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The effect of zeolite and diatomite on the corrosion of reinforcement steel in 1 M HCl solution

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ABSTRACT

The greatest disadvantage of reinforced concrete structures is the corrosion occurring in the reinforcement which, over time, causes a reduction in the reinforcement-concrete adherence and eventual sectional loss. The purpose of this study was to reveal the corrosion mechanism of ribbed reinforcement inside additive-free (reference), 20% zeolite-doped and 20% diatomite-doped concrete samples after exposure to 1 M HCl over 240 days. Electrochemical impedance spectroscopy (EIS) measurements were made every 10 days. Consequently, it was determined that the 20% zeolite-doped concrete samples had higher concrete and reinforcement resistance compared to the 20% diatomite-doped and the reference concrete, i.e. they exhibited less corrosion.

Introduction

Steel reinforced concrete has been extensively used for over a century. As a composite material, it incorporates many of the advantages of concrete and steel, being economical and suitable for on-site fabrication as well as possessing enhanced tensile strength [1]. Concrete is the most widely produced construction material on earth, with an annual consumption in the dozens of billion tons [2,3]. In spite of the advantages of reinforced concrete, corrosion of the steel bars remains its most common durability problem [4]. The reinforcement steel in concrete is usually inactive because the concrete provides a desirable high pH (∼13) medium and also acts as a physical barrier isolating the steel from aggressive elements in the environment [5]. However, steel will begin to corrode once aggressive ions penetrate through the concrete cover and reach a certain concentration.

The combination, or bonding, of the reinforcement and the concrete is called adherence. One of the major factors weakening the adherence of the concrete and reinforcement is corrosion. The bonds between the concrete and the reinforcement in an existing reinforced concrete structure are adversely affected in direct proportion to the amount of corrosion, and significant decreases in the strength of the construction elements may also be noted [6,7].

Internal stresses develop and cracks are observed on the concrete because of the volume enlargement resulting from the corrosion of the reinforcing bars. Generally, reinforcement corrosion is a major problem that occurs in reinforced concrete bridges, viaducts, onshore and offshore structures and structures in industrial regions [8–10]. Corrosion occurring in reinforced concrete elements is a significant factor that indisputably threatens and even negates the safety of the structure [11,12].

One of the main causes for deterioration in concrete structures is the corrosion of the concrete due to its exposure to harmful chemicals found in nature and in the environment, such as in some ground water, industrial effluents, acid rain, acid mist, and seawater [13,14].

Today, it is known that hydrochloric acid is a considerably harmful chemical for reinforced concrete structures. It is used in almost every field, from the manufacturing of PVC to iron–steel production and from the production of organic material to the food sector industries [13]. Meanwhile concrete has contact with HCl during manufacturing process.

Zeolite, a natural pozzolana, achieves a bonding property by reacting with $Ca(OH)_2$ such as is found in the fly ash and silica fume in concrete. Previous studies have shown that the porosity in cement paste samples prepared with zeolite was reduced over time, and in addition to the positive physical and mechanical properties of zeolite, it was found to be a factor affecting the durability of concrete [15–17].

Diatomite is a pozzolanic substance containing small amounts of amorphous silica, cristobalite, and waste minerals [18]. Diatomite is an important industrial ore and may develop in pure, sandy, alluvial, clayey, calcareous, marly, and tuff type media.

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Table 1
Composition of the low carbon steel sample used in the experiment.

Elements	C	Mn	Si	P	S	Ni	Cr	Mo	Sn	Fe
Wt. (%)	0.36	0.23	0.20	0.61	0.025	0.11	0.12	0.01	0.02	98.315

Table 2
Chemical structure and physical properties of the concrete samples.

