Influence of cement content on concrete performance in corrosive environments (sea water)

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ABSTRACT: In this study, the effect of cement content on concrete performance in corrosive environments is investigated on concrete mixtures having the same water/cement (w/c) ratio. Three w/c ratios (0.40, 0.45 and 0.50) were used and for each w/c ratio three mixtures were prepared with cement contents 350, 400 and 450 kg/m^3. The compressive strength, electrical resistivity and chloride diffusivity of the samples without steel reinforcement were determined. In addition, the half-cell potential of samples with steel reinforcement in 5% NaCl solution was measured to evaluate the rebar corrosion. It is found that although w/c ratio is kept constant, strength increases and corrosion probability of steel reinforcements decreases when cement content in the mixture decreases from 450 to 350 kg/m^3.

INTRODUCTION

The unique combination of steel and concrete has made concrete one of the most popular construction principles in the world. However, the lack of knowledge about the long-term performance of concrete and the severity of environmental impacts has caused serious problems. One of these problems is the corrosion of reinforcing bars that is the most common cause of deterioration of concrete structure in corrosive environments such as sea water (Pal *et al.,* 2002). Corrosion of reinforcing bar damaged the reinforced concrete structures in two ways. First, it is reduces the cross-sectional area of steel bar. Secondly, it produces corrosion products with a larger volume than the steel itself. The volume increase induces the tensile stress in concrete, which results in cracking and eventual structural failure.

Concrete normally provides a high degree of protection to the reinforcing bar against corrosion, by virtue of the high alkalinity (12.5 and higher) of pore solution. This high alkalinity enables the formation of a passive film on the rebar surface which prevents the development of an active corrosion process. In addition, well-consolidated and properly cured concrete with a low w/c ratio has a low permeability, which minimizes penetration of corrosion inducing agents, such as chloride, carbon dioxide, moisture, etc. to the steel surface. Further, the high electrical resistivity of concrete restricts the rate of corrosion by reducing the flow of electrical current from anodic to the catholic sites (Ahmad, 2003). Thus, concrete with high quality can be considered as a primary factor that controls corrosion process in corrosive environments.

There are several factors that influence on concrete performance in corrosive environments. One of these factors is the amount of cement in the mixture. Ahmad (Ahmad, 2003) pointed out that due to inadequate amount of cement in mixture the concrete is not consolidated properly leading to the formation of honeycombs and other surface defects. Theses honeycombs and other surface defects help in penetration and diffusion of deteriorating agents, such as Cl$^-$, H$_2$O, CO$_2$, O$_2$, etc., in concrete. Kolias and Georgiou (Kolias and Georgiou, 2005) reported that high amount of cement in mixture by increasing paste content, the main factor of porosity, causes the increase of concrete porosity.

This paper presents the first results of a continuing investigation on the effect of cement content on compressive strength and some durability parameters of concrete from the view point of steel reinforcement corrosion in more details.

MATERIALS AND METHODS
Materials
Type II Portland cement produced from Hegmatan cement plant in Iran, were used in this study. The chemical composition and some physical and mechanical properties of cement are given in Table 1. The coarse aggregate was a crushed limestone

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with a maximum particle size of 19 mm whereas the fine aggregate was a mix of natural sand and crushed limestone sand. Properties of aggregates are presented in Table 2. A polycarboxylate type super plasticizer was also used to get a workable fresh concrete.

Mixture details
Concrete mixtures with three w/c ratios (0.40, 0.45, and 0.50) were studied. For each w/c ratio three mixtures were prepared with cement contents 350, 400 and 450 kg/m^3. Grading of the aggregate mixture was kept constant for all concretes. All concrete mixtures were designed to provide the slump 16±2 cm for the ease of handling, placing and consolidation. The super plasticizer was added at the time of mixing. Mix composition and properties are given in Table 3.

Table 1: Chemical, physical and mechanical properties of cement

Chemical composition (%)		Physical properties	
SiO_2	21.44	Specific gravity	3.1
AL_2O_3	4.52	Expansion (%)	0.1
Fe_2O_3	3.69	Specific surface (cm^2/gr)	3570
CaO	63.54	Mechanical properties	
MgO	1.48		
Na_2O	0.52	Compressive strength (kg/cm^2)	
K_2O	0.72	7 days	250
SO_3	2.26	28 days	376
Cl$^-$	0.026	91 days	502

