
RESEARCH NOTE

CORROSION OF CONCRETE IN SEA WATER

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Abstract Attack and disintegration of concrete structures under the influence of aggressive fluids, wet gases, etc. are understood as corrosion of concrete. The corrosion of concrete is a chemical, colloid-chemical process, yet often a physico-chemical one, while that of reinforced concrete is mainly electrochemical. Many sea harbor jetties, docking facilities and concrete supported oil platforms are subjected to marine environment in the Persian Gulf and therefore corroded. In the present study we have tried to investigate the time required for corrosive agents such as chloride and oxygen to penetrate through the concrete using an aerated synthetic sea water representative of Persian Gulf environment. The influence of the concrete's cover depth on corrosion rate of the rebar has also been studied.

Key Words Concrete, Reinforcement, Concrete Cover, Sea Water, Corrosion

چکیده آسیب دیدگی و تجزیه ساختارهای بتنی تحت تأثیر سیالات خورنده، گازهای مرطوب و غیره بعنوان خوردگی بتن شناخته شده است. خوردگی بتن یک فرایند شیمیایی و گاهی فیزیکی - شیمیایی است. در حالی که فرایند خوردگی بتن مسلح، صرفاً الکتروشیمیایی است. بسیاری از اسکله های دریایی، تسهیلات بارانداز و سکوهای نفتی در خلیج فارس که با بتن ساخته شده اند در معرض محیط دریایی قرار گرفته و در نتیجه خورده می شوند. در این مقاله سعی بر این است که با استفاده از آب دریای مصنوعی جایگزین محیط خلیج فارس، زمان مورد نیاز برای نفوذ یونهای خورنده همانند کلر و اکسیژن به درون بتن اندازه گیری شود. همچنین تأثیر ضخامت پوشش بتنی در سرعت خوردگی آرماتور نیز مورد مطالعه قرار گرفته است.

INTRODUCTION

In recent year the performance of concrete in marine environments has received considerable attention because of the offshore activity for gas and oil explorations in various countries and have been investigated by several researchers [1,2,3].

The interaction between the concrete service environment and the concrete itself can lead to the deterioration of reinforced concrete structures and in some cases can render the structures unsuitable for its designed purpose. The interaction is often with the

chemical species in the environment [4].

For concrete in a marine environment, there appear to be a direct correlation between low permeability, high strength and good durability. Therefore, concrete sea structures such as harbor structures and offshore platforms are built using high quality concrete [5]. In general, concrete is a finely porous material, pore sizes varying from a few angstroms to several millimeters. This pore system is more or less filled with a solution which contains varying quantities of different salts.

The problems associated with the application of

reinforced concrete in marine environment are well known. These problems have led to extensive research on corrosion of metal in concrete structure.

Reinforcement is usually protected from corrosion by the highly alkaline environment (pH about 11.5) of the concrete surrounding it. As a result, the steel surface frequently receives a very dense oxide layer which is difficult to dissolve, hence limits further disintegration [7,8,1]. This normally happens either by the carbonation of the concrete around the steel which reduces the alkalinity or the presence of even small quantities of chlorides in the concrete around the steel.

The depth of penetration of chloride is a function of time and the permeability of moisture and oxygen near the steel surface [10,11]. In the absence of either of these, corrosion will not occur.

The corrosion of steel causes the metal to be converted at different stages to various ferric oxides and ferric hydroxides [12]. This change leads to an increase in volume. Damage resulting from corrosion can also be seen in the form of cracks parallel to embedded steel which finally causes cracking and spalling of the concrete which, in turn, accelerates the rate of corrosion.

The corrosion of reinforcing steel in concrete results from an electrochemical process [13] accompanied by anodic and cathodic reaction. Iron is transferred in the solution as hydrated ions with two electrons left in the reinforcing steel. These two electrons are transferred to the cathodic area to assimilate in the cathodic reaction.