Chemical components%	Reference	Pure Diatomite	Pure Zeolite
SiO_2	18.68	79.56	68.85
Al_2O_3	4.67	6.54	11.71
Fe_2O_3	3.53	2.76	1.29
CaO	64.56	2.45	3.97
MgO	0.98	0.79	1.06
SO_3	3.00	0.48	0.18
Na_2O	0.14	2.63	0.29
K_2O	0.73	0.69	2.19
Loss of ignition	3.92	3.88	10.00
Free lime	1.74	–	–
Insoluble residue	0.50	75.98	37.32

Physical properties	Reference	Pure Diatomite	Pure Zeolite
Blaine size (cm^2/g)	4249	13,640	5740
Specific weight(g/cm^3)	3.17	2.28	2.18
90 μm Sieve analyses (%)	4.08	9.80	17.60
45 μm Sieve analyses (%)	–	28.60	35.80

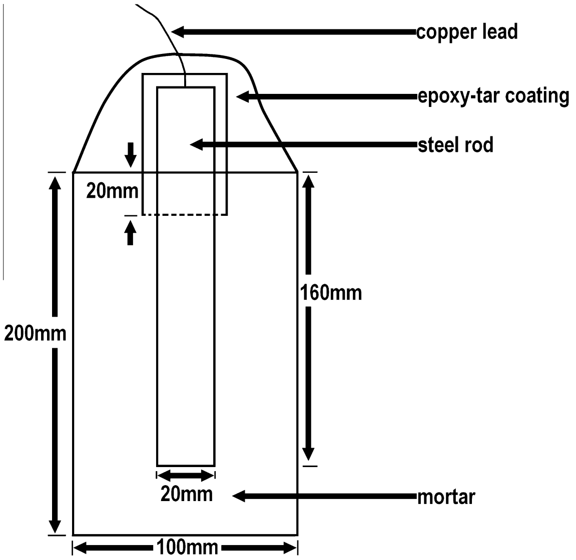

Fig. 1. Schematic view of the concrete reinforcement.

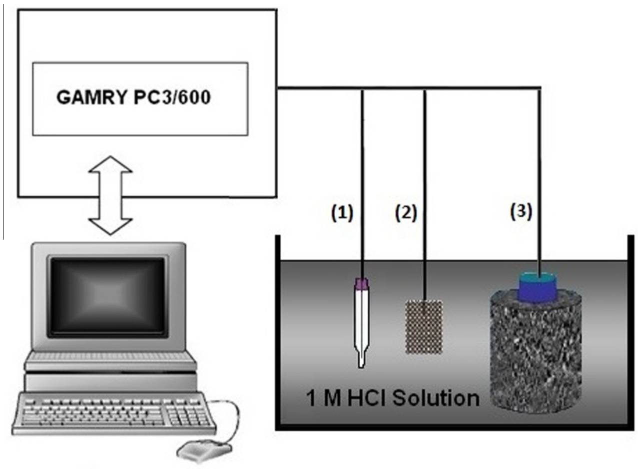

Fig. 2. Experimental setup: (1) Ag/AgCl electrode; (2) Pt wire; (3) Working electrode.

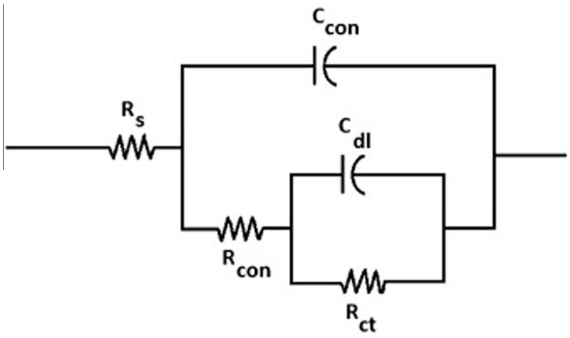

Fig. 3. *R(C(R(CR)))* circuit.

Lately, there has been extensive research on the usage of diatomite as a cement additive [19,20]. The studies conducted have proved that diatomite increases the resistance of blended cements [21,22].

Gerengi et al. comprehensively investigated the corrosion of ribbed reinforcement inside additive-free (reference), 20% zeolite-doped, and 20% diatomite-doped concrete samples in a solution of 0.5 M H_2SO_4 in order to simulate and examine the effect of acid rain [23].

