

Investigation of corrosion assessment of hydrogen-rich water based cement mortars

Byung Wan Jo^a, Muhammad Ali Sikandar^{a,*}, Sumit Chakraborty^{a,b} and Zafar Baloch^a

^aDepartment Civil and Environmental Engineering, Hanyang University, Seoul 133-791, South Korea

^bDepartment of Civil Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah 711103, India

This study primarily investigates the effects of hydrogen-rich water (HRW) on the rebar corrosion embedded in Portland cement mortars. We comparatively assessed the performances of reinforced HRW-based mortars (HWMs) with respect to cement mortars fabricated from control water (CWM). The results indicate that the use of HRW significantly improves the anticorrosion properties of rebars embedded in cement mortars. Lower electronegative corrosion potential and the galvanic current were observed in HWMs compared to CWM. The electrical resistivity (ER) of HWMs was observed to be higher than those of CWM. Moreover, the HRW reduces the setting times and improves mechanical properties. The generally improved mechanical and anti-corrosion properties of HWMs are attributed to the formation of more cement hydrates with fewer voids in the hydrogen-rich environment. Based on X-ray diffraction (XRD), Fourier transform infrared (FTIR), and scanning electron microscope (SEM) analyses it was deduced that the use of HRW in Portland cement mortars produces a more compact, dense, and durable microstructure with fewer voids due to a higher degree of hydration. The higher degree of hydration in HRW leads to precipitation of greater amount of cement hydrates especially calcium hydroxide (Ca(OH)_2) which helps maintain passive condition for reinforced bars.

Key words: Cement, Sustainable, Electrical resistivity, Compressive strength, Mortars, corrosion.

Introduction

Portland cement-based concrete is the most widely used construction material. Corrosion of concrete is the major cause of deterioration of reinforced concrete structure [1]. The ingress of chloride and carbonate ions into concrete cause damage to passive layer around rebars, thereby promoting corrosion. Steel in concrete is in a passive condition, protected by a thin layer which is either ferrous or ferric in nature. The carbonation reduces the pH of concrete which causes damage of this protective layer, which in turn leads to corrosion at the anodic site of rebar by Cl^- or CO_3^{2-} ions [2]. Additionally, the quest for shorter setting times and high early strength has led researchers to modify Portland cement using innovative chemical and mineral admixtures to meet those demands. The need to produce more sustainable concrete has led researchers to formulate complex mixes that use secondary mineral additions and a wide variety of chemical admixtures to improve concrete performance. Conventionally, set accelerators (both chloride and non-chloride) are used to reduce the setting time and increase the early strength of concrete materials. However, chloride-based set accelerators have the disadvantage of passivating steel reinforcements.

Various types of corrosion inhibitors are used in concrete to retard the electrochemical corrosion reactions. Corrosion inhibitors are generally classified as anodic, cathodic, and mixed inhibitors, depending upon their electrochemical mode of action [3]. Anodic inhibitors are generally oxidizing in nature, which oxidizes ferrous to ferric compound, which leads to the formation of the thin passive layer around rebar. This passive layer serves to protect the dissolution of the anodic site and suppresses the anodic half reaction. Anodic inhibitors being oxidizing in nature are required in sufficient quantity to work effectively. The sufficient level of anodic inhibitors is determined from the amount of Cl^- ions. Calcium nitrate is the most common anodic inhibitor used. Alkali salts of nitrite, benzoate, and chromate have also been used. Cathodic inhibitors slow down the reduction of oxygen at the cathodic site by depositing insoluble salts of metals. Cathodic inhibitors include carbonates, phosphates, polyphosphates, and silicates. Mixed inhibitors suppress both the anodic and cathodic reactions. They adsorb on the entire surface of steel and form a protective layer. That is why they are called ‘film-forming inhibitors’ or adsorption inhibitors. Effective mixed inhibitors are generally organic in nature. Organic compounds containing polar groups containing nitrogen, sulfur, and a hydroxy group. Lowering concrete porosity and permeable voids is the key to limit ingress of Cl^- ions. The use of certain mineral admixtures such as fly ash and metakaolin are known to reduce Cl^- ions into concrete.

*Corresponding author:
Tel : +821021657167
E-mail: muhammadalisikandar@yahoo.com

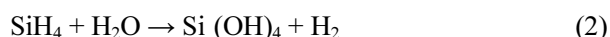
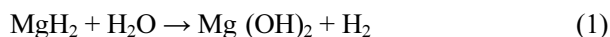
Low-calcium fly ash geopolymers are also known to reduce concrete permeability [4]. The reinforced concrete requires both chemical and physical protection. Steel embedded in good quality concrete perform well against corrosion, owing to the high alkaline environment. However, ingress of harmful ions deteriorates the passive environment around steel.