Table 2: Physical properties of aggregates

Physical properties	Fine aggregate (Sand)	Coarse aggregate	
	≤ 4.75 mm	No. I ≤ 12.5 mm	No. II ≤ 19 mm
Specific gravity	2.667	2.596	2.607``
Water absorption (%)	1.9	2.2	2.0

Table 3: Composition and properties of mixtures investigated

W/C	Constituent (kg/m^3)					SP*	Paste content (lit/m3)	Slump (mm)	Compressive strength (MPa)	
	Cement	Water	Fine Aggregate (sand)	Coarse aggregate					28 days	91 days
				No. I	No. II					
0.50	450	225	784	180	669	0.00	370.16	180	43.42	50.30
0.50	400	200	836	192	714	1.00	329.03	175	44.49	51.63
0.50	350	175	888	203	758	1.89	287.90	180	46.28	53.45
0.45	450	202.5	812	186	694	0.45	347.66	165	46.08	51.58
0.45	400	180	861	197	735	1.72	309.03	175	47.31	53.25
0.45	350	157.5	910	208	777	2.97	270.40	175	55.79	63.10
0.40	450	180	841	193	718	0.76	325.16	175	53.19	56.28
0.40	400	160	886	203	757	2.28	289.03	140	55.99	62.62
0.40	350	140	932	214	796	3.67	252.90	165	56.76	64.76

* SP: Super plasticizer

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Casting and curing the test specimens

The concrete mixtures were prepared using a pan mixer. Cubes having dimensions of 100×100×100 mm were cast for the compressive strength and electrical resistivity tests, and 150×150×150 mm for chloride ion diffusion test respectively. The reinforced concrete specimens for the half-cell potential test were 70×180 mm concrete cylinders in which a 12 mm diameter steel bar was centrally embedded. The steel bar was embedded into the concrete cylinder such that its end was 50 mm above the bottom of the cylinder, and it was coated with epoxy at the exit from the concrete cylinder in order to eliminate crevice corrosion at these locations. Rebars were cleaned with a wire brush to remove the rust from the surface just before casting the reinforced concrete specimens. Twelve 100 mm cubes, three 150 mm cubes, and three reinforced concrete specimens were cast from each concrete mixture. Test specimens were cast in three layers and compacted using a vibrating table. After casting, the moulded specimens were covered with a plastic sheet and left in the casting room for 24 h. They were then demoulded and cured under the following conditions:

• 100 mm cubes were immersed in 20±2°C water until the test age.
• 150 mm cubes were immersed in 20±2°C water for 7 days and then cured in 5% NaCl solution at 20±2°C for 91 days.
• Reinforced concrete specimens were coated with wet burlap for 6 days and then immersed in a 5% for 25 weeks. The NaCl solution height was 140 mm from the bottom of the cylinder.

Test details

Compressive strength: The 100 mm concrete cubes were used for the compressive strength tests at 7, 28 and 91 days, where three specimens from each mixture were tested at each testing age. The test procedure followed during the test was in conformity with BS 1881: part 116: 1983.

Chloride ion diffusion: The chloride ion diffusion test was performed on three 150 mm cubes for each mixture. On completion of the 7-day water curing, the cubes were coated on five of six faces with a coal tar epoxy to simulate unidirectional chloride ingress and then immersed in a 5% NaCl solution. Following exposure periods of 91 days, the specimens were put in a well-ventilated oven at 105°C for 72 h. The specimens were then placed at room temperature for 48 h. After this period, four holes each with a diameter of 12 mm were dry drilled at the depth of 0-5 mm, 5-10 mm, 10-15 mm, 15-20 mm, and 20-30 mm from the uncoated exposed surface with a hand drill. The drilling machine was fixed in a vertical

alignment and was kept normal to the specimen surface. A scale was fixed on the drill to measure the depth of drilling. The drilling machine was started and stopped once it drilled into the specimen by 5 mm. the pulverized materials were then collected before the next drilling. The procedure was repeated until all the samples were collected. The pulverized materials collected from four holes at each depth of three specimens were combined to give a test sample. The resultant sample was then sieved through a 75 µm sieve. The water soluble chloride ion content in each sieved sample was determined in accordance with ASTM C 1218. These values were then plotted against the average sampling depth from the surface of the ponding to determine the chloride profiles.