In the present study, instead of using a 0.5 M H_2SO_4 solution, ribbed reinforcement inside additive-free (reference), 20% zeolite-doped, and 20% diatomite-doped concrete samples were exposed to a solution of HCl similar to that common in industrial use. The corrosion was measured via electrochemical impedance spectroscopy (EIS) every 10 days over a period of 240 days and the results were evaluated.

Materials and method

Preparation of the working electrode

Table 1 illustrates the composition of the ribbed structural steel sample used in the experiment. Table 2 illustrates the chemical composition and some physical properties of the materials used in the preparation of the concrete samples. Additional ratios of the three types of concrete samples that were prepared (20% diatomite-doped, 20% zeolite-doped and additive-free reference) are shown in Table 2. The total cross-sectional area of each sample was equal to 94.2 cm^2 (Fig. 1). The experimental samples were prepared by using Portland cement TS EN 197-1 [24] CEM I 42.5 R concrete binder [25] in accordance with the standards. The diatomite and zeolite were procured from the Turkish regional sources of Kütahya and Balıkesir, respectively. Well water obtained from Düzce was used in the mixture and the water/cement ratio was fixed as 0.5. Porosity values were measured 15 days after the samples were immersed in the solution, in accordance with ASTM C642 [26] standards. The lowest porosity values were determined as 0.85, 2.05, and 4.67 for the zeolite, reference and diatomite samples, respectively.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a method that has been successfully used for corrosion rate measurements for the past 30 years. This electrochemical measurement technique is operated by alternative current (AC) and is used in nearly every sector because it provides extensive information about the electrochemical structure of a system [27]. In recent times, EIS has been widely used to determine the corrosion rate of the reinforcement inside concrete [28,29]. Because EIS contributes less damage to the working electrode as compared to electrochemical measurements performed by using direct current sources [30], the same sample can be used repeatedly for EIS measurements [31]. This method, via a suitable equivalent circuit, measures the electrical response of the metal/solution interface within the specified frequency range and enables the determination of the electrochemical parameters required to evaluate the corrosion mechanism [32].

The corrosion mechanism of the three differently composed concrete samples (20% diatomite-doped, 20% zeolite-doped and additive-free reference) in 1 M HCl was analyzed over 10-day periods for 240 days by using the EIS method. Fig. 2 shows the experimental apparatus. In the triple electrode system, low carbon steel was used as the working electrode, Ag/AgCl as the reference electrode and Pt wire as the counter electrode.

Measurement of the corrosion potential of the steel in the concrete samples was performed within the 0.01–100 kHz frequency range using the GAMRY PC3/600 potentiostat/galvanostat/ZRA system; ZsimpWin 3.21 software was used to conduct the impedance