A review of the literature shows that mineral and corrosion inhibitors inhibit the rebar corrosion in concrete materials. Hydrogen rich water is a type of water with the high amount of molecular hydrogen species (H_2). In hydrogen-rich water, H^+ ions react with environment faster than OH^- causing an alkaline boost after electrolysis. In our earlier work, we demonstrated that hydrogen-rich water controls the physical and mechanical properties of cement mortars, by the formation of a greater amount of cement hydrates [5]. The prime aim of this investigation was to evaluate the effectiveness of HRW as a corrosion inhibitor in cement mortars. The set accelerating tendency of HRW favors its use instead of calcium chloride which is related to corrosion of reinforced and pre-stressed concrete. HRW on the hand is believed to be sustainable development in the field of chemical admixtures, which not only shortens the setting time but also improves the strength and anti-corrosion characteristics of mortars.

Experimental

Materials

Portland cement (21.95 wt.% SiO_2 , 6.59 wt.% Al_2O_3 , 2.81 wt.% Fe_2O_3 , 60.12 wt.% CaO , 3.32 wt.% MgO , 2.11 wt.% SO_3 , and 2.58 wt.% LOI) conforming to ASTM C150 having specific gravity of 3.09 was used as the primary binding material in this study. River sand with an average particle size of 2.34 mm and specific gravity of 2.72 conforming to the grading requirements of ASTM C-33 was used. HRW was produced using a chemical mixture provided by H_2 Vision Inc., Korea. This chemical produces hydrogen in normal water. The chemical composition of the mixture consisted of 95% glycerol, 4% MgH_2 , and 1% SiH_4 . The chemical mixture produces hydrogen rich water according to following reactions,



Mix proportions and fabrication of specimens

For cement paste preparation for determination of initial and final setting times, 100 g of cement was mixed with 48.5 ml water (control or HRW). Five mortar mixtures each (for plain as well as reinforced specimens) having a water-to-cement ratio and the sand-to-cement ratio was kept constant for each mix

Table 1. Mix proportions of mortars for 1 m³.

Mixture	Cement (kg)	Sand (kg)	Water (kg)	Hydrogen conc. (ppm)
CWM0	542	1490.5	262.87	0
HWM0.2	542	1490.5	262.87	0.2
HWM0.3	542	1490.5	262.87	0.3
HWM0.4	542	1490.5	262.87	0.4
HWM0.5	542	1490.5	262.87	0.5

formulation at 0.485 and 2.75, respectively. CWMs were produced using normal water, and HWMs were produced using HRW. The HRW concentrations were kept as 0.2, 0.3, 0.4, and 0.5 ppm. The hydrogen concentration in water was monitored using a hydrogen water needle sensor ENH-1000 provided by Japan. The redox potential and pH of the water was measured using pH-ORP digital meter provided by DKK- TOA., Japan. The mortars were labeled as follows: normal water (control) was CWM0, and the mortars fabricated from 0.2, 0.3, 0.4, and 0.5 ppm of concentrated HRW were HWM0.2, HWM0.3, HWM0.4, and HWM0.5, respectively. The formulation summary for the mortar mixes is in Table 1. Cement and sand were dry-mixed in the mixer with a rotating speed of 80 rpm for one minute. Then water (HRW for the HWM mortars) was added, and it was further mixed for one minute. The prepared mortars were cast into molds in three layers, with each layer tamped 32 times. For electrochemical tests reinforced CWM and HWMs cylindrical mortar samples of dimension (5 × 10 cm) were fabricated by centrally placed a 6-mm dia steel rebar. The specimens (plain as well as reinforced) were removed from the molds after 1 day and placed in normal water for curing at 23 ± 2 °C at 100% RH.

Testing methods

Initial and final setting times of cement pastes were determined using Vicat instrument conforming to ASTM C191 [6]. Compressive and tensile strength tests were performed on 50 mm side cubes and 70 mm side prismatic specimens, respectively. The compressive and splitting tensile strength of the mortar specimens were determined in accordance with ASTM C109 [7] and BS1881 [8], respectively, at 28 days. Test for determination of permeable voids in cubic specimens was performed after 28 days of curing on 50 in accordance with ASTM C642 [9].