EXPERIMENT

The experiments performed were designed with two purposes: the first was to study the time that corrosive agent takes to penetrate through the concrete cover to the reinforcing steel and the second purpose was to investigate the influence of the depth of cover for a

embedded symmetrically. The steel bar embedded 50mm into the mortar and to avoid the formation of different aeration cells, the end of the embedded bars were insulated with an adhesive tape. The portland

TABLE 1. Chemical Composition of Artificial Sea Water Used.

NaCl	MgCl ₂ · 6H ₂ O	MgSO ₄ · 7H ₂ O	CaSO ₄ · 2H ₂ O	KHCO ₃
32 g/l	6 g/l	5 g/l	1.5 g/l	0.2 g/l

fixed water-cement ratio.

The tests were performed on mortar specimen partially submerged in an erated sea water the composition of which is given in Table 1. The mortar specimens were made with ordinary portland cement and had water-cement ratio of 0.4, 0.5, 0.6, 0.7 with the cement-sand ratio of 1:3.

The aggregate used were crushed stone and used in a saturated surface dry condition when mixed in concrete and the sand was the ordinary local river sand. The specimens made were 20×55×80 mm with two round carbon steel bars of 7mm diameter

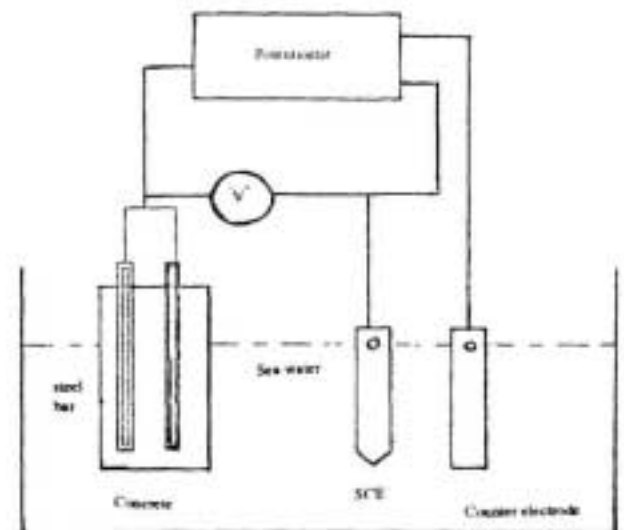


Figure 1. Schematic illustration of polarization measurements.

cement was cured at 20°C for 28 days. Since the procedure of this test required a constant current density (mA/mm²) over the reinforcement surface, the specimens were exposed to distilled water in the tank for several days to obtain a uniformity of moisture in concrete before the impressed current was applied. Direct current was impressed on the specimen from a DC rectifier of a constant voltage and a potentiometer was used to control the current applied to each specimen. Current direction was so arranged that the reinforcing steel bars served as anode and a stainless steel rod was employed as counter electrode served as cathode (Figure 1). The potential of each specimen was measured daily using a saturated calomel electrode with a voltmeter twice a day and any drift was corrected by adjustment of the potentiometer. Potential readings were taken with the power on, which represented the polarization potential of the reinforcement plus the voltage drop across any corrosion product film at the reinforcement-cement interface.

In order to study the effect of different cover depths on the corrosion rate of reinforcing steel, specimens of 200×300×125mm slab were made from Portland cement at water cement ratio of 0.5. Each specimen contained 2 carbon steel electrode rods of 3mm diameter embedded at four depths of cover i.e. 10, 20, 30 and 40 mm.

The electrochemical corrosion measurements of the embedded steel reinforcement were carried out by means of polarization resistance measurement and the rest potential. The corrosion rates were calculated from polarization resistance value using Stern-Geary equation i.e.:

$$I_{\text{corr}} = I_{\text{appl}} / 2.3 \Delta E (\beta_c \beta_a / (\beta_c + \beta_a))$$

I_{corr} has been calculated on the assumption that both the anodic and cathodic Tafel constants β_a and β_c had values of 120 mV/decade.

RESULTS AND DISCUSSION

The corrosion of concrete reinforcement in an aerated sea water is expressed in terms of potential and current in the embedded rebar as a function of exposure time. Temperature and oxygen content of the sea water have been checked regularly. The temperature has been varied from 20°C to 25°C, depending on the time of the year, while oxygen content has been kept about 7ppm at all times. The electrochemical potential is measured via a high impedance millivoltmeter against a calomel electrode.