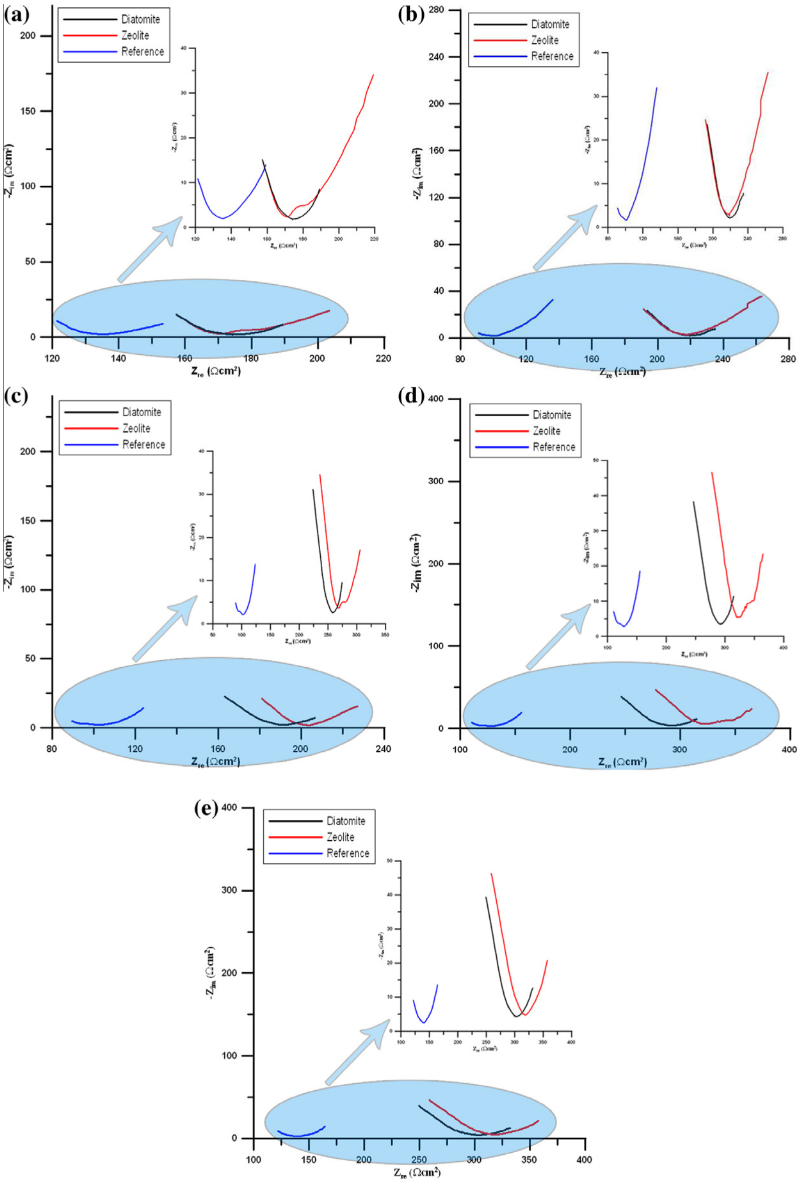

Fig. 4. Nyquist curves obtained at the end of (a) 1, (b) 30, (c) 60, (d) 120 and (e) 240 days.

analyses, and the resistance values were calculated using the *R(C(R(CR)))* circuit model (Fig. 3). In the electrical circuit, R_{ct} was the change transfer resistance, C_{dl} the capacitance of the double layer, C_{con} the concrete capacitance, R_{con} the resistance of the concrete, and R_s the solution resistance [33].

Results and discussion

In the experiment, Zeolite- and diatomite-doped and reference concretes were subjected to 1 M HCl over 10-day periods for 240 days. At the end of 240 days, the resistances of the concrete and the reinforcement inside were measured and the results were compared. The resistance of the reinforcement and concrete in reference to these samples can be seen in Fig. 4(a–e), which shows the Nyquist curves of the samples at the end of 1, 30, 60, 120, and 240 days, respectively.

It was observed that all the Nyquist curves given in Fig. 4 had similar configurations. Nyquist curves similar to a half arch that formed in high frequency and low frequency regions have also been reported in previous studies [33–35]. Ping Gu et al. [36] gave an explanation for the pattern shown in Fig. 5. The first arch within the high-frequency range is formed by the effect of the concrete matrix [37]. The second arch in the low-frequency range defines the corrosion process on the reinforcement surface. The reduction in the size of the arch formed in the high-frequency region is based on the increase in the porosity of the concrete samples and the ion concentration in the cement paste [38].

As can be seen in Fig. 4(a–e), the scale of the arch formed in the high-frequency region depending on exposure time in the reference sample decreased on average from 13 to 8 Ω cm^2, while the arch formed in the low-frequency region depending on exposure time enlarged. This difference showed that the porosity of the reference sample had increased with time. The difference in the R_{con} value measured over time in Fig. 6 verifies this as well. While the resistance of the reference sample (R_{con}) decreased over time, an increase was observed in the diatomite and zeolite samples, subject to the decrease in porosity.