The effective chloride diffusion coefficient D_e from the chloride profiles was calculated by non-linear regression analysis outlined by Poulsen (Poulsen, 1990), based on Fick's Second Low (Nt Build 443):

$$C(x, t) = C_s - (C_s - C_i)\,\text{erf}\left(\frac{x}{\sqrt{4D_e t}}\right) \tag{1}$$

where $C(x, t)$, C_s, C_i are the chloride concentration at depth x and exposure time t, the surface concentration of chloride and the initial chloride concentration measured in concrete sample all in (mass %), respectively. X is the depth blow the espoused surface in (m), D_e is the effective chloride diffusion coefficient in (m^2/s), t is the exposure time in (s) and erf is the error function given by Eq. 2 below.

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-u^2}\,du \tag{2}$$

Electrical resistivity: The electrical resistivity of three 100 mm concrete cubes was determined at each age of 7, 28, and 91 days. At the test time, the specimens were removed from the water tank and after testing, again returned to the water. For this purpose, an electrical resistivity meter was used, which produced 100 Hz AC. Two copper plates (120×100×2 mm) with a thin layer of low slump cement paste were laid on two opposite faces of each saturated surface dry specimen, and the resistance was measured between them (see Fig. 1). The electrical resistivity was then obtained by multiplying the measured resistance with cross-sectional area of specimen and dividing it into the height of specimen.

Half-cell potential: The measurements were performed by a high impedance voltmeter with a saturated calomel reference electrode (SCE) for 25 weeks (see Fig. 2).

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The probability of corrosion was estimated by following ASTM C 876 standard. Because this reference electrode is a saturated calomel electrode (SCE) and the ASTM standard is base on copper/copper sulfate (CSE), the conversation from CSE to SCE is conducted according to values in Table 4.
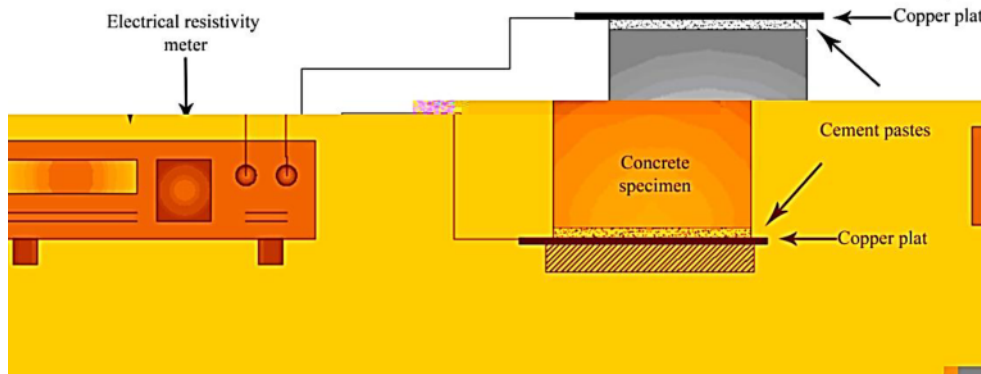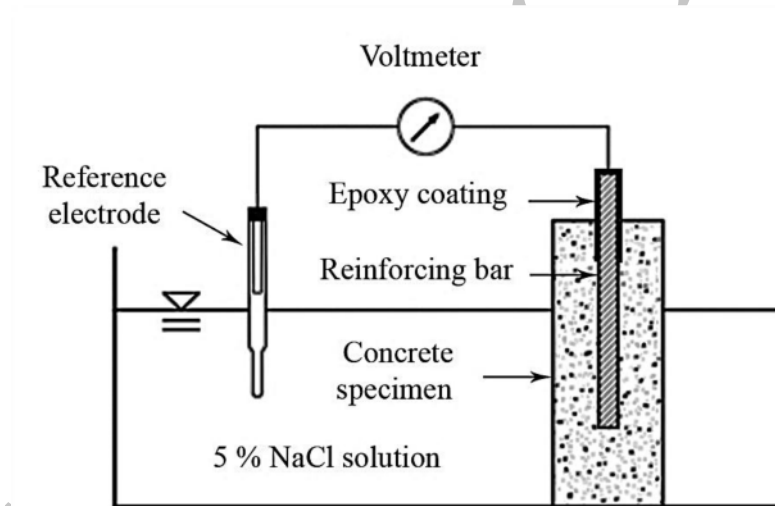

Fig. 1: Electrical resistivity measurement

Fig. 2: Half-cell potential measurement

Table 4: Corrosion condition relation to half-cell potential measurements
(Song and Saraswathy, 2007, Leelalerkiet *et al.,* 2004)

Measured potential		Corrosion probability
(mV vs. CSE)	(mV vs. SCE)	
-200 <	-125 <	90 no corrosion
-200 to -350	-126 to -275	Uncertain
< -350	< -276	90 % corrosion