Figure 2 shows a typical half-cell potential vs. time behavior of embedded steel reinforcement in an aerated sea water. It shows that the time required for the reinforcing steel to be in the active potential is about 3.5 weeks for water-cement ratio of 0.7 and increases to about 13 weeks for water-cement ratio of 0.4. In other words the time for corrosion agent to reach the embedded steel is the time the steel reinforcement changes from passive potential to an active potential which occurs when there are sufficient chloride ion and oxygen present to cause corrosion of the steel bar. Therefore, one can assume

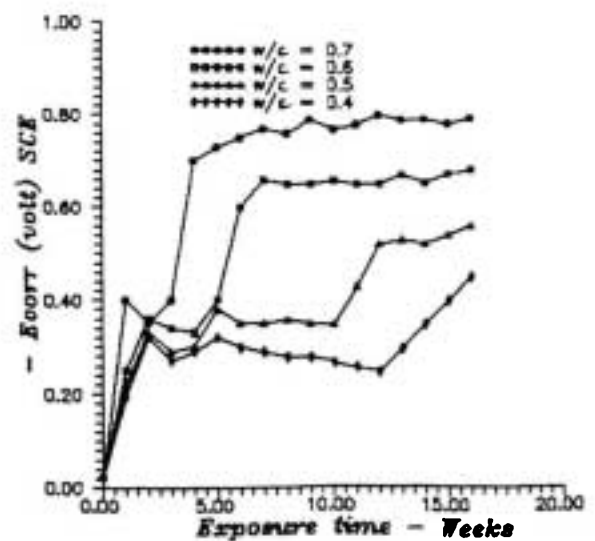


Figure 2. Corrosion potential vs. Exposure time.

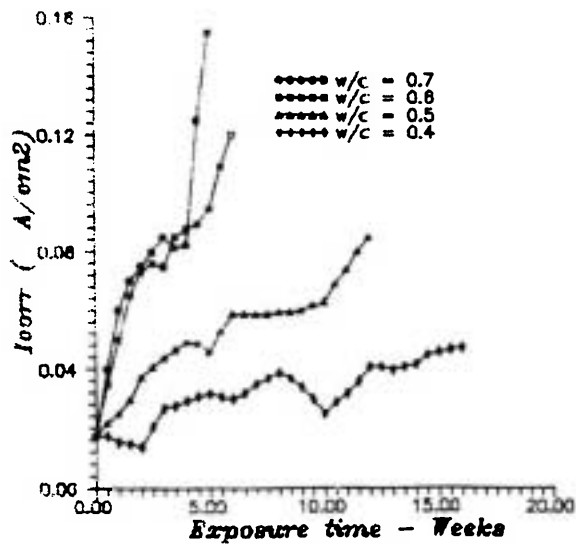


Figure 3 Corrosion current density (I_{cor}) vs. exposure time

that a high water-cement ratio makes the concrete permeable enough for the corrosive agent to penetrate the reinforcing steel and then to make it depassivated. Thus as the water-cement ratio increased the potential of the reinforcing steel bar became less noble.

In general, decrease in the observed corrosion current was found with decreasing the water-cement ratio (Figure 3). In order to accelerate the corrosion

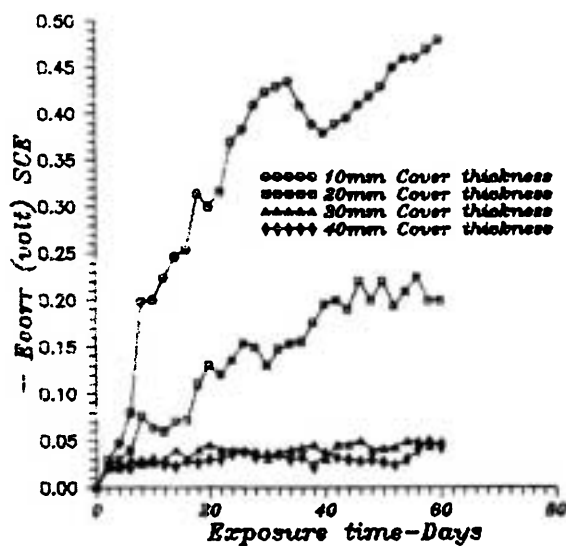


Figure 4 Corrosion potential vs. exposure time.

process, a constant electrical potential of 3.5 volt was impressed into the embedded steel bar.

