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Effect of Oxide Compositions in the Portland Cement on Corrosion **Behavior of Reinforcing Steel Embedded in Concrete**

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ABSTRACT

In this study, corrosion behavior of reinforcing steel embedded in concrete samples obtained from CEM II /B-M 32.5 R Portland cement type which has been taken from various factories in order to determine effect of oxide compositions in the cement has been examined. For this purpose, the mixture ratio of concrete samples has been prepared according to ACI 211.1 and the same type and amount of materials have been used for the samples. The unique difference among samples was CEM II /B-M 32.5 R Portland cements on various producing center. The corrosion experiments were conducted in two stages. In the first stage, the corrosion potential of steels in the concrete was measured every day for a period of 90 days in accordance with ASTMC 876 standard. In the second stage, anodic and cathodic polarization values of these steels were obtained and then the corrosion currents were determined with the aid of cathodic polarization curves. As a result of this study, it was found that corrosion rate of reinforcing steel embedded in concrete affected with the change of oxide compositions in the cement.

Key Words: Corrosion, Cement, Concrete, Reinforcing Steel.

INTRODUCTION

Concrete and reinforced concrete are the most widely used construction materials [1]. High quality and durable concrete is required to reduce the rapid deterioration of concrete in severe conditions. Among the factors related to declining concrete durability such as carbonation, corrosion, alkali-silica reaction, freezing/thawing, and so on, the penetration of chloride-ions into concrete has been regarded as the major deterioration problem. Ingress of chloride ions destroys the natural passivity of the surface of reinforcing steel, and often leads to the corrosion of steel in concrete structures. Thus, insufficient concrete cover or poor quality concrete accelerates reinforcement corrosion [2]. These corrosion problems lead frequently to early deterioration and eventually to risky situations for the stability of structures. In any case, the economic costs inherent to reparation works are considerable [3].

Numerous research studies have been performed on the factors affecting the corrosion of reinforcing steel embedded in concrete in recent years [1-12]. During studies on real concrete samples or in equivalent alkali solvent, the corrosion rate of reinforcing steel usually at chloride ion concentrations and the minimum limit value that results in the corrosion of chloride ions were determined. For the studies about the effect of cement on the corrosion of reinforcing steel, different types of cement were compared and their effects on steel corrosion were investigated.

In this study, instead of using different types of cement, only the effect of CEM II /B-M 32.5 R Portland cement, which is widely used in the construction industry, on the corrosion of reinforcing steel was investigated. The aim of the study is to determine the effects of small changes that take place during the oxide composition of raw cement material on the corrosion rate.

For this purpose, the corrosion potential of reinforcing steels embedded in concrete samples prepared with CEM II /B-M 32.5 R Portland cement which were obtained from different regions were measured every day for a period of 90 days in accordance with ASTMC 876 standard and then corrosion rates of the steel were determined by using the galvanostatic method. At the end of the experiments, the effect of various oxide compositions in the cement on the corrosion behavior of reinforcing steel has been interpreted.

MATERIAL AND METHOD

The effect of variations oxide compositions in the CEM II /B-M 32.5 R Portland cement, which was – acquired from factories in five different cities at different regions of Turkey, on the corrosion behavior of – reinforcing steel, has been investigated on 25 pieces _ concrete samples.

Prepare of Electrodes

As an electrode, Ereğli Iron and Steel Factories in Turkey product SAE1010 steel bar, which is the fundamental construction material of construction industry, was selected for the present study. The asreceived material was in the form of 10 mm diameter hot rolled bar with a ferritic-pearlitic structure. The chemical composition of SAE1010 is given in Table 1.

Table 1. Chemical composition of the steel (wt.%)

С	Mn	Si	Р	S	Fe
0,176	0,250	0,050	0,005	0,046	Balance

50 pieces of reinforcing steel were machined to 8 mm diameter and 130 mm length and the sample surfaces were polished with 1200 mesh sandpaper. The polished surfaces were cleaned with ethyl alcohol. 10 cm² surface areas were left open in the tips of electrodes which would be embedded in the concrete. Screw thread was machined in other ends of steel electrodes and cables were connected to these ends in order to easily make measurements during the experiment. Remaining sections of the electrodes were protected against external effects by covering with epoxy resin at first and then with polyethylene wrap.

Design of Concrete Samples

The steel electrodes prepared in advance were embedded in 100x100x200 mm concrete samples to evaluate corrosion behavior.

CEM II /B-M 32.5 R Portland cement which was acquired from factories in five different cities at various regions of Turkey was used in order to prepare all concrete samples included in the experiments in scope of the study. Tap water was used as mix water while preparing the concrete blocks. 3.5% NaCl was added into the mix water of the concrete mortar for the sake of creating corrosive environment. The concrete samples were kept in molds for 24 hours, and then unmolded. In order to prevent the samples from losing their conductivity nature and standardization purpose, they were cured at 90% relative humidity and 20 ± 2 °C for 90 days.