RESULTS AND DISCUSSION

Compressive strength
The results are shown in Fig. 3 in terms of strength versus cement content. Each point on Fig. 3 is the mean value of measurements of three specimens. It is observed that for constant w/c ratio the strength increases as the cement content in the mixture decreases. It can be usually attributed to the longer path the crack needs to follow when the aggregate volume in the concrete is higher, thus having to move around greater number of aggregates, a fact which makes the energy absorbed higher. When the volume of the paste is higher and the volume of the aggregates is smaller, the length of the path becomes straighter, thus smaller, and the amount of energy absorbed becomes smaller. The similar results have been also observed in other research works (Yiğiter *et al.,* 2007).

Chloride ion diffusion
The chloride diffusion coefficients after 91 days of exposure are shown in Fig. 4. It is found that for each w/c ratio, reduction of cement content from 450 to 350 kg/m^3 decreases the chloride diffusion coefficient. This is explained due to significant improvement of the micro structure attributed to the use of low cement content as well as the significant reduction of the capillary pore volume. Moreover, it can be attributed to the increment of dilution (blocking) and tortuosity (redirecting) effects of aggregate that have low permeability and diffusivity rather than cement paste.
Therefore, since the most cause of initiation of corrosion of steel in concrete is the presence of chloride ions (ACI 222R-01, 2001), it is expected the use of low cement content (350 kg/m^3) delays the onset of corrosion.

Electrical resistivity
The data concerning the variation of electrical resistivity with cement content are plotted in Fig. 5. The highest value was obtained from the concrete with lowest cement content and w/c ratio, whereas the concrete with highest cement content and w/c exhibited the lowest electrical resistivity.
Test results indicate that cement content has significant effect on electrical resistivity of concrete. As expected, for a constant w/c ratio, decrease of cement content increases the electrical resistivity. The increase in the electrical resistivity is mainly due to the denser microstructure of concrete resulting from low cement content. Additionally, the high volume of aggregates also increases the electrical resistivity of the concrete. Aggregates have greater electrical resistivity than cement paste, and does not release noticeable amount of ions (that decreases the electrical resistivity) into pore solution of concrete (Shi, 2004).
The resistivity of concrete and corrosion rate of reinforcement after depassivation is related. Ion transport between anodes and cathodes on steel surface is one of the rate controlling factors. Based on the simplifying Bazants model (Bazant, 1979), the corrosion rate is inversely proportional to the resistivity, although this relationship may vary with concrete composition. Thus, it can be expected that the reduction of cement content in concrete reduces the corrosion rate of steel reinforcing bars after initiation of corrosion.
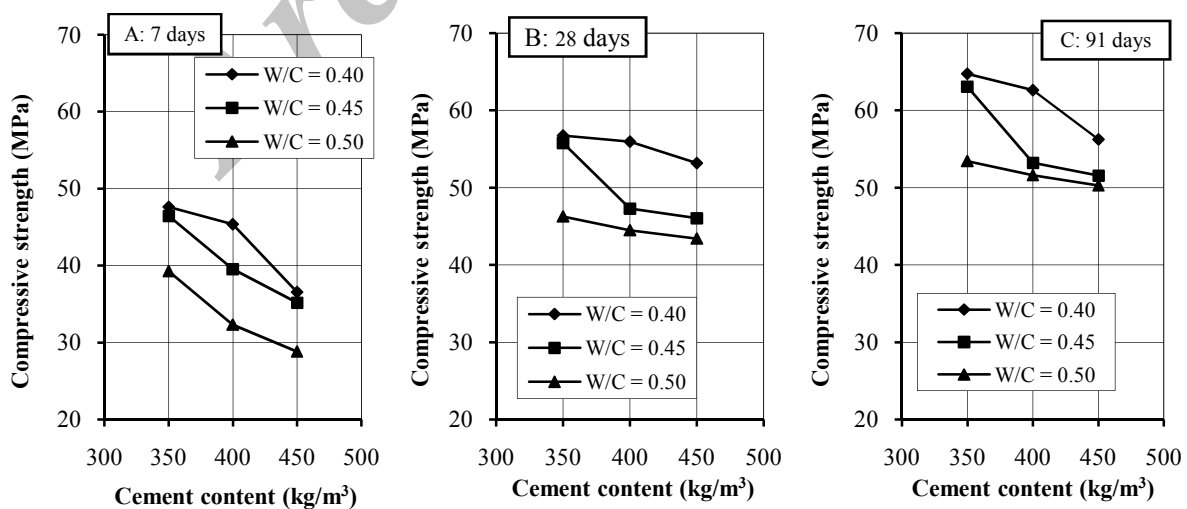