The changes measured in the Nyquist curves of the diatomite and zeolite concrete samples (Fig. 4(a–e)) were the reverse for the reference sample. The size of the arch formed in the high-frequency region increased on average from 15 to 42 Ω cm^2, while the size of the arch formed in the low-frequency region decreased approximately from 35 to 20 Ω cm^2. All these results supported the increase in the R_{con} changes of the diatomite- and zeolite-doped concrete samples given in Fig. 6.

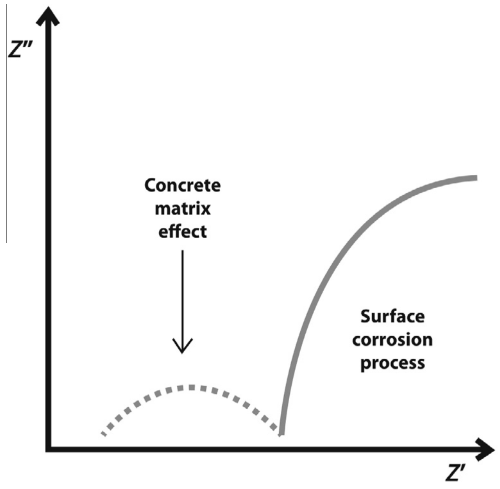

Fig. 5. Nyquist curves showing the general corrosion mechanism of the reinforcement inside the concrete.

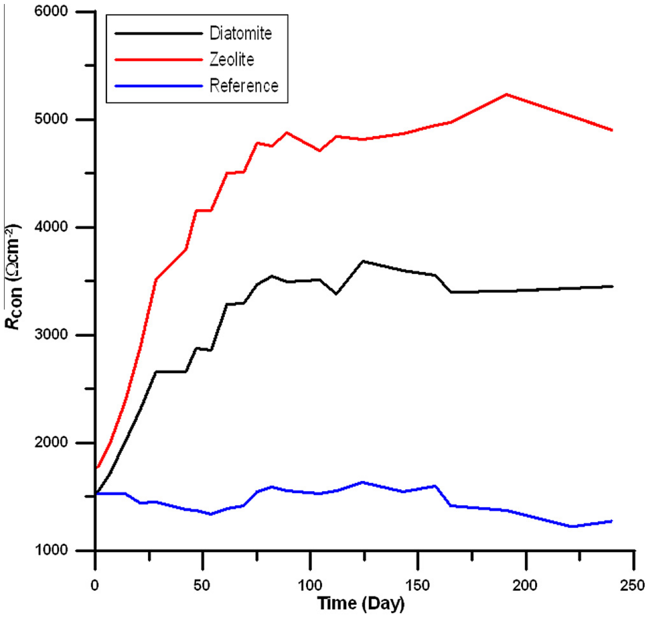

Fig. 6. Graphical representation of the changes occurring in the concrete resistance during the measurements.

At the end of the 240 days, the R_{con} values had increased from 1790 to 4700 Ω cm^2 in the zeolite samples and from 1540 to 3450 Ω cm^2 in the diatomite samples, whereas this value had decreased from 1620 to 1420 Ω cm^2 in the reference sample. As can be seen, the difference in the other samples was considerably higher than that in the reference sample.

Fig. 7 shows the changes occurring over time in the resistance of the reinforcement inside the concrete samples (R_{ct}). At the end of 240 days, the measured R_{ct} value increased from 3970 to 4276 Ω cm^2 for the zeolite sample and from 1245 to 2300 Ω cm^2 for the diatomite sample, while this value decreased from 6520