The electrical resistivity (ER) test on specimens was performed after every week for 12 weeks using an ER measuring device with two electrodes. The reinforced samples were corroded to the same degree under exposure to 5% NaCl solution. For measuring corrosion current density, the resistance to polarization was determined using commercially available potentiostat. The reinforced bars were polarized to 10 mV at the rate of 3 mV. The corrosion potentials of reinforced CWM

and HWMs specimens were determined as a function of time using standard copper/ copper sulfate electrode (CSE) in accordance with ASTM C876. The corrosion potential of the specimen was determined after every week for 12 weeks. High impedance voltmeter was used for recording corrosion potentials of steel electrodes embedded in mortars.

For the FTIR and XRD analyses, the 28-day hydrated mortar samples (CWM0 and HWM0.5) taken from fractured mortar specimens after compressive strength testing were used. The samples were ground and treated with acetone to remove water and thereby mitigate the hydration reaction. FTIR was performed using a spectrometer (Nexus 870, Thermo Nicolet Corp., USA). Exactly 1 mg of sample was mixed with 100 mg KBr to make a pallet. The structural characteristics of the hydrated cement mortar samples were evaluated using an XRD diffractometer (Ultima III, Rigaku Inc., Japan) operated with a Cu-K α radiation (40 kV, 30 mA) element to record the XRD of the hydrated cement sample in the 2θ range of 10 to 50 degrees at a rate of 1 degree per min. To observe the morphology and the extent to which hydration products formed at the micro level, SEM analysis (backscattered mode) was performed 28-day hydrated samples (CWM0 and HWM0.5) using a field emission scanning electron microscope (Nova Nano SEM 450, Field Electron and Ion Co., USA). The samples were coated with platinum to prevent charging and analyzed at 15kv at 12kx magnification.

Results and Discussion

Setting time of cement paste in HRW

Results of initial and final setting time (IST and FST) of cement pastes are shown in Fig. 1. In this figure, with the increase in HRW concentration, reduction in IST and FST is observed. The initial and final setting time for fresh cement paste prepared from control were

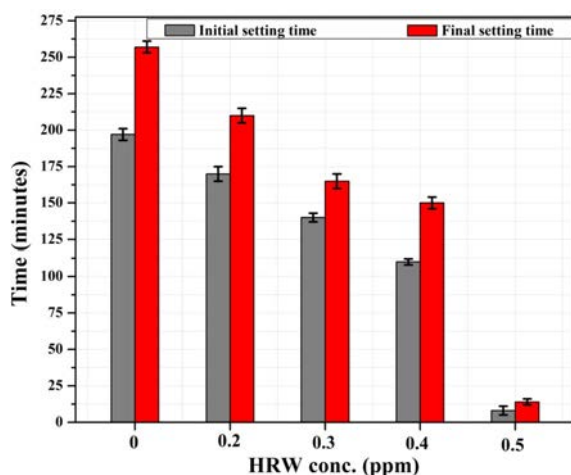


Fig. 1. Initial and final setting times of cement pastes with varying hydrogen-rich water concentration.

observed to be 197 ± 3 and 122 ± 2 minutes, respectively. Moreover, a gradual increase in HRW concentration reduced both the initial and final setting time. For cement paste prepared using 0.5 ppm HRW, the initial and final setting time is found to be 14 ± 2 and 8 ± 2 minutes, respectively. It is ascertained that HRW acts as a set accelerator which reduces the induction time by greater precipitation of cement hydrates at a faster rate.