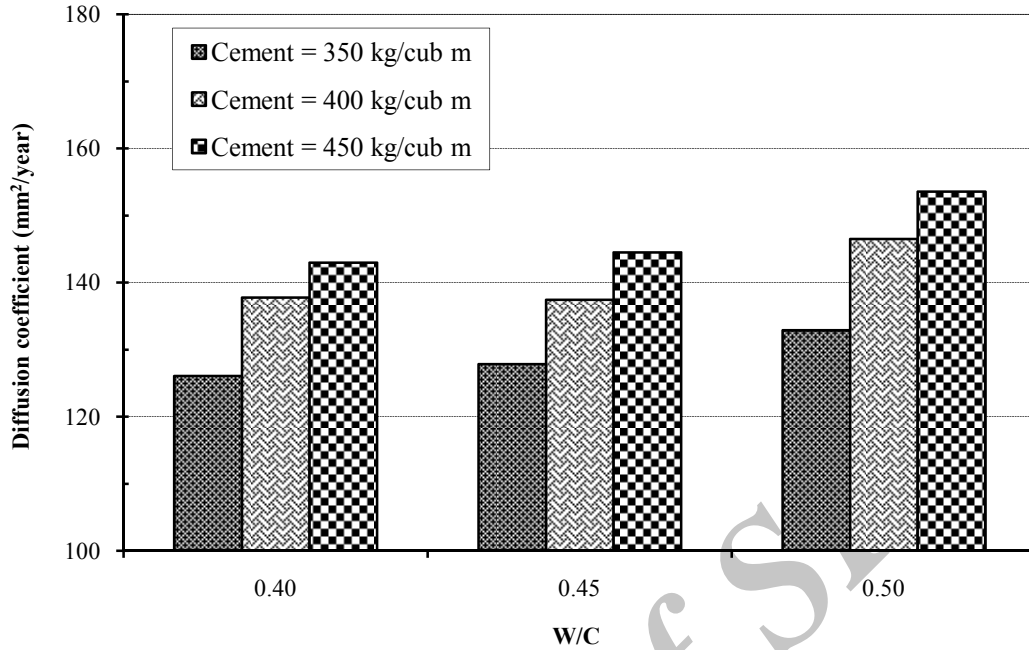Fig. 3: Relationship between compressive strength and cement content

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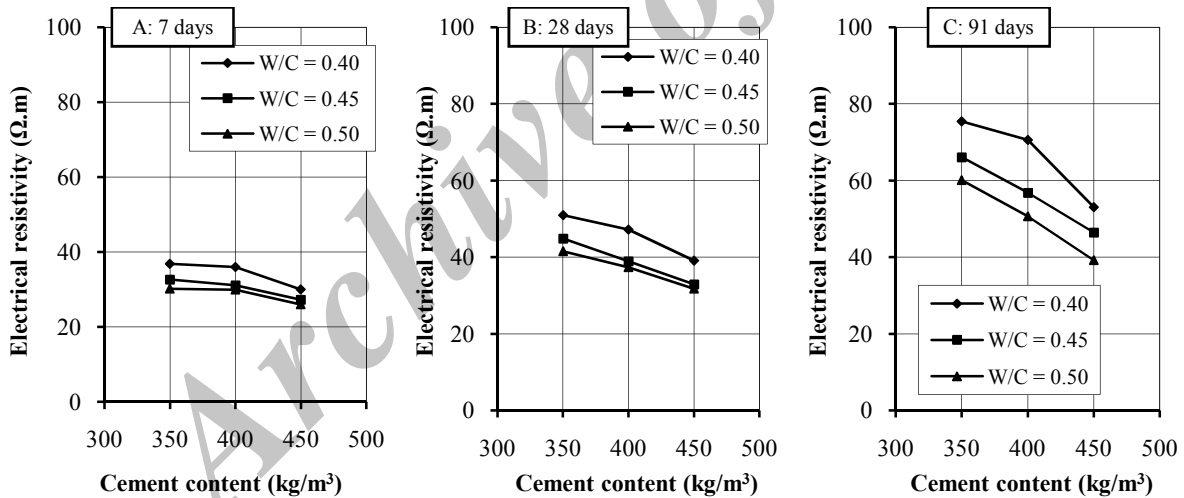Fig. 4: Average diffusion coefficient

Fig. 5: Relationship between cement content and electrical resistivity

Half-cell potential measurements

Half-cell potential readings of specimens subjected to 5% NaCl solution were recorded to compare the performances of the different concrete mixtures. The half-cell potential results are illustrated in Fig. 6.

