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THE EFFECTS OF SULPHATE ION ON CONCRETE AND REINFORCED CONCRETE

A.B. Yılmaz
Faculty of Fisheries
Mustafa Kemal University, 31200 İskenderun Türkiye

B. Yazıcı and M. Erbil
Department of Chemistry, Faculty of Science and Art
Çukurova Üniversity, 01330 Adana Türkiye

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ABSTRACT

The effects of the sulphate ions and the pH on the strength of concrete and reinforcement steel have been investigated. Concrete and reinforced concrete samples prepared by using mixing water having different sulphate ion concentrations (standard, 400 ppm and 3500 ppm) were cured in a water bath containing the same ion concentrations of mixing water or distilled water at two different pH values (8 and 5). The samples were exposed to the environments for 90 days. The compressive strength of concrete, pH values of bath, galvanic current changes and potentials (vs. Ag/AgCl) of reinforcing steel were measured. It was observed that the compressive strength of the concrete decreases as the $SO^{=}_4$ ion concentration increases. The galvanic currents were high for the first 28 days and then these currents decreased steadily. It was found that the potentials have been rising up to the passive potential of the reinforcing steel where the $SO_4^=$ concentration is low. © *1997 Elsevier Science Ltd*

Introduction

The effects of the $SO_4^=$ ions to the cement and consequently to the concrete have been the subject of investigations for many years (1, 2, 4, 6, 11). Cement contains calcium silicates (C_2S, C_3S), tricalcium aluminate (C_3A) and tetracalcium aluminoferrite (C_4AF). Ions in the mixing water or ions diffusing into the concrete structure can lead to the formation of new solids. Sulphate ions, for example, react with the C_3A in the cement composition and form ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) which reduces the strength of the concrete due to the expansion in the volume (1, 2).

The diffusion of the chloride ions into the concrete has been studied by many investigators and put forward by Fick's law (3, 14, 15). The diffusion rate of sulphate ions appears to be much lower than that of chloride in the 4% Na_2SO_4 solution at pH 7. It has been reported that the penetration depth of ions into concrete was measured as ~0.5 mm (2). Diffusivity values for sulphate ions were calculated as 0.56 – 1.34 × 10^{-14} m^2/s for different types of cement pastes.

Sulphate ions from external sources react with calcium hydroxide in the pores by penetrating into the concrete depending on the diffusivity value of concrete. This, in turn, speeds up the penetration of sulphate ions (4). As the sulphate ion concentration is high enough in the pores, ettringite is formed (7). On the other hand, sulphate ions from internal sources, such as from mixing water, forms the same product by reacting with C_3A. The degree of this effect depends on the amount of C_3A, the ratio of water/cement, and pore matrix (4, 6, 14).

The pH value of the concrete pores was found to be high at normal conditions ($pH \cong 12.6 - 13.8$) (5). The maturation reactions are formed at these pH values. The strength of the concrete weakens if the environment of the concrete is acidic. The effect of the acidity on the concrete strength depends on the ions diffused into the concrete. Similar effect is realized by the diffusion of the SO_2 and CO_2 gases from the atmosphere. It is stated that these negative effects occur at values of pH below about 6.5 and this effect will increase at the lower pH values (6).

Reinforcing steel is also affected from these chemical reactions and from the ions diffused into the concrete (8). In practice, it is desired that concrete and reinforcing steel should be fused. But the pores and ionic solvents accumulated in these pores are in contact with metal. The steel, expected to be passive at normal pH, may lose its passivity due to the composition of the pore solution (5, 8). According to the ASTM C 876, if the measured voltage, referenced to the copper-copper sulphate (CSE) is -0.20 V or higher, 90% or more of the reinforcing steel is passive. However, if the potentials over an area are in the range of -0.20 to -0.35 V CSE, corrosion activity of the reinforcing steel is uncertain. If the voltage is below the -0.35 V CSE, 90% of the reinforcing steel is active.

In this study, the effects of the SO_4^- ions on the strength of concrete and on the corrosion of reinforcing steel have been studied. It has also been investigated whether the $SO_4^=$ ion can be diffused away from concrete in order to eliminate its effects. Depending on the $SO_4^=$ ion concentrations, the compressive strength of the concrete specimens, prepared at two different initial pH, were tested. The potentials and galvanic currents of the reinforcing steel were observed for the reinforced concrete specimens, which were prepared at the same conditions. The transport of $SO_4^=$ ions from the concrete pores into the distilled water by diffusion was investigated by changing the parameters mentioned above.