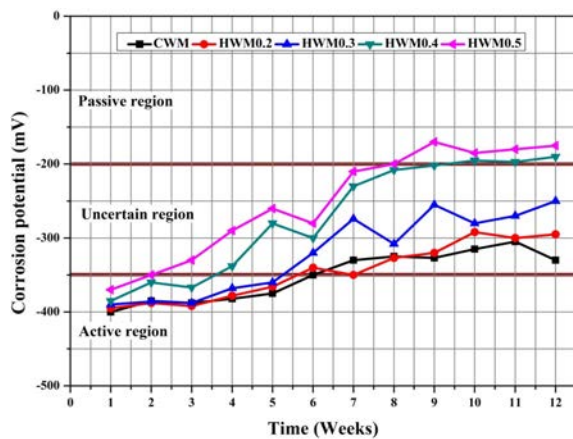
Mechanical and Physical properties

Table 2 presents the results of compressive strength, tensile strength, and permeable voids performed on hardened mortar specimens performed after 28 days of curing. In this table, it is observed that the compressive strength is observed to be increasing with the increase in HRW concentration. The percent increase in compressive strength for HWM0.2, HWM0.3, HWM0.4, and HWM0.5 with respect to CWM0 was found to be 8.45%, 12.21%, 15.42%, and 23.97%, respectively. Similarly, significant enhancement in tensile strength of HWMs is also observed compared to control. A percentage increase of 25% in tensile strength for HWM0.5 compared to CWM0 is observed. The results indicate enhanced mechanical properties for HWMs compared to CWM. The enhanced mechanical performance of HWMs compared to CWM is attributed to the formation of more cement hydrates in HRW environment. The HRW increases the pH of the normal water and makes it alkaline. It is stated elsewhere [10] that at a pH value below 8.5, calcium essentially exists as Ca^{+2} , whereas silica species are in their weakly ionized state. However, at an increased pH value, calcium and silicate species exist as hydroxylated species ($\text{Ca}(\text{OH})_2$) and silicate anions, respectively. Therefore, interstitial CSH forms through a combination of ($\text{Ca}(\text{OH})_2$) and silicate ions at the grain surface. During the hydration phase, the cement pore solution is rich in species such as Na^+ , Ca^+ , K^+ , SO_4^- , and OH^- . Aluminum, silicate, and iron are also present in the lower amount [11]. The increased concentration of OH^- ions that HRW brings to the pore solution results in increased dissolution of Ca^{+2} ions, causing rapid nucleation and growth of CH and CSH. Additionally, it is presumed that HRW produces more compact and dense microstructure with fewer permeable voids. Moreover, it is presumed better degree of hydration in HRW leads to formation of CSH gel pores

The permeable voids are an important property of concrete materials, as it governs the ingress of harmful ions into it which causes carbonation and deterioration of passive layer of reinforcement. Permeability induces corrosion mainly by the destruction of the alkaline environment by fall of pH. Once pH falls below 14 the corrosion initiates. The results for the content of permeable voids reveal that increase in HRW concentration reduced the permeable voids in mortars. This phenomenon is

Table 2. Compressive strength, tensile strength, and permeable voids of 28 days hydrated mortars.

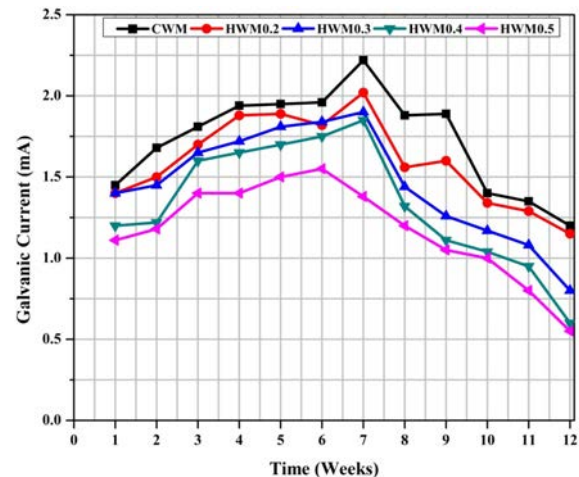
Property	Mixture ID				
	CWM0	HWM0.2	HWM0.3	HWM0.4	HWM0.5
Compressive strength (MPa)	30.28 ± 1.25	32.84 ± 1.11	33.98 ± 1.08	34.95 ± 1.20	37.54 ± 1.25
Tensile strength (MPa)	2 ± 0.25	2.2 ± 0.21	2.22 ± 0.15	2.23 ± 0.15	2.5 ± 0.15
Permeable voids (%)	16 ± 2.56	15.69 ± 2.69	13.58 ± 1.58	12.59 ± 1.39	12.01 ± 1.52

**Fig. 2.** Variation in corrosion potential of mortars with time.

because of formation of a greater amount of hydration products which fill in the gaps and permeable voids in cement sand matrix. Concrete with less permeable voids resists penetration of moisture into a concrete matrix which tends to depassivate reinforcement.

Corrosion potential

Corrosion potential is the most common corrosion index used in field and laboratory due to its easy application. Corrosion potential is a qualitative measure and there is no direct relationship between corrosion potential and current density. The corrosion tendency of steel bars in specimens was assessed by measuring corrosion potential change over time. The plot of corrosion potential versus time is shown in the Fig. 2. According to ASTM C-876 [12] probability of rebar corrosion in concrete would be greater than 90%, if its corrosion potential is less than -350 mV vs SCE. Initially, the corrosion potential for all specimens was near -400 mV. Thereafter, recovery started for all specimens towards less electronegative behavior. The corrosion potentials taken from rebars embedded in CWM0, HWM0.2, HWM0.3 were lower than -350 mV until 5 weeks, but after that remained between -350 and -200 mV till 12 weeks; a range referred to be as uncertain corrosion range according to ASTM C876 guidelines. In this corrosion potential range chloride ions may ingress into mortar system and can passivate the reinforcement bars. Similarly, corrosion potential for HWM0.4 and HWM0.5 was in uncertain corrosion range until week 7 but thereafter showed passive behavior as corrosion potential was measured to be

