OPC by RHA showed pitting as potential kept on drifting down to E_{corr} of -693 mV. Increasing RHA to 20% by weight of OPC improved the E_{corr} values to a region of -330 mV. This specimen did not show any pit on visual inspection.

RHA (20% by weight of OPC) aids in cement hydration i.e., more C-S-H formation and hence more release of $Ca(OH)_2$ in the pore solution. Accelerated hydration by RHA is supported by other researchers^[14, 18]. Hausman^[3] has stated that a critical Cl^-/OH^- ratio must be maintained to ensure passivity of steel in concrete.

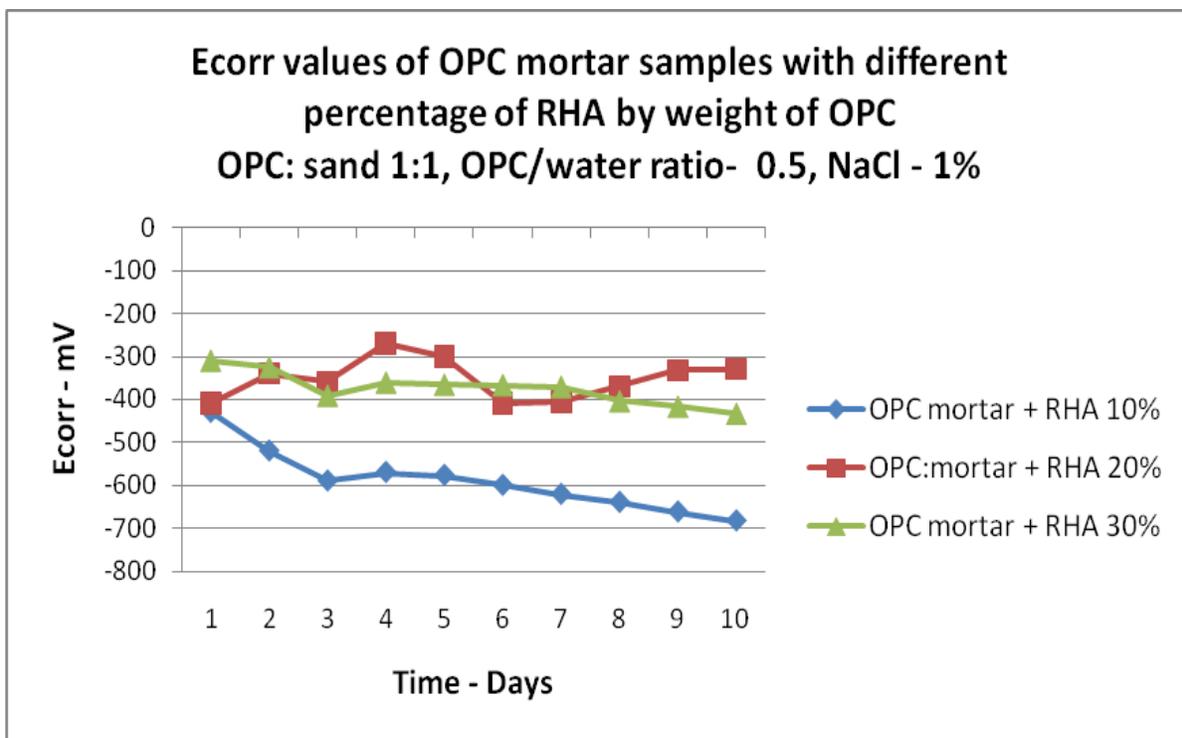


Fig. 2. Comparison of mortars with different OPC: sand: RHA ratios

Increasing the RHA further to 30% also shows the same i.e., more noble potentials than the sample with 10% RHA. However, it keeps declining very slowly. It seems that some corrosion activity is present but at a very slow rate.