Experimental

Materials. Chemical composition of the cement used in the experiments is shown in Table 1. Natural aggregate was used in the experiments. Ideal mixing water (IMW) was prepared with chemicals added to the distilled water and its pH was adjusted with NaOH and HCl. The chemical components of IMW are 10 mg/l NH_4^+ (NH_4Cl), 100 mg/l Mg^{+2} [$Mg(NO_3)_2$],

TABLE 1

Chemical Composition of Cement (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O, Na_2O	Free lime
24.20	7.80	2.90	57.00	2.90	2.11	0.54	1.6

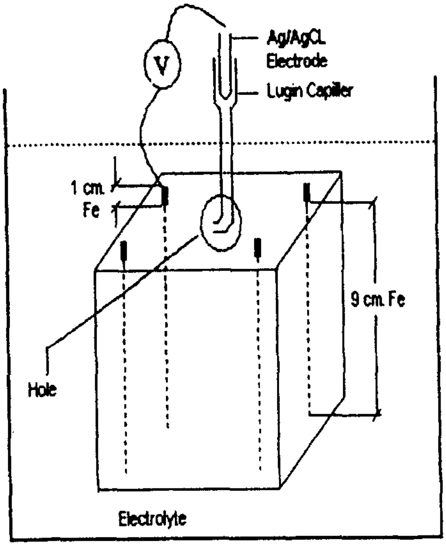

FIG. 1.
Experimental arrangement.

200 mg/l $SO_4^=$ (Na_2SO_4) and 100 mg/l Cl^- (NaCl). The steel rods used in the experiments were composed of 0.13% of C, 0.65% of Mn, 0.030% of S, 0.013% of P and 0.017% of Si. Ag/AgCl electrode was used as a reference electrode for all potential measurements. The compressive strength in MPa (σ) was measured with Tonitecnic.

Test Specimens and Conditioning. In the experiments, cubic shaped concrete specimens (10 × 10 × 10 cm) were used as shown in Figure 1. The compositions of the mixing water and external solution in which specimens were cured are given in Table 3. The strength tests were carried out at the 1, 3, 5, 7, 14, 21, 28, 60 and 90th day of the curing period by using three specimens for each day, and the average value is accepted. Embedding the steel rods into the concrete specimen having the same composition as given in Table 2, the potentials and galvanic currents were measured and the changes during the experiments were observed by the experimental arrangement shown in Figure 1.

TABLE 2

Composition of the Concrete

	Mass (kg)	Density (kg/dm^3)	True volume (dm^3)
Water	167	1.00	167
Cement	304	2.94	103
Air	---	---	20
0/4 Agr	1019	2.71	376
0/16 Agr	892	2.67	334

TABLE 3

The Compositions of the Mixing Water and External Solution, Initial pH Values and the Measured Compressive Strength of the Concrete Specimens After 90 Days Curing

Symbol	Environment		Initial pH	σ(Mpa) 90th day
	Mixing water	External solution		
A	IMW	IMW	8	41.5
B	IMW	IMW	5	40.5
C	IMW+400 ppm $SO_4^=$	IMW+400 ppm $SO_4^=$	8	40.2
D	IMW+400 ppm $SO_4^=$	IMW+400 ppm $SO_4^=$	5	39.3
E	IMW+3500 ppm $SO_4^=$	IMW+3500ppm $SO_4^=$	8	35.2
F	IMW+3500 ppm $SO_4^=$	IMW+3500ppm $SO_4^=$	5	34.7
K	IMW	Distilled water	8	42.3
L	IMW	Distilled water	5	41.6
M	IMW+400 ppm $SO_4^=$	Distilled water	8	40.4
N	IMW+400 ppm $SO_4^=$	Distilled water	5	39.7
O	IMW+3500 ppm $SO_4^=$	Distilled water	8	36.2
P	IMW+3500 ppm $SO_4^=$	Distilled water	5	36.6

Results

The Environments with the Same External Solution and Mixing Water. The graph of compressive strength of concrete specimens, pH of external solution, potentials of reinforcing steel and galvanic currents vs. time (day) are shown in Figure 2. The compressive strength increased rapidly for the first 28 days in all experimental conditions; the increasing rate slows down in the forthcoming days. After the first 28-day period, the environments (C through F) having higher $SO_4^=$ ion concentrations, which were prepared with the IMW, showed smaller compressive strengths than that of the environments having lower $SO_4^=$ ion concentrations. The lowest compressive strengths were measured in the environments E through F for 3500 ppm $SO_4^=$ ions in the 90th day (Table 3).