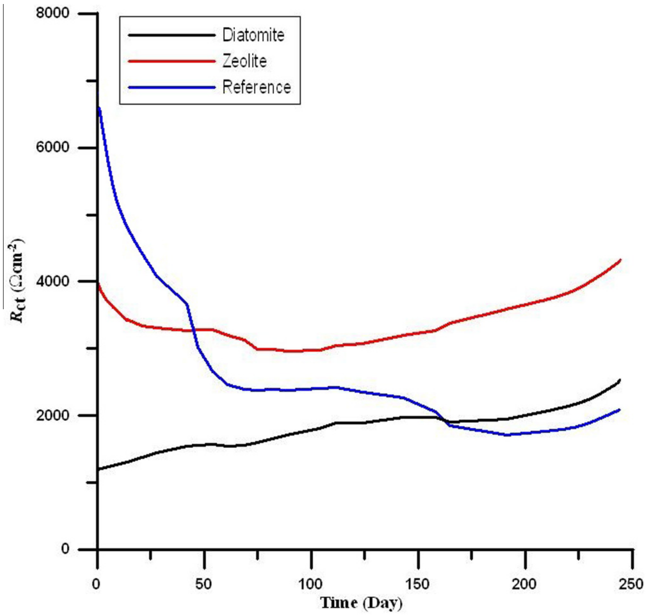

Fig. 7. Graphical representation of the changes occurring in the reinforcement resistance during the measurements.

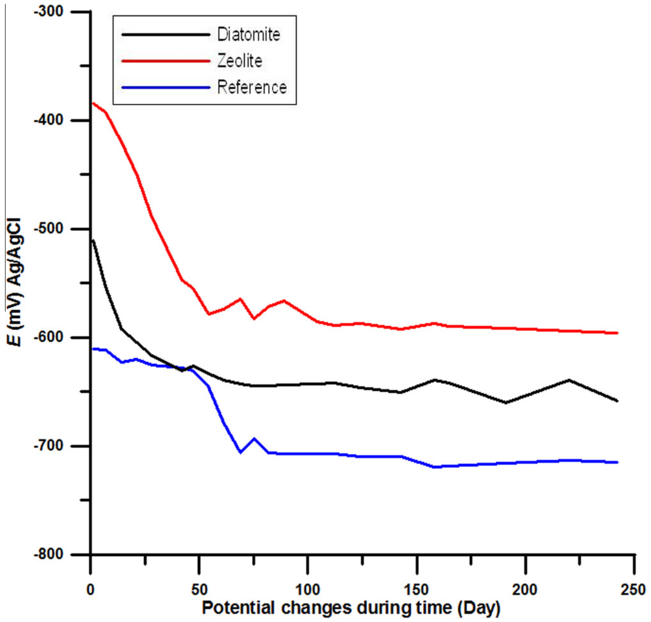

Fig. 8. Graphical representation of the changes occurring in the potential during the measurements.

to 1750 $\Omega\,\text{cm}^2$ in the reference sample. These data supported the changes in the R_{con} data. The increase in the R_{con} and R_{ct} values of the diatomite and zeolite samples showed that the porosity had decreased and thus, the reinforcement was exposed to fewer corrosive effects.

Regular measurement of the reinforcement potential is one of the most common procedures used for the routine supervision of reinforced concrete structures [39]. Fig. 8 shows the open circuit potentials measured for 240 days. According to ASTM C876-09 standards, if the open circuit potential value measures are more negative than 270 mV/SCE [40] or 225 mV/Ag,AgCl, there is a 90% probability that corrosion is present. All of the samples in this experimental study were below this potential value. While the potential of the reference sample decreased to -685 mV at the end of 240 days, this value in the diatomite and zeolite samples was measured more positively as -643 and -585 mV, respectively. These data supported the R_{con} and R_{ct} changes. The potential change of the reinforcement in the zeolite sample showed that it was exposed to less corrosion by being in a more positive region compared to the diatomite and reference samples.

Conclusion and recommendations

1. The results obtained in this study showed that the additives to the concrete were important for the corrosion behavior of the reinforcement in 1 M HCl.
2. The EIS measurements showed that the electrical parameters (R_{con}, R_{ct} and E) were compatible with and supportive of each other.
3. It was observed that the reinforcement inside the zeolite-doped concrete in the 1 M HCl medium exhibited less corrosion compared to the diatomite-doped and reference samples.
4. It was thought that use of the zeolite and diatomite additives reduced the concrete porosity over time and thus, the reinforcement corrosion was less than in the reference sample.
5. Based on these results, in terms of high corrosion resistance, zeolite-doped concrete is recommended for use in environments where 1 M HCl is present.