**Fig. 3.** Variation in the galvanic current of mortars with time.

higher than -200 mV till week 12. Therefore, it was ascertained that increase in HRW concentration lowered the electronegative corrosion potentials of mortars. Moreover, the less electronegative corrosion potential values for HWMs indicate the formation of the stable passive layer around rebar. The less negative potential for HWMs shows the less thermodynamic conditions for corrosion to occur in them. The results show electronegative potential was much lower in HWMs compared to CWM. Large reductions in electronegative potential were observed as the HRW concentration was increased. Corrosion potential is a qualitative measurement and provides an indication of the possibility of steel corrosion in specimens.

Galvanic current

The plot for galvanic corrosion versus time for all specimens is shown in Fig. 3. The galvanic current provides a much precise estimate of construction life. In this figure, greater anti-corrosive properties of HWMs are observed, which causes high corrosion resistance of reinforcing steel. The highest galvanic current is observed for CWM0. This anti-corrosion property of HWMs is attributed to dense and compact microstructure with fewer voids. It is presumed that HRW results in precipitation of greater amount of cement hydrates i.e $\text{Ca}(\text{OH})_2$ and CSH. The maximum galvanic current recorded for HWM0.5 was 1.54 mA compared to 2.22 mA of CWM0. At the end of the experimental duration, the galvanic current observed in HWM0.5 was observed to be 0.55 mA compared

to 1.2 mA of CWM0. The decrease in current density may be ascribed to the formation of the thick and anodic film in the presence of more calcium hydroxide. The increased precipitation of cement hydrates is the main reason of decreased corrosion potential of HWMs. Cement hydrates such as calcium hydroxide help to maintain an alkaline condition in a mortar, which in turns leads to passive condition for reinforcing bars.

Electrical resistivity (ER)

The ER results of all mortar mixtures are shown in Fig. 4. In this figure, a significant increase in ER is noticed with age for all mixtures. Initially, at the end of week 1, the ER values of all mortars are near 7 k Ω -cm but, thereafter an improvement in ER is observed till the end of 12 weeks for all specimens. According to ACI 222 [13], corrosion is less likely to take place when ER is equal to or greater than 10 k Ω -cm. The ER for CWM and HWM0.2 remained in the range at the high risk of corrosion until 7 weeks. The ER values for HWM0.3 entered the safe region after week 4. Whereas, the ER values for HWM0.4, and HWM0.5 were found to be in the range corresponding to low risk of corrosion after the second week. It is ascertained that the increase in HRW concentration enabled mortars to develop a denser and more compact microstructure, which reduced the interconnectivity between pores and thus resulted in higher ER. That is, the denser microstructure, less-continuous pore system, and reduced porosity allowed the HWMs to demonstrate higher ER. ER is an important parameter that governs the corrosion of reinforcement in concrete. It is presumed that alkaline environment in the pore solution HWMs would provide an appropriate environment for the steel bars embedded, so that they can passivate and remain passivated against corrosion. The increased alkalinity leads to a denser pore structure, which apparently is outweighing the increased ionic concentration in pore water. The increased ER of concrete was also observed

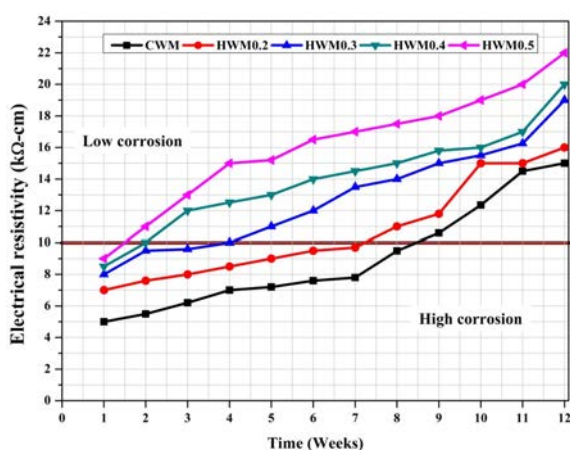


Fig. 4. Variation in electrical resistivity of mortars with time.

by Pruckener et al. [14] in the alkaline environment provided by NaOH.