The initial pH values of the external solution increased rapidly until the 21st day in all conditions, as shown in Figure 2b. The pH's were around ~11-12 at the 21st day. The pH values started to decrease after the 28th day and it stayed between 9.0 and 10.5 in the 90th day. The potentials shifted to the positive values by the time they were around -0.5V in all conditions at the beginning of experiments. Rate of this shift is small for the solutions having high $SO_4^=$ concentration. For example, the measured potentials in the 90th day for A, B, C, D, E and F were -0.287, -0.263, -0.323, -0.303, -0.358 and -0.402 V respectively (Figure 2c).

Galvanic current variations vs. time are given in Figure 2d. Galvanic currents were between +50 μA and -35 μA in the first days of experiments. But in the forthcoming days, these values changed irregularly. These values were between +10 μA and -10 μA in the 90th day.

The Environments with Distilled Water as an External Water. Experimental results for the environments from K to P are given in Figure 3. The compressive strength increased independently from the external solution and the initial pH. The increasing rate slowed down after the 28th day as seen in Figure 3a. The compressive strength of concrete specimens, in the K and L environments, prepared with the IMW and cured in the distilled water for 90 days, increased up to the values 42.3 (pH = 8) and 41.6 (pH = 5) respectively. Concrete

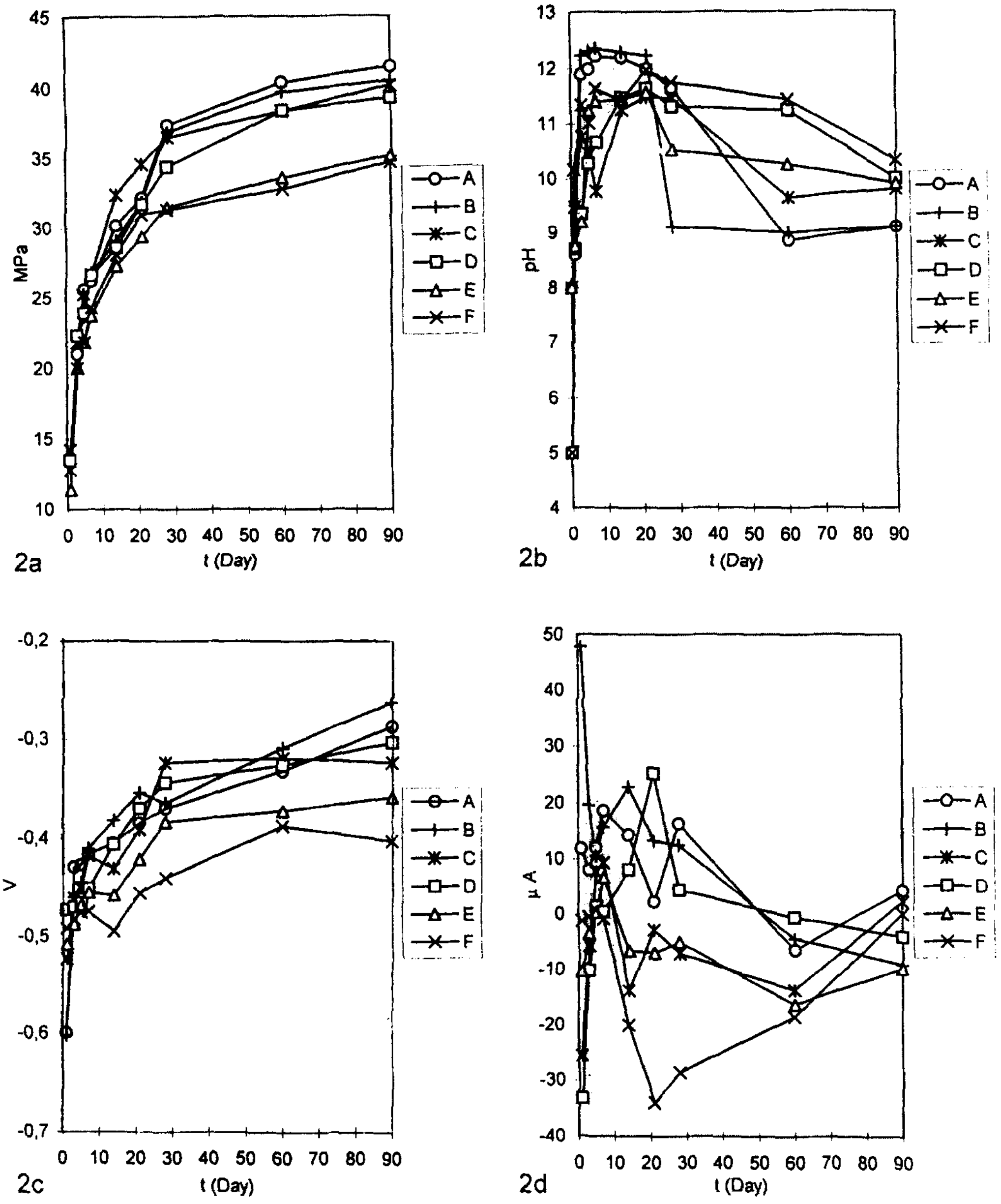

FIG. 2.

Experimental results for environments A through F, (a) compressive strength of the concrete specimens, (b) pH of external solution, (c) potentials of reinforcing steel, and (d) galvanic currents of the reinforcing steel.

specimens prepared with the mixing water of higher $SO_4^{=}$ concentrations could not reach to the same strength values during the same time (Table 3). On the 90th day in the environment having 400 ppm $SO_4^{=}$ ion concentration, the measured strengths were 40.4 MPa (pH = 8) and 39.7 MPa (pH = 5). In the environments of 3500 ppm $SO_4^{=}$ ion concentration, a remarkable