Concrete cracking due to the corrosion of the reinforcement was observed after 14 weeks for water-cement ratio of 0.4 and 10.5 weeks for $W/C = 0.5$, 4.5 weeks for $W/C = 0.6$ and 4 weeks for $W/C = 0.7$. Therefore, the sharp rise in current in Figure 3 is related to the time when the appearance of the cracks were observed. However the failure of the concrete specimen due to the corrosion of steel reinforcement is related to the initial current of the steel bar, and as can be seen the initial current of the steel bar depends upon the water-cement ratio of the concrete. Therefore, for the reinforced steel embedded in the concrete with lower water-cement ratio, the initial current was lower and it took a longer time for the corrosive agent to reach the steel reinforcement and cause corrosion failure. The results of the measurement of the distribution of corrosion potential and corrosion current density of the reinforcing steel after 70 days of exposure for different cover thicknesses are shown in Figures 4 and 5.

In the case of cover thickness of 10mm, the degree of corrosion was large and the specimen had a crack

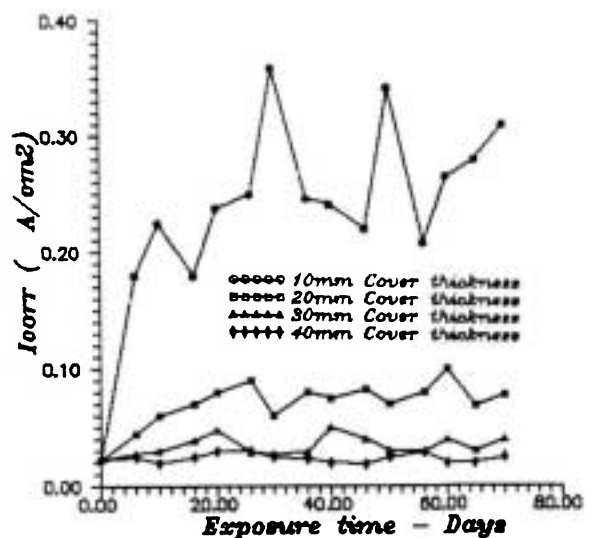


Figure 5 Corrosion current density vs. exposure time.

of about 0.2 mm produced due to the corrosion of the reinforcing steel and the corrosion of the steel rebar at the location of the crack was particularly remarkable. On the other hand, with increasing the cover thickness to 40mm a very little corrosion of the reinforcing steel bar was observed.

Visual examination of the reinforcement bar after 70 days revealed a white deposit on the surface and the amount of the deposit varied with the depth of the cover thickness. On microscopic examination, the deposit appeared crystalline in structure and was very dense in nature (Figure 6).

Chemical analysis of the deposit showed that it consists of a mixture of calcium carbonate and magnesium hydroxide. Since sea water contains a lot of magnesium sulfate which is the most harmful salt as far as attacking the cement is concerned, it reacts with calcium hydroxide and by substitution of magnesium for calcium secondary gypsum in flat prisms and brucite $Mg(OH)_2$ in superimposed platelets are formed (Figure 7).

CONCLUSION

Since sea water contains a lot of chloride in various forms and sulfate salts, the initial period of the attack is the time taken for chloride and sulfate ions to penetrate from the surface through the concrete cover and reach the reinforcement steel bar. During this period, the steel is in the passive state until the threshold value of these aggressive ions is reached for corrosion to initiate in the presence of oxygen.