FTIR, XRD, and SEM investigation

FTIR spectra, XRD patterns, and SEM images of 28-days hydrated CWM0 and HWM0.5 samples are shown in Fig. 5. The FTIR, XRD, and SEM analysis were performed to compare the extent of formation of hydration products especially calcium hydroxide in both the samples. Fig. 5(a) shows that the XRD patterns of both the HWM0.5 and CWM0 mortar samples mostly contain peaks at the same positions but with different intensities. The more intense peaks at 2θ values of 18.09° , 34.09° , 47.12° , and 50.77° in the XRD pattern of HRW0.5 indicate the greater formation of calcium hydroxide [15,16]. The formation of calcium hydroxide at larger scale helps to maintain the alkaline environment in the mortar matrix, which in turns lead to protect the passive layer of ferrous or ferric oxide formed around rebar.

In the Fig. 5 (b), the FTIR spectrum of HWM0.5, the reinforced band at 3638 cm^{-1} due to O-H of $\text{Ca}(\text{OH})_2$ indicates the formation of a greater amount of hydration product in HWM0.5 [17]. The same band appears with lower intensity in the FTIR spectrum of CWM0. Hence, based on FTIR, XRD, and SEM analysis, it is revealed that formation of cement hydrates especially calcium hydroxide in HWM0.5 helps to maintain an alkaline environment in a cement matrix. The presence of $\text{Ca}(\text{OH})_2$ helps to maintain an alkaline environment in cement pore solution. The alkaline environment leads to increased pH of pore solution and causes passive protection for reinforced steel cars. Moreover, the formation of hydration products at larger scale produces more compact and dense microstructure. Figs. 5(c and d) show the SEM images of 28-day hydrated samples of CWM0 and

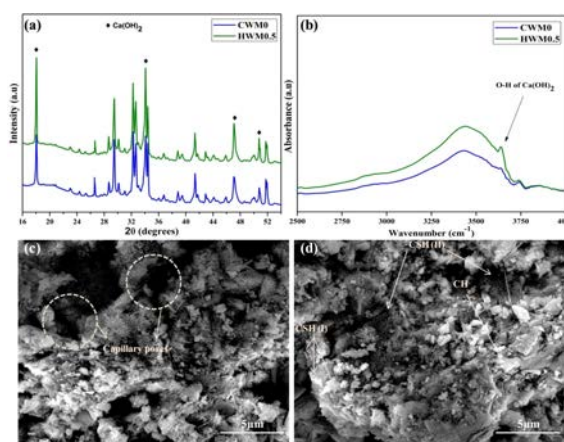


Fig. 5. (a) XRD patterns of un-exposed CWM0 and HWM0.5 mortars cured for 28 days (in the 2θ range of 16° – 52°), (b) FTIR transmission spectra of un-exposed CWM0 and HWM0.5 mortars cured for 28 days and (c) SEM image of CWM0 cured for 28 days (d) SEM image of HWM0.5 cured for 28 days.

HWM0.5, respectively. From the SEM micrographs, it is revealed that HRW promotes the degree of hydration by forming a greater amount of cement hydrates, which help to maintain the alkaline environment, which helps to passivate the rebar. Moreover, the formation of a greater amount of hydrates cause pore filling effect, resulting in the development of compact and dense microstructure which inhibit the ingress of harmful ions (Cl^- and CO_3^{2-}) in HWM0.5. The SEM image of CWM0 is characterized by lower extent of hydrated products with intermittent voids.

Inhibiting mechanism of HRW

The corrosion of rebar in concrete is an electrochemical process, which involves the chemical reactions taking place at electrodes and flow of current. The actual loss of metal takes place at anode where iron atoms (Fe) are ionized to ferrous ions (Fe^{+2}), which dissolve in the water around the steel. These electrons are deposited on the steel surface and raise its electrical potential. The electron then flows to the area of lower potential (i.e. cathode) and combines with O_2 and water to produce OH^- . Apart from corrosion current flowing from anode to cathode, there is also movement taking place through concrete pore solution. The external current involves the movement of OH^- ions from the cathode to anode and Fe^{+2} from the anode to cathode. If concrete is dense enough with less permeable voids, then it would lead to a halt in the flow of corrosion current.

