



The Effect of Caspian Sea Water on Corrosion Resistance and Compressive Strength of Reinforced Concrete Containing Different SiO₂ Pozzolan

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Many parameters are influenced by the diffusion of chloride on concrete in marine environments and these can affect concrete quality. In this study, the effect of water to cement ratio of 0.35, 0.40 and 0.45 on corrosion resistance and compressive strength of reinforced concrete was evaluated. Moreover, different percentages of micro silica (SiO₂) including 5, 7.5 and 10% were utilized, in order to investigate the effect of pozzolanic materials on the corrosion of steel in concrete. Then cubic samples reinforced with steel bar spacing of 2.5, 5 and 7 cm from the cube surface were made and put in Caspian sea water for 5 months. During this period, corrosion potential of steel was measured by a calomel half cell (SCE). In order to finalize the evaluation of the mechanical strength of the samples, concrete pressure test was conducted and the result showed that after 40, 44 and 59 days for the bars with depth of 2.5, 5 and 7 cm, respectively and the samples prepared with water-cement ratio of 0.35, the corrosion potential was -350V versus SCE, while the compressive strength was approximately 450 kg/cm². This result showed longer life span of this sample in comparison with other water-cement ratios. By adding micro silica to the samples up to 7.5%, the time for obtaining a corrosion potential of -350V, bars with depth of 2.5, 5 and 7 cm, was 43, 50 and 86 days, respectively, and the compressive strength of this sample was approximately 480 kg/cm². Consequently, it is arguable that in order to achieve longer life span of corrosion and suitable compressive strength, the optimum ratio of water to cement should be 0.35 and the percentage of pozzolan SiO₂ should be 7.5%.

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1. INTRODUCTION

Concrete is one of the strongest and cheapest building materials [1] that possesses low tensile strength [2, 3]. When concrete is combined with steel bar, it forms reinforced concrete structures, further enhancing the mechanical properties [4, 5]. The composites have better properties than base materials [6-8]. Many researches have worked on the methods for increasing the strength of concrete, among which is the addition of pozollanas to concrete such as fly ash, ground granulated blast furnace slag, silica fume, metakaolin, rice husk ash, granite slurry waste, etc [9]. However, irrespective of several advantages, it is not resistant against corrosive chemical agents; hence it gradually

corrodes and fails [10-14]. Corrosion phenomenon, by definition, is a chemical or electrochemical reaction between a material, usually metal and its surroundings [15, 16], which ultimately changes the material properties due to the chemical reaction and this chemical reaction is generally destructive in nature. Acids and salts [10, 17, 18] (including chlorides [19], sulfate [20-22] and nitrates [23]) and gas (such as oxygen [24] and carbon dioxide [25]) are the main causes of corrosion in concrete [26-28]. Most significantly on a beach that is moist and full of minerals, concrete corrosion is so severe that inner bars are also destroyed [29]. Therefore, life of concrete structures is much shorter in coastal areas than anywhere else [30].

Temperature and high humidity are the most important aspects of a corrosive environment [31]. The

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examining of concrete is noteworthy in marine environments considering that both factors mentioned above present [18]. For many reasons, the effect of sea water on concrete is remarkable; firstly, coastal and offshore structures are exposed to physical and chemical damage simultaneously [24], and secondly, oceans cover 80% of earth's surface, therefore a lot of structures are directly or indirectly exposed to sea [32]. Concrete piers, breakwaters' decks and retaining walls are widely used in the construction of harbors and docks. Therefore, it is pertinent to study the issues pertaining to durability of reinforced concrete structures.

When designing concrete structures in the marine environment, it is necessary to take into consideration, destructive factors that affect the concrete over the years [33]. The vulnerability of a concrete structure by a beach is highly dependent on the location of the concrete with respect to sea level. Therefore, a structure placed along a beach could be grouped into five categories namely; atmosphere, splash, tidal, immersion and mud areas [34]. The atmosphere area is the part of the structure that is out of the sea and under the influence of the surrounding area. The splash and tidal area are due to the rise and fall of sea water and the collision of waves with the structure. Finally, the mud zone is the part of structure located in the sand and soil [35]. This study deals with major factors resulting in the destruction of concrete structures before their minimum expected lifespan in Caspian sea water.