A possible form of corrosion attack on the reinforcement in the initial stage was pitting corrosion. However, there is a good reason to assume that the number of pits is fairly high as in case of 10 mm cover thickness and since the amount of available cathodic current is constant, regardless of the number of pits, the average anodic current will be small. Therefore, the most important consequence of pitting

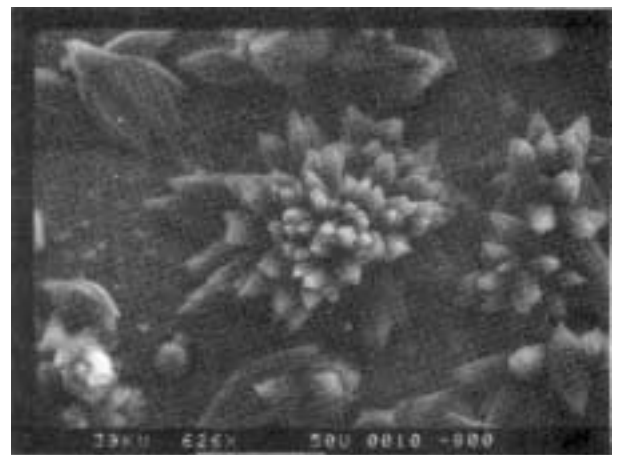
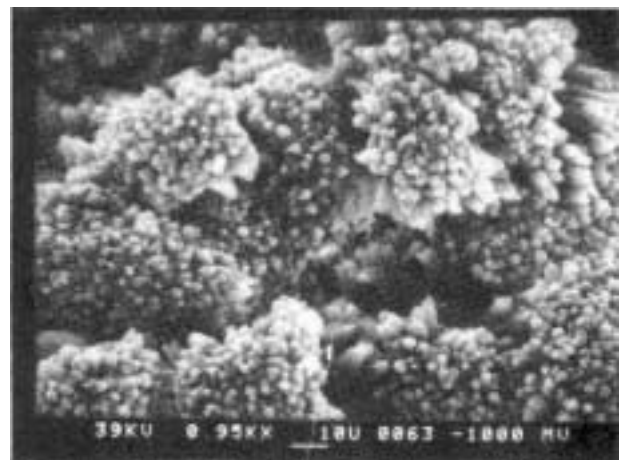
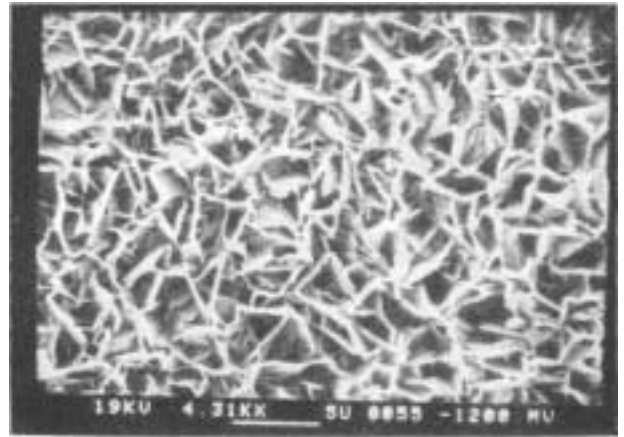


Figure 6. Morphology of calcareous deposits after seventy days of exposure to sea water, (a) Crystallization of brucite layer, (b) Aragonite deposit on brucite layer, (c) Magnified aragonite.



Figure 7. The dissolution of calcium hydroxide and formation of secondary gypsum.

is that oxygen is consumed, the steel potential drifts to a negative value and corrosion takes place. Hence the availability of oxygen is one of the main controlling factors of the corrosion of steel rebar in the concrete. The amount of corrosion discovered when the reinforcement was removed was insignificant as the depth of cement cover increased and small spots of corrosion products were in a few instances visible at the surface.

A high water-cement ratio makes concrete permeable enough for the aggressive ions to penetrate the reinforcing steel easily and therefore makes the reinforcement depassivated. Thus, as the water-cement ratio of the concrete increases, the potential of the reinforcing steel becomes less noble and the electrical resistance of wet concrete becomes lower due to high permeability which accelerates the corrosion of reinforcing steel.

NOMENCLATURE

I_{cor} Corrosion current density
 I_{app} Applied current density

ΔE Potential difference
 β_a, β_c Tafel slopes of anodic and cathodic reactions respectively

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