Acknowledgments

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References

[1] MacGregor JG. Reinforced Concrete Mechanics and Design. 2nd ed. New Jersey: Englewood Cliffs; 1992.
[2] Pradhan B. Corrosion behavior of steel reinforcement in concrete exposed to composite chloride–sulfate environment. Constr Build Mater 2014;72:398–410.
[3] Montemor MF, Simoes AMP, Ferreira MGS. Chloride-induced corrosion on reinforcing steel: from the fundamentals to the monitoring techniques. Cem Concr Compos 2003;25:491–502.
[4] Hussain SE, Rasheeduzzafar. Corrosion resistance performance of fly ash blended cement concrete. ACI Mater J 1994;91:264–72.
[5] Montemor MF, Simoes AMP, Salta MM. Effect of fly ash on concrete reinforcement corrosion studied by EIS. Cem Concr Compos 2000;22:175–85.
[6] M. Erbil, Korozyon İlkeler Önlemler, Ankara, 2012 (in Turkish).
[7] Togcu IB, Boga AR. Effect of corrosion on adherence between reinforcement and concrete for reinforced concrete. Eng Arch Fac Eskisehir Osmangazi University 2008;21:23–38.
[8] Cakır O, Effect of ground granulated balast furnace slag on the durability of concrete and reinforced concrete, Istanbul; 2006 (in Turkish).
[9] Lee HS, Noguchi T, Tomosawa F. Evaluation of the bond properties between concrete and reinforcement as a function of the degree of reinforcement corrosion. Cem Concr Res 2002;32:1313–8.
[10] Coskan S, Yüksel İ, Betonarme binalarda mevcut donatı korozyonunun deprem davranışına etkileri, 2. Türkiye Deprem Mühendisliği ve Sismoloji Konferansı, MKÜ, Hatay, 25–27 Eylül; 2013.
[11] Cil I. Corrosion measurement of rebars by electrical methods, D.E.U.. J Sci Eng 2006;8:59–63.
[12] Cheng A, Huang R, Wu JK, Chen CH. Influence of GGBS on durability and corrosion behavior of reinforced concrete. Mater Chem Phys 2005;93:404–11.
[13] Huang P, Bao Y, Yao Y. Influence of HCl corrosion on the mechanical properties of concrete. Cem Concr Res 2005;35:584–9.
[14] Shannand MJ, Shaia HA. Sulfate resistance of high-performance concrete. Cem Concr Compos 2003;25:363–70.
[15] Karakurt C, Topçu IB. Effect of blended cements with natural zeolite and industrial by-products on rebar corrosion and high temperature resistance of concrete. Constr Build Mater 2012;35:906–11.
[16] Valipour M, Pargar F, Shekarchi M, Khani S. Comparing a natural pozzolan, zeolite, to metakaolin and silica fume in terms of their effect on the durability characteristics of concrete. Constr Build Mater 2013;41:879–88.
[17] Valipour M, Pargar F, Shekarchi M, Khani S, Moradian M. In situ study of chloride ingress in concretes containing natural zeolite, metakaolin and silica fume exposed to various exposure conditions in a harsh marine environment. Constr Build Mater 2013;46:63–70.
[18] Ergun A. Effects of the usage of diatomite and waste marble powder as partial replacement of cement on the mechanical properties of concrete. Constr Build Mater 2011;25:806–12.
[19] Xu S, Wang J, Ma Q, Zhao X, Zhang T. Study on the lightweight hydraulic mortars designed by the use of diatomite as partial replacement of natural hydraulic lime and masonry waste as aggregate. Constr Build Mater 2014;73:33–40.
[20] Yi-qiu T, Lei Z, Xing-you Z. Investigation of low-temperature properties of diatomite-modified asphalt mixtures. Constr Build Mater 2012;36:787–95.
[21] Degirmenci N, Yilmaz A. Use of diatomite as partial replacement for Portland cement in cement mortars. Constr Build Mater 2009;23:284–8.
[22] Yılmaz B, Ediz N. The use of raw and calcined diatomite in cement production. Cem Concr Compos 2008;30:202–11.
[23] Gerengi H, Kocak Y, Jazdzewska A, Kurtay M, Durgun H. Electrochemical investigations on the corrosion behaviour of reinforcing steel in diatomite- and zeolite-containing concrete exposed to sulphuric acid. Constr Build Mater 2013;49:471–7.
[24] Cement- Part 1: Compositions and Conformity Criteria for Common Cements, TSE EN 197–1, Ankara; 2002.
[25] Tkaczewska E, Mroz R, Łoj G. Coal-Biomass fly ashes for cement production of CEM II/A-V 42.5R. Constr Build Mater 2012;28:633–9.
[26] Kuo WT, Wang HY, Shu CY, Su DS. Engineering properties of controlled low strength materials containing waste oyster shells. Constr Build Mater 2013;46:128–33.
[27] Cogger ND, Evans NJ, An Introduction To Electrochemical Impedance Measurement Technique Report, Solartron Instrument; 1999.
[28] Sobhani J, Najimi M. Electrochemical impedance behavior and transport properties of silica fume contained concrete. Constr Build Mater 2013;47:910–8.
[29] Bragança MOGP, Portella KF, Bonato MM, Marino CEB. Electrochemical impedance behavior of mortar subjected to a sulfate environment – A comparison with chloride exposure models. Constr Build Mater 2014;68:650–8.