TABLE 1. Samples of concrete reinforced with bar in different ratios of water to concrete and different percentages of micro silica (sample codes are C_{ij} and S_{mj} where i, j and m indicate the codes assigned to water-cement ratio, steel bar distance from concrete surface and micro silica percentage, respectively)

Sample code	C ₂			C ₃			C ₄			S ₁			S ₂			S ₃		
	C ₂₁	C ₂₂	C ₂₃	C ₃₁	C ₃₂	C ₃₃	C ₄₁	C ₄₂	C ₄₃	S ₁₁	S ₁₂	S ₁₃	S ₂₁	S ₂₂	S ₂₃	S ₃₁	S ₃₂	S ₃₃
Space of steel bar from concrete surface (cm)	2.5	5	7.5	2.5	5	7.5	2.5	5	7.5	2.5	5	7.5	2.5	5	7.5	2.5	5	7.5
Water-cement ratio	0.35			0.4			0.45			0.4			0.4			0.4		
Micro silica (%)	-			-			-			5			7.5			10		

In order to reduce environmental problems, such as rocks and seaside, the specimens were placed in a large polymer container, allowing draining and replacing the fresh water. Conditions for installations were in such a way that first, the samples were transferred to the research center, thereafter the reinforced concrete samples were put into a large container filled with water from the Caspian sea by chemical analysis as shown in Table 2 such that three-quarters of their height were submerged in the water (Figure 2) and the water was evacuated and replaced with new water every 24 h.

Finally, after 150 days, samples were removed from sea water and underwent pressure test by a device with maximum capacity of 30000 kN.

2. RESEARCH METHODOLOGY

In this study, 18 samples of concrete reinforced with steel bars (10 mm diameter and 24 cm length) were prepared as shown in Table 1. The grade of cementitious materials in whole mix design was considered consistent and equal to 400 kg/m³.

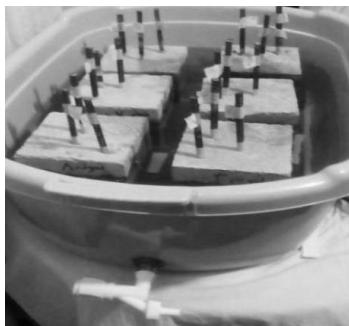
Thereafter, concrete cube blocks of 15×15×15 cm were built in order to investigate the corrosion potential of samples in immersed exposure conditions in the Caspian sea as shown in Figure 1. Also in the mix design of blocks, the super plasticizer based on poly carboxylate is used. Processing time was 3 days at ambient conditions of Mazandaran region and the thickness of the concrete coating on the reinforcements from the sample surfaces was 2.5, 5 and 7 cm, respectively. Different thicknesses of concrete were chosen due to the impact of concrete coating on the start of corrosion and for comparison. Finally, the test blocks were submerged in water in the Caspian sea to examine corrosion over time. In order to undertake an evaluation of the corrosion stages of bars, corrosion potential method [36-38] was used, and corrosion potential of each bar was read every 12 h for 150 days by a saturated calomel half-cell.



Figure 1. Reinforced concrete during molding and the location of steel bars

TABLE 2. Compounds of Caspian sea in mg/L

Element	K ⁺	Ca ⁺⁺	Mg ⁺⁺	SO ₄ ²⁻	Na ⁺	Cr
Content (mg/L)	180	205	619	1875	5002	6208

**Figure 2.** The reinforced concrete samples semi-submerged in the Caspian sea water

The image of the compression testing machine during testing of the samples under test is shown in Figure 3.

ASTM C876 standard [39] has specified the starting of corrosion activities as probability according to Table 3. Hence, this study shows that with the help of examining the corrosion potential, the probable percentage of bar corrosion inside the concrete could be predicted. It is obvious that this test only offers the potential difference which is called the corrosion potential and never displays corrosion rate or corrosion magnificence of bar.

**Figure 3.** Measuring device of concrete compressive strength during testing of samples after 150 days of exposure to Caspian sea water**TABLE 3.** The range of the corrosion potential in order to predict the probability of starting corrosion activity according to ASTM C876 standard [39]

Corrosion initiation probability	Electrochemical potential vs SCE
More than 90%	> 350 V
About 50%	> 200V and 350 V>
Lower than 10%	200 V >

ANOVA and Dunken's Post Hoc tests were used to compare the means of the data compression of samples at 5% significance level. Statistical analyses were performed using SPSS software.