Mixture ratio of concrete blocks in accordance with ACI 211.1 [13] is presented in Table 2.

Table 2. Mixture proportion of the concrete blocks (kg/m^3)

Cement	Sand (0-4 mm)	Gravel (4-8 mm)	Water	NaCl
460	900	850	266.75	8.25

While the specimens were being prepared, cement dosage, water/cement ratio, aggregate amount and NaCl amount which was added for creating a corrosive environment were kept constant. Experiments were conducted by using A, B, C, D and E for naming the samples, instead of naming them according to the factories they were acquired from in order to avoid commercial problems. Chemical compositions of these cements are given in Table 3.

Table 3. Chemical compositions of the cements (wt.%)

Compositions	Composition Amounts					
Compositions	Α	В	С	D	E	
Silicon dioxide (SiO ₂)	29.12	27.74	23.51	27.08	23.45	
Aluminum oxide (Al ₂ O ₃)	8.63	7.27	6.15	6.24	8.55	
Iron oxide (Fe ₂ O ₃)	6.00	3.96	4.00	5.01	7.50	
Calcium oxide (CaO)	43.85	49.97	58.51	52.54	50.82	
Magnesium oxide (MgO)	3.74	2.85	2.27	4.38	3.61	
Sulfur trioxide (SO ₃)	2.14	2.21	2.37	2.81	2.92	
Chloride (Cl [*])	0.006	0.0102	0.10	-	-	
Loss of Ignition (LOI)	2.50	4.99	2.04	1.17	2.43	
Unknown	4.02	-	-	0.71	0.25	
Non-melting residue	-	-	12.46	13.03	14.74	
Free Lime (f.CaO)	1.57	1.06	0.55	1.28	-	
Total additive amount	30.00	28.99	24.49	29.01	24.38	

Corrosion Tests

Corrosion experiments were conducted in two stages. In the first stage, the corrosion potential of steels embedded in concrete was measured every day for a period of 90 days in accordance with ASTM C876 method [14]. Saturated Copper/Copper Sulfate (Cu/CuSO₄) was used as a reference electrode, and a high impedance voltmeter was used as a measurement device in corrosion potential measurements. Changes in corrosion potentials versus time were indicated as graphics in order to determine whether the steel is in active or passive state. Recommendations on evaluation of potential measurement results in ASTM C876 experiment method are stated in Table 4 [6, 10, and 15]. In the second stage, anodic and cathodic polarization values of steel in the concrete samples were obtained by using the galvanostatic method and then the corrosion currents were determined with the aid of cathodic polarization curves.

 Table 4.
 Estimation of corrosion probability as determined by half-cell potential test

Potential, (mV),	Probability of the Presence of Active		
(CSE)	Corrosion		
> -200	The probability for corrosion is very low		
-200 ~ -350	Uncertain		
< -350	The probability for corrosion is very high		

Experimental setup used for the application of galvanostatic method is shown schematically in Figure 1.

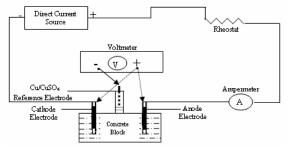


Figure 1. Schematic representation of the polarization measurement using galvanostatic method

Black areas on the electrodes displayed in Figure 1 indicate the areas kept under protection. In this circuit, the electrode which connected to the positive terminal was the anode and the electrode which connected to the negative terminal of the DC power source was cathode. DC power source applied as 20 volt fixed stress to the system.

RESULTS AND DISCUSSION

Corrosion potential changes versus time of the reinforcing steels embedded in the concrete samples are shown in Figure 2.

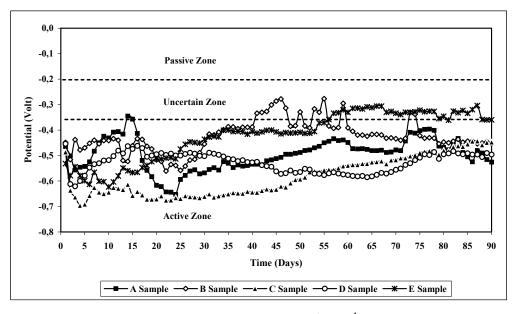


Figure 2. The change of corrosion potential on the concrete samples

As seen from Figure 2, positive potential increasing of the steels embedded all the concrete samples stayed very low during 90 days. As known, the corrosion of steel in concrete is essentially an electrochemical process. Iron is oxidized to ferrous ion which passes into solution in the anode region. In the cathode region, oxygen is reduced to hydroxyl ions. Anode and cathode form a short-circuited corrosion cell, with the flow of electrons in the steel and ions in the pore solution of the concrete [16]. In the anodic region, ferrous iron will react with hydroxyl group and generate ferrous hydroxide. Then it will be oxidized as ferric iron. Eqs. (1) and (2) show these processes.