[30] Bereket G, Gerengi H, How truly electrochemical measurements are evaluated in corrosion researches? In: XIII. International corrosion symposium, Fırat University, Turkey, 15–17; October 2014.

[31] Gerengi H, Akcay C, Ozgan E, Arslan I. Investigation on the corrosion of low carbon steel placed in asphalt concrete in 3.5% NaCl environment. J Graduate School Nat Appl Sci Mehmet Akif Ersoy Univ 2012;3:5–11.

[32] Techniques for Monitoring Corrosion and Related Parameters in Field Applications, Item No. 24203; NACE International Publication 3T199. (1999) 1–41.

[33] Gurten AA, Kayakirilmaz K, Erbil M. The effect of thiosemicarbazide on corrosion resistance of steel reinforcement in concrete. Constr Build Mater 2007;21:669–76.

[34] Choi YS, Kim JG, Lee KM. Corrosion behavior of steel bar embedded in fly ash concrete. Corros Sci 2006;48:1733–45.

[35] Qiao G, Ou J. Corrosion monitoring of reinforcing steel in cement mortar by EIS and ENA. Electrochim Acta 2007;52:8008–19.

[36] Ping G, Elliott S, Hristova R, Beaudoin JJ, Brousseau R, Baldock B. A study of corrosion inhibitor performance in chloride contaminated concrete by electrochemical ımpedance spectroscopy. ACI Mater J 1997;94:385–94.

[37] McCarter WJ, Brousseau R. The A.C. response of hardened cement paste. Cem Concr Res 1990;20:891–900.

[38] Xu Z, Gu P, Xie P, Beaudoin JJ. Application of A.C. impedance techniques in studies of porous cementitious materials, (II). Relationship between ACIS behavior and the porous microstructure. Cem Concr Res 1993;23:853–62.

[39] Pour-Ali S, Dehghanian C, Kosari A. Corrosion protection of the reinforcing steels in chloride-laden concrete environment through epoxy/polyaniline–camphor sulfonate nanocomposite coating. Corros Sci 2015;90:239–47.

[40] Standard test method for corrosion potentials of uncoated reinforcing steel in concrete. ASTM C876–09; 2009.