3. RESULTS AND DISCUSSION

3. 1. Corrosion Potential Test Results

Diagram of electrochemical potential versus saturated calomel electrode for bars spaced at 2.5, 5, and 7.5 cm, and water-cement ratios of 0.35, 0.4, and 0.45%, and micro-silica percentages of 5, 7.5, and 10% are illustrated in Figure 4. It is clearly illustrated that in graphs with different concrete coatings, the least amount of corrosion potential difference in negative direction versus saturated calomel electrode (SCE), belongs to bars with the highest concrete coatings (7.5 cm). This shows that although the thickness of the concrete coating increases the corrosion resistance of the steel bars, the percentage of water to the cement and the presence of micro silica in the concrete can have a significant effect on the resistance to corrosion of steel in the concrete.

The results regarding the lifetime of samples are illustrated in bar graphs in Figure 5 until the concrete potential difference of -350 V to SCE was obtained. As samples with the same coating could be observed in the corrosion potential-time diagrams, C_j sample (j=1, 2, 3) reinforcements with the highest percentage of water-cement ratio (0.45) and without micro silica has attained the corrosion threshold (-350 mV to SCE) sooner than all other samples. Also, the reinforcements of S_{2j} sample with 0.4% of water-cement ratio and 7.5% of micro silica replaced with cement reached corrosion threshold later than all other samples. This indicates that micro silica is effective in decreasing the rate of permeation of invader ion and corrosion speed and it can be concluded that 7.5% of micro silica is a good alternative for cement.

3. 2. Concrete Compression Test Results

Samples of compressive strength after 150 days of immersion in sea water are also shown in Figure 6. According to the results from Figure 6 (a), among concrete mix plans without micro silica with different ratios of water to cement at the age of 150 days, the sample with the least water-cement ratio (0.35) has the highest compressive strength. The results show that increasing water-cement ratio leads to reduction in compressive strength in destructive salt environments. As the water to cement ratio increases, the porosity in the concrete will be increased. According to Equation (1) the concrete strength is inversely proportional to the amount of porosity [40]:

$$\sigma = \sigma_0 \left(1 - \frac{P}{P_{cr}}\right) \quad (1)$$

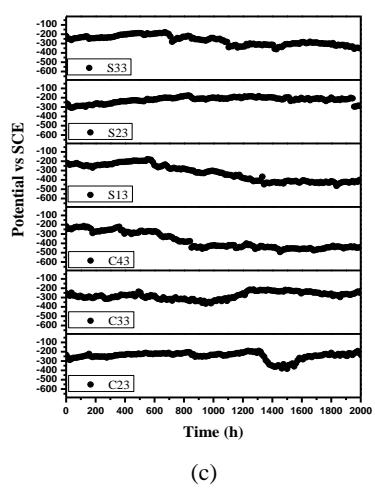
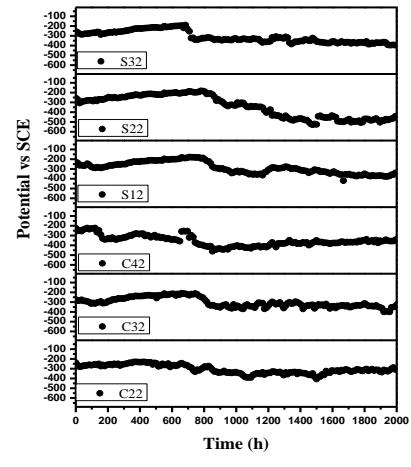
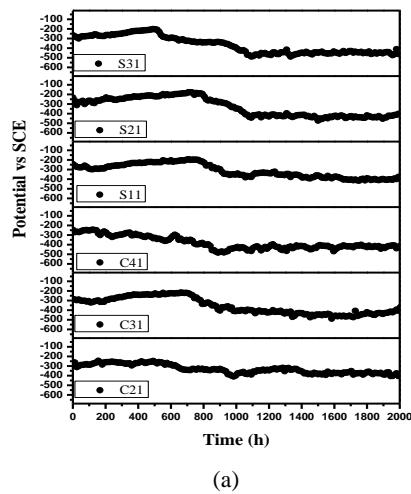


Figure 4. Diagram of corrosion potential-time versus saturated calomel electrode pertaining to samples with different water-cement ratios and different percentages of micro silica with a) 2.5 cm coating, b) 5 cm coating and c) 7.5 cm coating