The Fe^{2+} and OH^- moving towards each other react to form $\text{Fe}(\text{OH})_2$, this can further react with oxygen and OH^- to form rust. There are primary two types of rust are red rust (Fe_2O_3) and black rust (Fe_3O_4). These reaction products may not essentially deposit on the anode. Steel can react with oxygen to form a thin protective layer as thick as 10 nm. As far as passive layer remains intact the steel is considered not-corroding. The steel can form passive layer if aqueous solution surrounding is rich in OH^- ions. However, the carbonation of concrete and ingress of Cl^- may lead to depletion of OH^- ions. The passive layer formed over steel is ferrous and ferric in nature. However, ferric oxide is more stable, especially in Cl^- environment. The ferric oxide is referred to be $\gamma\text{-FeOOH}$. The reaction taking place at anodes and cathodes are as under

Anodic Reactions

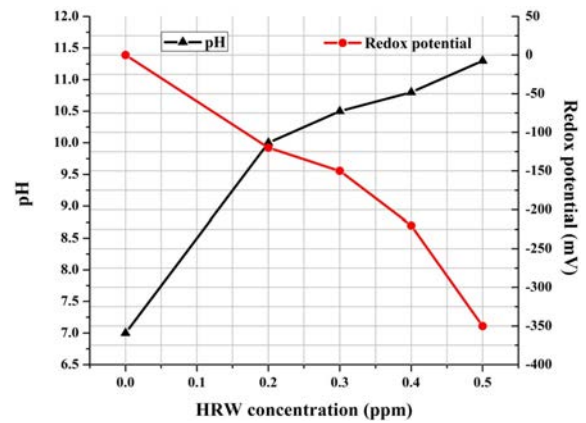
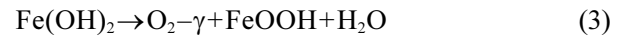


Fig. 6. Variation in pH and Redox potential of hydrogen-rich water.

(rust)



(passive layer)

Cathodic reactions



Neither ferrous nor ferric oxide layer would remain passivated if pH is below 11.5 in pore solution. It is presumed that the alkaline environment in HRW environment leads to protection of passive layer around reinforcement bars. Formation of calcium hydroxide to a greater extent in the case of HRW leads to maintain pore solution alkaline. One another explanation of increased inhibiting properties of HWMs is the low-redox-potential value of HRW. In a low redox potential solution the Fe^{+2} act as strong reducing agent and reduce oxygen to form Fe^{+3} . It is known that inhibition is either associated with thickening of the oxide film at high pH or formation of particulate deposits of the ferric oxide. The above state phenomenon was also observed when an iron bar was placed in 0.1 M NaOH solution having pH and ORP of 12.5 and -350 mV, respectively [18]. The figure shows the variation in redox potential and pH of HRW of various concentrations. pH and ORP for 0.5 ppm HRW was found to be 11.4 and -350 mV, respectively. It is observed from the figure as the pH of HRW increases, its ORP decreases. One another explanation for the inhibiting effect of HRW can be due to the presence of $\text{Mg}(\text{OH})_2$. It is stated elsewhere [3] that $\text{Mg}(\text{OH})_2$ can deposit on cathodic site and thus can retard the cathodic reaction from taking place. It is presumed that $\text{Mg}(\text{OH})_2$ in HRW acts as a cathodic inhibitor, which blocks the cathodic sites, which leads to retard the

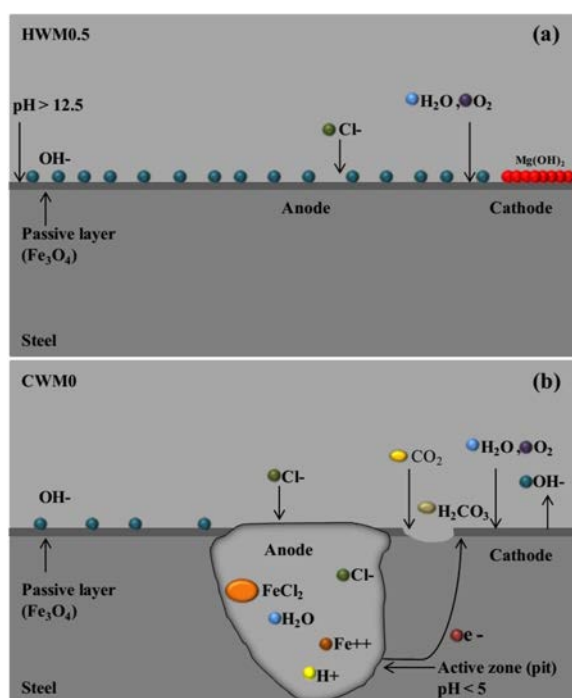


Fig. 7. (a) Model showing protection of steel embedded in HWM0.5 and (b) Model showing corrosion and pitting of steel embedded in CWM0.

cathodic reaction.