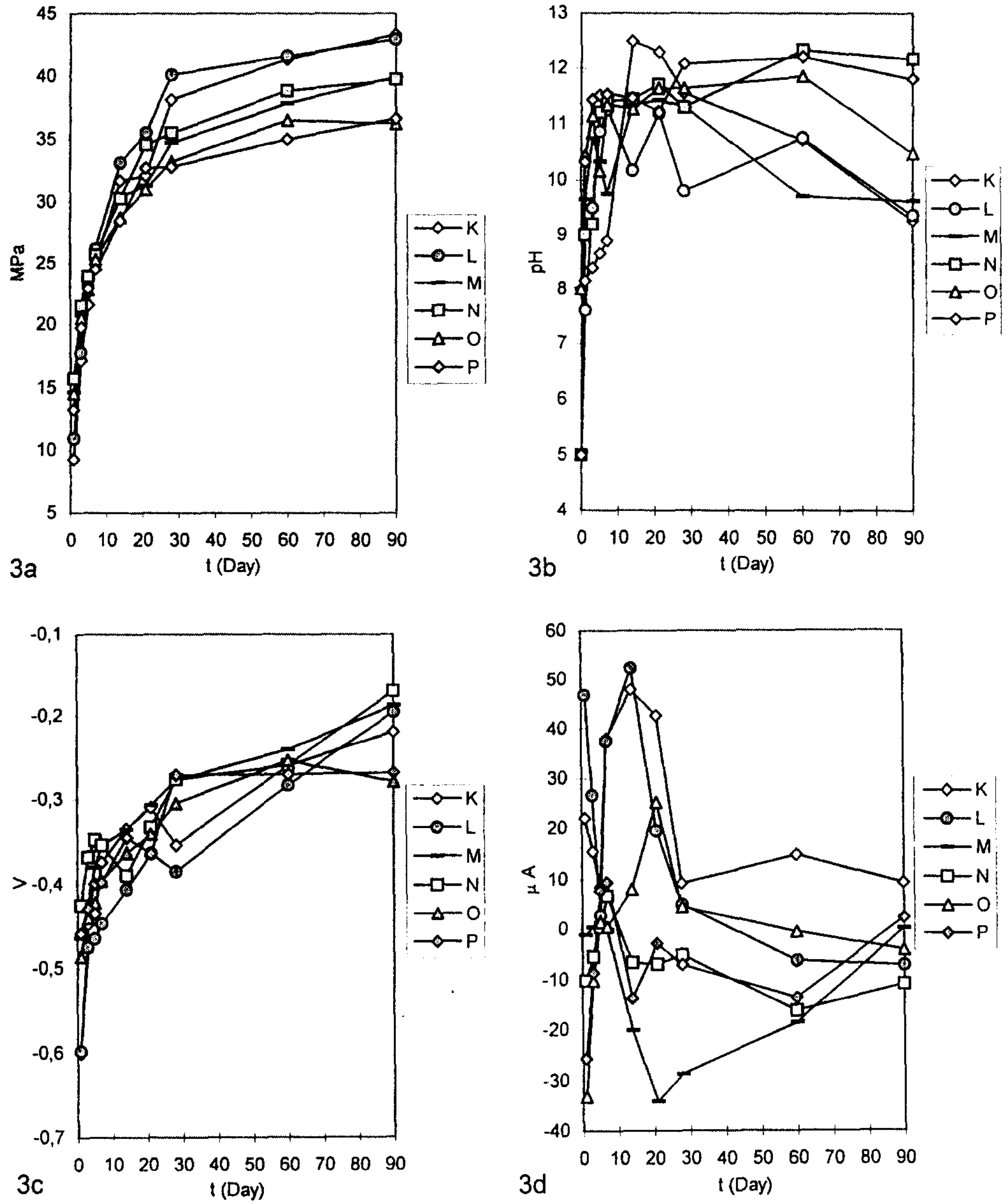

FIG. 3.

Experimental results for environments K through P, (a) compressive strength of the concrete specimens, (b) pH of external solution, (c) potentials of reinforcing steels and (d) galvanic currents of the reinforcing steel.

decrease in the strength was observed. The strengths were 36.2 MPa (pH = 8) and 36.6 MPa (pH = 5).

As seen in Figure 3b, the pH value of distilled water increased rapidly in all environments and reached to pH = 11-12 at the 21st day. The pH values in the 90th day were between 12 and 9. In the IMW environments, while the pH values were as low as 9 at the last measurement, the pH values of environments, having initial pH value 5 and higher $SO_4^=$ ion concentrations were much higher, such as 11-12.

Potentials shifted to the more positive values, while they were negative (-0.4, -0.6 V) initially, as seen in Figure 3c. For example, the potentials for K, L, M, N, O and P environments were -0.219, -0.195, -0.187, -0.170, -0.279 and -0.268 V at the 90th day, respectively.

The galvanic current changes are seen in Figure 3d, while the galvanic currents were between + 48 μ A and -35 μ A initially, these values changed irregularly by the time and measurements were between +10 μA and -20 μA in the 90th day.

Discussion

Figures 2 and 3 show the effects of the mixing water and external water composition in the concrete specimens. The compressive strengths for mixing and external water at various pH and $SO_4^=$ concentrations for the 90th day are also shown in Figure 4. At these experimental conditions (A-F and K-P), it can be seen that the compressive strength decreases as the $SO_4^=$ ion concentration increases and pH decreases. One of the parameters that causes a decrease in compressive strength is the $SO_4^=$ ion concentration.

It has been shown that this negative effect is more pronounced when the sulphate ion concentrations are more than 2000 ppm (6). As it can be seen from Figure 4, the largest decrease in compressive strength was obtained when the $SO_4^=$ ion concentration was 3500 ppm (E, F and O, P). This is in good agreement with the previous studies. It is claimed that $SO_4^=$ ion from external solution or mixing water goes into the concrete and then forms ettringite with C_3A which can cause an expansion or formation of capillary cracks in the concrete structure (1, 2, 4, 11, 14).

Another parameter that causes a decrease in compressive strength is the pH. When pH is lower than 6.5, it has an effect on the maturation reactions of concrete that occurs at basic conditions (5, 6). Figures 2b and 3b show that there is a normal decrease in compressive strength when the pH is adjusted to 5.0 as an initial pH. However, this decrement is small