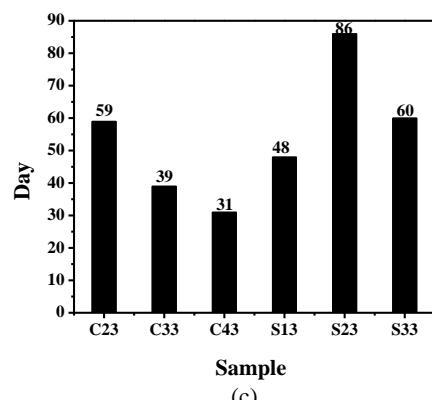
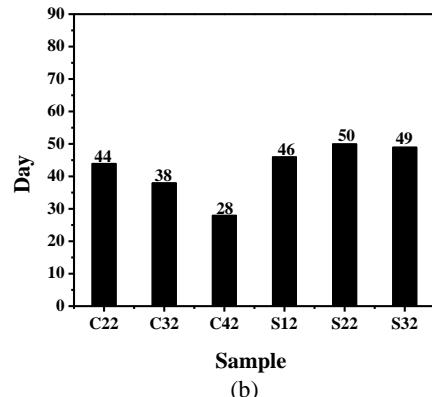
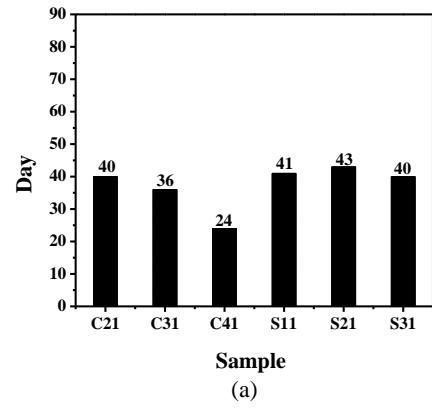


Figure 5. Bar graph of corrosion threshold of samples' reinforcement with coatings of a) 2.5 cm, b) 5 cm and c) 7 cm

where σ and σ_0 are strength and strength attained at zero porosity, respectively. P is porosity and P_{cr} shows the critical porosity. Therefore, with the water to cement ratio increasing, the "P" increases and the " σ " reduces.

It should be noted that, the permeation of chloride into the concrete depends on the capillary pores of the cement matrix, which itself is highly dependent on the water-cement ratio. In general, it can be stated that for a certain degree of hydration, chloride permeability in concrete with lower cement water ratio is low [41].

According to Figure 6 (b), among concrete mix plans containing different micro silica with 0.40 water-cement ratios at the age of 150 days, the concrete containing combination of 7.5% micro silica has the highest compressive strength. Generally, when comparing different samples containing micro silica (S_1 , S_2 , and S_3) with the sample without micro silica (C_3), while all have the same conditions, C_3 has the minimum compressive strength. The presence of micro silica in all mix plans adequately increased the strength. It should be noted that the bending strength test results are also consistent with the compressive strength test results.

When water-cement ratio is consistent and micro silica is added instead of cement, the compressive strength of samples containing different percentages of micro silica replacement at the age of 150 days is more than that of similar sample without micro silica. This can be attributed to the use of micro silica; as its usage is somewhat effective in decreasing long-term water absorption. Moreover, by decreasing the cement content, capillary absorption coefficient of concrete is reduced. The presence of micro silica in concrete also reduces absorption coefficient.

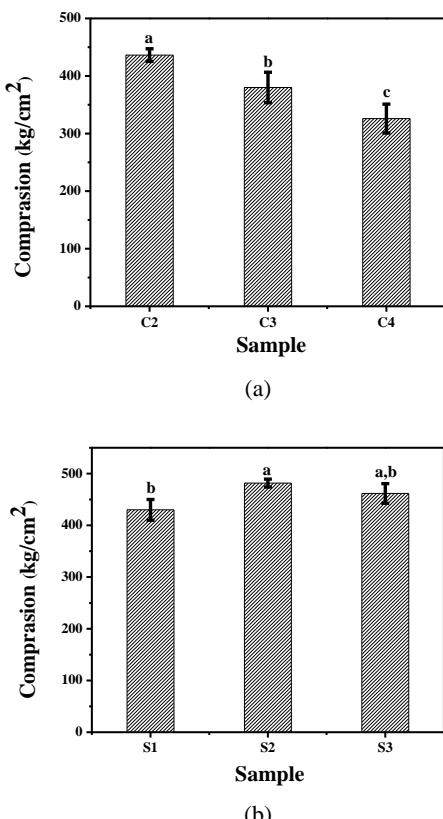


Figure 6. Compressive strength of samples within 150 days a) without micro silica and b) containing micro silica. The bars show mean ($n = 5$) \pm SD. Different letters on the bars represent the significant difference at 5% level of probability

On the other hand, the compressive strength of the sample containing 10% micro silica is less than that of the sample containing 7.5% replacement of micro silica at the age of 150 days. This can be attributed to the excessive usage of micro silica which may lead to separation of aggregates, concrete water bleeding, long delay in setting time, occurrence of cracks caused by the delay in the setting, suspension in time required to achieve compressive strength at the ages of 3, 7 and 28 days and even complete death of concrete.