A plausible model in favor of inhibiting the effect of HRW is shown in Fig. 7. It is seen that alkaline environment tends to protect the reinforcement from depassivation in HWM. In addition, the ingress of Cl^- and CO_3^{2-} is prevented due to compact and dense microstructure. Additionally, deposition of $Mg(OH)_2$ blocks the cathodic reaction from taking place at the cathode. Whereas, in control concrete ingress of harmful ions tend to deteriorate the passive layer, which in turns lead to the formation of pits (due to Cl^- ion) and removal of steel section altogether (carbonation). In the light of above discussion, it could be deduced that HRW controls the inhibition of steel in cement mortars. It is believed that HRW is a novel addition to the family of chemical admixtures which not only accelerates the setting process of cement but also serves to protect the steel reinforcements from being corroded. For the depassivation of steel, only the free chlorides of pore solution are of directly relevant. Chlorides ions penetrating into concrete can be bound physically or chemically in the pore system of concrete. Thus, only a fraction of the total (acid-soluble) chloride content is free. A number of bound chlorides (related to the mass of concrete) depend on the chloride content, the cement type and content, the porosity and pore size distribution, and the pH of the pore solution. The hydroxide concentration (i.e., the pH of the pore solution) has a significant effect on chloride binding because the hydroxides compete with chloride ions for the binding sites.

Conclusions

1) The initial and final setting time of cement paste reduce significantly in HRW. Thus, HRW can be used as a substitute for calcium chloride for accelerating the hydration rate of cement, which causes chloride-induced corrosion in reinforced structures.

2) The enhanced mechanical performance of HRW specimens with fewer permeable voids is an indication of development dense microstructure, which reduces ingress of harmful species into cement matrix. The HRW promotes the precipitation of greater amount of cement hydrates.

3) The increase galvanic current resistance and lower corrosion potential is obtained for HRW based mortars compared to control water mortars, indicate anti-corrosive properties. This was attributed to the formation of more cement hydrates with fewer voids. The HWMs demonstrated higher ER values than CWM on account of refined pores structure and dense microstructure

4) FTIR, XRD, and SEM analysis revealed the formation of greater amount calcium hydroxide, which serves to maintain alkalinity in a cement matrix, which in turns lead to protect the reinforcement by forming a passive layer.

5) Lower ORP value and higher pH (alkaline environment) in HRW protect the passive layer around the rebar hydrogen-rich water mortars.

References

1. M.A. Baccay, N. Otsuki, T. Nishida, S. Maruyama, Corrosion. 62[9] (2006) 811-821.
2. A. Aguirre, R. Mejía de Gutiérrez, Materiales de Construcción 63[309] (2013) 7-38.
3. C.G. Dariva, A.F. Galio. Develop. Corr. Prot. InTech (2014).
4. M. Babaei, A. Castel, Cem. Concr. Res. 88 (2016) 96-107.
5. B.W. Jo, S. Chakraborty, M.A. Sikandar, H. Kim, K.H. Kim, Constr. Build. Mater. 100 (2015) 31-39.
6. ASTM C191. Standard method for normal consistency and setting of hydraulic cement.
7. ASTM C109. Standard test method for compressive strength of hydraulic cement mortars (using 2-in. or 50-mm] cube specimens).
8. BS 1881-1883. Testing concrete-part 120: Method for determination of the compressive strength of concrete cores.
9. ASTM C 642. Standard test method for density, absorption, and voids in hardened concrete.
10. A. Ramachandran, M.W. Grutzeck, J. Amer. Ceram. Soc. 76[1] (1993) 72-80.
11. C.L. Page, M.M. Page. Durability of concrete and cement composites (Elsevier, 2007).
12. ASTM C 876-2009. Standard test method for corrosion potentials of uncoated reinforcing steel in concrete [S].
13. Committee A, editor Guide for the design and construction of concrete reinforced with FRP bars2001: American Concrete Institute.
14. F. Pruckner F, O. Gjörv, Cem. Concr. Res. 34[7] (2004), 1209-17.

15. P. E. Stutzman .Guide for X-ray powder diffraction analysis of Portland cement and clinker: US Department of Commerce, Technology Administration. 1996.
16. F. Kontoleontos, P. Tsakiridis, A. Marinos, N. Katsiotis, V. Kaloidas, M. Katsioti, Mater. Res. 16[2] (2013) 404-16.
17. M.A. Trezza, Mater. Res. 10[4] (2007) 331-4.
18. J. Mayne, S. Turgoose, Brit. Corr. J. 10[1] (1975) 44-6.