In accordance with ASTM C 876, after 25 weeks of exposure, steel bars embedded in samples with w/c ratio 0.50 and cement contents 400 and 450 kg/m^3 are showed high probability of corrosion. Also, steel bars in specimens with w/c ratios 0.40 and 0.45 and cement contents 350 and 400 kg/m^3 are exhibited

low corrosion probability. In the case of other rebars, the uncertain corrosion probability was achieved. These results indicated that concretes with low cement content (near to 350 kg/m^3) can reduce the probability of steel corrosion in concrete structures and the effect is more pronounced for higher w/c ratios. Therefore, the low cement content with improvement of the micro structure of concrete can delay salt attacks in aggressive environment for the protection of steel reinforcements from corrosion.
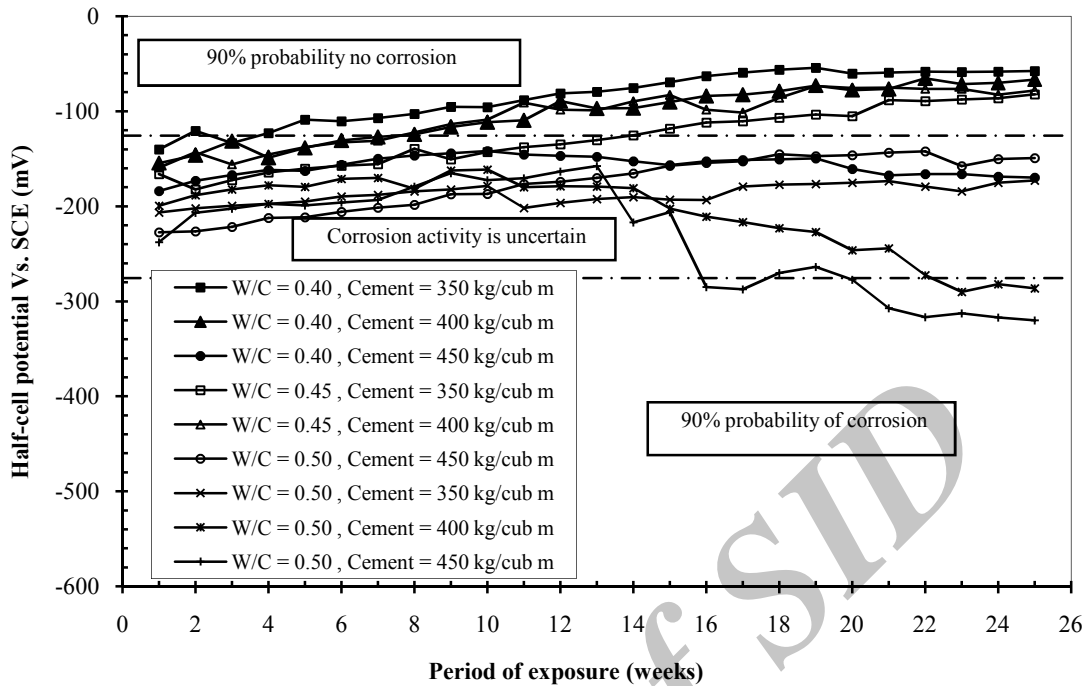
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Fig. 6: Variation of half cell potential of reinforcing steel bar immersed in solution of 5% NaCl

CONCLUSION

Taking into the limitations of the work concerning the primarily the max aggregate size used (19 mm) and the w/c ranged from 0.40 to the 0.50, the following conclusions can be drown:

1. Compressive strength of the mixtures increases when the cement content decreases from 450 to 350 kg/m^3 at constant w/c ratio and the effect is more pronounced for lower w/c ratios.

2. Chloride ion diffusion coefficient also decreases with decrease of cement content at each w/c ratio.

3. Decrease in cement content at all w/c ratios increases the electrical resistivity considerably.

4. In general, the reduction of cement content from 450 to 350 kg/m^3 decreases the corrosion probability of steel bars in aggressive environments and the effect is more pronounced for higher w/c ratios.

5. Based on the results of the tests it seems that optimum cement content at all w/c ratios is 350 kg/m^3 for this study. In cases where the mix proportions of the concrete different from the usual ones then the effect of cement content on the performance of concrete should be carefully studied.

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