4. CONCLUSION

Considering the performed experiments in the research and regarding the laboratory tests and analyses carried out, the following conclusions were raised:

1. By increasing the concrete water-cement ratio, compressive strength of concrete decreases. This implies that the higher the water-cement ratio, generally the more short-term and long-term water absorption which will increase invader ion permeation in concrete and will decrease its compressive strength.

2. If water-cement ratio is consistent and micro silica replacing cement is added, then compressive strength of samples containing different percentages of micro silica replacement at the age of 150 days is more than that of the similar sample without micro silica.

3. Compressive strength of micro silica containing 5 and 10% of micro silica is less than that of the sample containing 7.5% micro silica replacement at the age of 150 days. Hence 7.5% micro silica for compressive strength of concrete structures in the Caspian sea is the right and suitable amount.

4. The use of concrete with high water-cement ratio in concrete structures in the Caspian sea causes the phenomenon of early corrosion in these structures. As observed, during a short time, corrosion began and was about to commence in samples with 0.4 water-cement ratio and more, with different thicknesses of concrete coating, without micro silica and without the use of surface coating and protectors such as cathodic protection.

5. It can be concluded that thermodynamically, the use of structures with low concrete coating thickness, leads to earlier or faster corrosion in steel.

6. The amount of 7.5% micro silica for cement replacement in concrete structures in the Caspian sea is a suitable amount.

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Steel Corrosion

Micro silica

عوامل زیادی بر میزان نفوذ یون کلر در بتن در محیط‌های دریابی تاثیرگذار می‌باشد که همه آنها را می‌توان در کیفیت بتن خلاصه نمود. در این تحقیق تاثیر نسبت آب به سیمان با سه نسبت ۰/۴۰، ۰/۳۵ و ۰/۴۵ مورد ارزیابی قرار گرفت. همچنین جهت بررسی تاثیراستفاده از مواد پوزولانی بر مقاومت به خوردگی فولاد در بتن، از میکروسیلیس با درصد های مختلف ۵٪، ۱۰٪ و ۷/۵٪ استفاده شد. سپس نمونه‌های مکعبی تقویت شده با میلگرد فولادی با فاصله‌های ۰/۲۵cm، ۰/۵cm و ۰/۷cm مطحه مکعب ساخته شد و به مدت ۵ ماه در آب دریای خزر قرار گرفتند. در طول این مدت پتانسیل خوردگی فولادها اندازه گیری شد. درنهایت به منظور بررسی استحکام مکانیکی نمونه‌ها، تست فشار بتن صورت گرفت. نتایج نشان داد نمونه‌های تقویت شده با نسبت آب به سیمان ۰/۳۵ پس از ۴۰، ۴۴ و ۵۹ روز به ترتیب برای میلگردهای با عمق ۰/۲۵cm و ۰/۵cm و ۰/۷cm به پتانسیل ۳۵۰V-۳۵۰V-۳۵۰V نسبت به الکترود کالومل اشباع (SCE) رسیدند که در مقایسه با نسبت‌های دیگر آب به سیمان عمر طولانی‌تری داشته و نیز استحکام فشاری آن حدوداً برابر ۴۵۰ MPa بود. با افزودن میکروسیلیس به نمونه‌ها تا ۷/۵٪ زمان رسیدن به پتانسیل خوردگی ۳۵۰V-۳۵۰V-۳۵۰V میلگردهای با عمق ۰/۲۵cm، ۰/۵cm و ۰/۷cm به ترتیب ۴۳، ۵۰ و ۸۶ روز رسید و مقاومت فشاری این نمونه نیز حدود ۴۸۰ MPa بود. در نتیجه می‌توان استدلال نمود که نسبت بهینه آب به سیمان به منظور رسیدن به عمر طولانی‌تر خوردگی و استحکام فشاری مناسب ۰/۳۵٪ و درصد پوزولان SiO_2 برابر ۷/۵٪ می‌باشد.

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