$$\operatorname{Fe}^{2^+} + 2\operatorname{OH}^- \to \operatorname{Fe}(\operatorname{OH})_2$$
 (1)

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$$
(2)

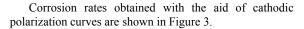
The deterioration effect of chloride iron during the electrochemical reaction is shown by Eqs. (3) and (4).

$$Fe^{2+} + 2Cl^{-} + 4H_2O \rightarrow 4FeCl_2.4H_2O$$
(3)

$$FeCl_2.4H_2O \rightarrow Fe(OH)_2 \downarrow + 2Cl_2 + H_2 \uparrow + 2H_2O \quad (4)$$

From the equations, we can see that the chloride iron neither participate reaction nor is it consumed by the reaction. But the chloride iron plays an important role in transporting the corrosion product. It is the catalyst of corrosion reaction. NaCl added in concrete mixture in order to create a corrosive atmosphere is the greatest factor preventing the steels in the concrete samples from becoming passivate during the period of experiment. Therefore, it was clearly seen from Figure 2 that corrosion potentials of the steels remained in the active zone in terms of corrosion. But, it is also understood from this figure that corrosion potential of the steel in E sample became more passive compare to the other samples and reached to uncertain zone in terms of corrosion at the end of the 2st month.

This situation was interpreted that the corrosion still continued even at the end of 90th day in A, B, C and D samples by taking ASTM C876 [14] as a reference. From the results of corrosion potentials by ASTM C876 standard, it can be said that the steels in the concrete sample which has been produced with E cement has higher corrosion resistance than the other concrete samples.



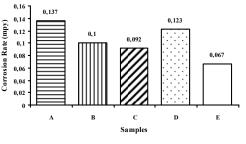


Figure 3. Corrosion rates of the samples

It is expected that the corrosion rate values of reinforcing steel embedded in concrete samples which were prepared with CEM II /B-M 32.5 R cement, should be practically similar. However, at the end of the 90th day, it was found that the corrosion rate of steel in sample A was the highest and corrosion rate of the steel in sample E was the lowest as seen in Figure 3. At the same time, the corrosion rate values of the B and C, A and D samples are close, which is also seen in Figure 3. Corrosion potential variations presented in Figure 2 are in nature supporting these results. In order to help interpreting the results, values for f.CaO, unknown, acid oxide, base oxide and total additives, which are encompassed by with CEM II /B-M 32.5 R Portland cements produced by A, B, C, D, and E factories, are presented in Table 5.

Table 5. f.CaO, unknown, acid oxide, base oxide and total additive amounts for the cements (wt. %)

	A B		С	D	Е
f.CaO	1.57	1.06	0.55	1.28	-
Unknown	4.02	-	-	0.71	0.25
Acid Oxide	31.26	29.95	25.88	29.89	26.37
Base Oxide	53.59	56.78	64.78	61.93	61.93
Total Additive Amount	30.00	28.99	24.49	29.01	24.38

As seen from Table 5, the amount of unknown components in the cement body is 4.02% for sample A, whereas, the highest unknown components amount in the cement body should be 1.0% according to the standard [17]. Furthermore, the amount of f.CaO in the cement body is 1.57% for sample A, whereas, the highest free lime amount in the cement body should be 1.0% according to the standard [17]. These situations may be some of the reasons which has highest corrosion rate of the sample A. Besides of these reasons, corrosion rate of the steel may have been change pH value of the sample. Because, acid oxide amount $(SiO_2 + SO_3)$ is higher and base oxide amount (Fe₂O₃ + CaO + MgO) is lower in specimen A in comparison to the other samples. This would be increased corrosion rate of the reinforcing steel in sample A by decreasing the pH value. Moreover, as understood from Table 5 that corrosion rates of the steel in samples have been affected from total additives amount.

CONCLUSIONS

which has highest corrosion rate.

As a result of this experimental study, it was found that the reason for the variation of corrosion rates of steels in concrete samples prepared with the same type of cement is the variety of cement raw material. The corrosion of steels embedded in concrete structures creates a major hazard and may cause dire consequences. Therefore, the most suitable raw material for CEM II /B-M 32.5 R cement type, which is widely used in the construction of today's structures in Turkey, should be identified and the negative consequences of cement type on corrosion of steel in concrete can be minimized by increasing cement quality.

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