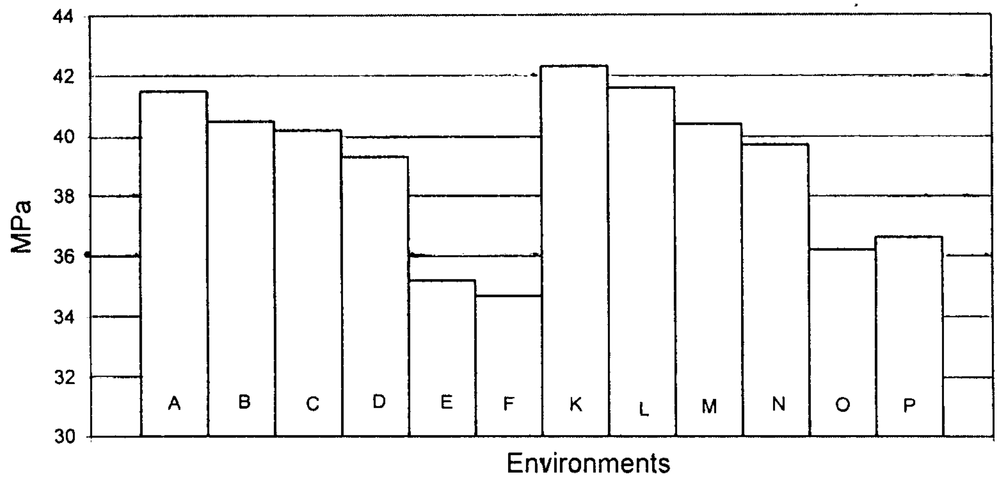

FIG. 4.

The comparison of the compressive strengths measured at the 90th day of curing in various environments, A through P.

since the pH value goes up rapidly from the beginning of the first day. In order to reduce the effect of ion diffusion into the concrete structure from contact enviroment, previous studies focused on the decrease of the porosity of concrete by the aid of some additives or changing the ratio W/C (2, 4, 11). Our aim was to force ions to diffuse out by increasing the concentration gradient of concrete against contact to water. Distilled water as an external water was used to provide this concentration gradient in this study (K-P). As a result, unbound $SO_4^=$ ions in pores diffused out and a small amount of increase in compressive strength was obtained (Figure 4). At high $SO_4^=$ ion concentrations, this increment is not at appropriate levels due to the low diffusion coefficient of $SO_4^=$ ion as shown in Figure 4 (2). When the $SO_4^=$ concentration in mixing water is 3500 ppm and the external solution is distilled water (O and P), insufficient increase obtained in compressive strength shows that the bound $SO_4^=$ does not diffuse outward.

Steel exhibits different corrosive activity at different environments as do all metals. If the reinforcing steel is kept at the same pH as in concrete, it shows a passive characteristic. However, it has been shown that the steel undergoes corrosion due to the deterioration of the passive film at low pH values (12). It is also possible that the ions accumulated in the pores may deteriorate the passive film in spite of high pH values. According to the Pourbaix diagrams, metal is expected to be passivated at pH 9-10 and at the potentials of -0.6 V (vs. Ag/AgCl) and -0.4 V (vs. SHE) (13). It has been found that the reinforcing steel in mature concrete is corrosive at the potentials lower than -0.3 V due to the complexity of concrete structure. The reinforcing steel in sea water is found to be non-corrosive at the potentials higher than -0.23 V, but corrosive at the potentials lower than -0.28 V (12). In our experimental conditions, the rate of potential shifting to the positive values slowed down as the $SO_4^=$ ion concentration increased. This is in good agreement with the literature (8, 10, 12, 13). The potentials for reinforcing steel were above -0.3 V in the conditions of IMW at the 90th day. When the $SO_4^=$ concentration is 400 ppm, this value was approximately the same as above, but, it was corrosive in the conditions having 3500 ppm $SO_4^=$ (Figure 2c). When the external water is distilled water, the potential of reinforcing steel shifted to more positive potentials and thus rises up to desired passive conditions in the concrete pH (Figure 3c). This result demonstrates that the outward diffusion of ions from concrete pores can be achieved by means of concentration gradient at longer period. At the first days, the homogeneity at the junctions of metals is lost due to the hydrolysis of salts in the concrete pores so new regions having different potentials at the metal surface are formed. Thus it is expected that a galvanic current will flow between the reinforcing steel rods (10, 12). Our results agree with this idea. Figures 2d and 3d show that the galvanic currents decrease and the potentials extent to a constant value due to the pores reaches to an equilibrium by the time.

Conclusions

The results have been interpreted as follows:

1. $SO_4^=$ ions cause a decrease of 12.5-15% in the compressive strength, when compared with IMW conditions.
2. Outward diffusion of $SO_4^=$ ions from inside the concrete pores to external solution has been partially achieved by forming a concentration gradient.
3. Reinforcing steel is found to be corrosive at the conditions of high $SO_4^=$ ion concentrations.

4. When the distilled water is used as an external solution, the potential of reinforcing steel reaches to more positive values. Therefore, it can be concluded that $SO_4^=$ ions cannot be completely eliminated from concrete due to the low diffusion coefficient of $SO_4^=$ ions.

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