The results of set 3 which shows the effect of increasing the sand content for the best sample i.e., 20% RHA mortar with 1 % NaCl are presented in Fig. 3. Increasing the sand in OPC mortars result in poor protection properties of steel in concrete. Higher OPC/sand ratios do not protect the steel at all. Though RHA replacement is done the E_{corr} continued to shift down showing pit activity. The studies show clearly that an increase in RHA does retards corrosion but OPC must be maintained at a certain level to mitigate corrosion in presence of NaCl. The same may be deduced by comparison of 1:3 OPC: sand mortar of Fig. 3 with Fig. 1. The RHA addition is of no help in presence of NaCl i.e., certain amount of OPC must be present to provide adequate amount of OH^- ions.

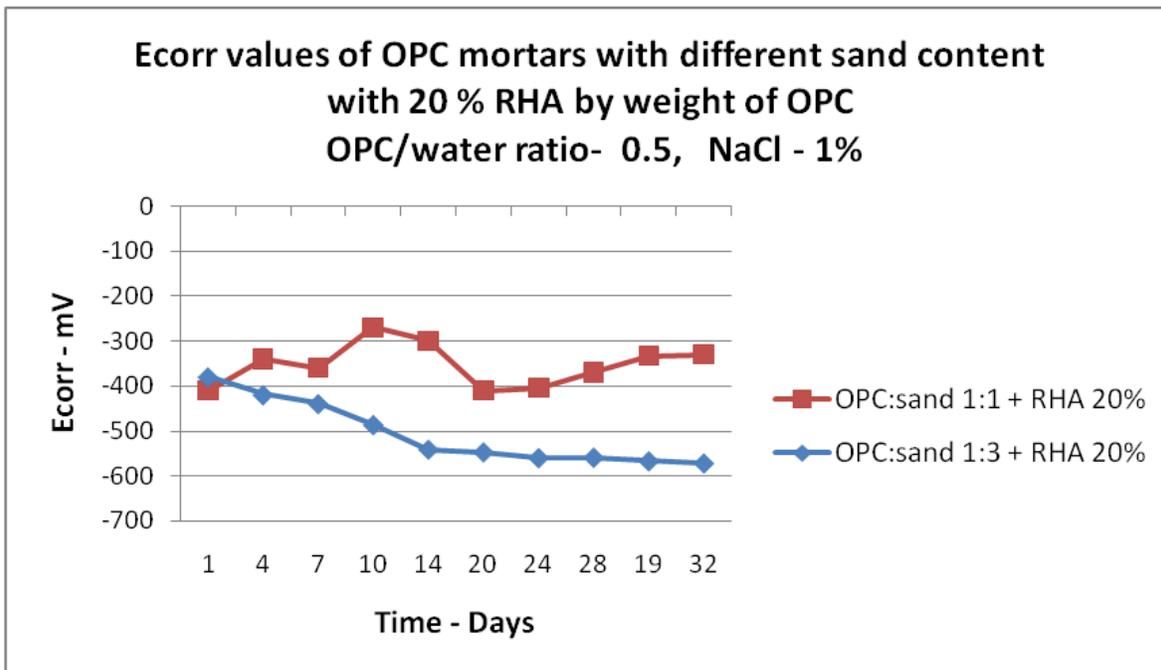


Fig. 3. Comparison of mortars with different OPC : sand ratios

Here RHA addition does not improve the condition for the NaCl is taken as an admixture when sand content is high. Hence, a high cement content is required for maintain passivity of steel when NaCl is present as an admixture^[19]. It is expected that RHA will be beneficial when chloride is present in the outside environment and has to diffuse to the steel surface to promote corrosion.

The present studies show that the use of RHA as a valuable replacement material for OPC that not only increases the strength and lowers the porosity but can also retard corrosion when taken in a selected RHA/OPC / sand blend.

Previous studies by G.C. Isaia (1999) have focused on the chloride ions from the outside of concrete, in which case RHA additions were found beneficial^[20]. Our findings are based upon preliminary results during the hydration period with NaCl as an admixture. The next phase of studies will take the Cl- penetration from the outside environment in OPC mortars with RHA additions to ensure the role of RHA additions on corrosion of steel in outside contaminated environments.

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