# Investigation of Chloride Diffusion Behavior of Concrete Manufactured with Blended Mineral Admixtures Using Electrochemical Technique

*Yong-quan Xiong*

School of Architectural Engineering, Sichuan University of Arts and Science, Dazhou, Sichuan Province, 635000, China
E-mail: xyq20110026@sina.com

Chloride-induced reinforcement corrosion has already been identified as a significant durability issue in reinforced concrete systems in the world. Here, the chloride ion diffusion in concrete structures blended with furnace slag (FS) and bottom ash (BA) admixtures were studied by soaking and electrochemical impedance spectroscopy (EIS) techniques. According to the EIS findings, increasing the volume of FS and BA improves resistance to chloride ion migration. The use of BA at 30% helped to increase the compressive strength of the concrete after 28 days of curing time. The soaking results revealed that the F-30BA sample significantly effect on the migration of chloride ions in concrete structures containing FS and BA additives. The surface morphology of steel rebar exhibited that a little corrosion product and slight pits were found on the surface of steel in F-30BA sample which was in the accordance with the results obtained from soaking and EIS tests.

## 1. INTRODUCTION

Corrosion of steel reinforcement is a significant issue in the long-term stability of reinforced concrete structures [1]. The transport of chloride, sulfate, and carbon dioxide by the interconnected pore space of concrete is known as a major property of the material and a corrosion rate controlling parameter [2, 3]. By minimizing diffusion and the permeability of aggressive species and moisture to the interface of steel concrete, Portland cement (PC) concrete containing Pozzolanic materials improves long-term durability and excellent mechanical properties [4]. The effect of different kinds of mineral admixtures on the corrosion resisting properties of concrete has been investigated by research and it has been reported that additives such as natural pozzolanic materials and industrial by-products are important materials for protection of reinforcing rebars in concrete [5, 6]. These mineral additives

are used to lower costs and improve the properties of concrete, especially its durability, which may help minimize reinforcement corrosion [7]. They are also more eco-friendly because they are made from industrial waste or need less energy to manufacture than traditional PCs.

Bottom ash (BA) is a coarse, incombustible, granular by-product composed from the furnace bottom. BA is used as construction materials, roofing granules, abrasive blasting grit, aggregate of concrete and so on [8]. Some researchers have published research on the use of BA in concrete as a cementitious supplementary material [9, 10] or as a partial replacement for natural aggregates [11, 12]. Furnace slag (FS) formed once molten blast-furnace slag is quickly chilled, as by dipping in water [13]. The combination of granulated-blast furnace slag may reduce the content of cement and be an alternative material in rigid economic structure.

The majority of current blended concrete research has focused on improving its stability to protect against the influence of damaging agents that may cause corrosion, as well as testing the material without taking reinforcing steel behavior into account [14]. Electrochemical techniques like electrochemical impedance spectroscopy (EIS) and linear polarization have, however, begun to be utilized in some recent concrete studies [15, 16]. While these methods were primarily used to research corrosion processes in metals and coatings, they can now be used to predict the behavior of concrete and reinforced steel [17].

Chloride diffusion is studied using experiments that assume either steady-state flows or non-steady-state flows through the sample [18]. The steady-state chloride diffusion experiments conducted with diffusion cells are time-consuming and impractical since cement paste samples are used instead of concrete samples [19]. Cyclic wetting and drying, as well as soaking experiments that mimic non-steady-state chloride flow in the sample, are time consuming but suitable for long-term studies. With these concerns in mind, this paper uses both EIS and soaking techniques to investigate chloride diffusion phenomena in mortars containing BA and FS mineral admixtures.

## 2. MATERIALS AND METHODS

Concrete was made in this study using Portland cement (PC), fine, coarse aggregates, and water under controlled conditions at room temperature. The cement replacing was done with BS and FS. Table 1 indicates the chemical compositions of PC, BS and FS. The ratio of water to cement was 0.45.

**Table 1.** Chemical compositions of PC, BA and FS

|  | PC (wt%) | BA (wt%) | FS (wt%) |
|---|---|---|---|
| $SiO_2$ | 20.45 | 51.26 | 33.87 |
| $Fe_2O_3$ | 3.12 | 4.28 | 1.22 |
| $Al_2O_3$ | 4.89 | 24.64 | 11.22 |
| CaO | 64.15 | 7.43 | 38.92 |
| MgO | 2.02 | 2.18 | 0.63 |
| $Na_2O$ | 0.25 | 0.75 | 0.37 |
| $K_2O$ | 0.67 | 1.65 | 1.62 |
| $SO_3$ | 2.98 | 0.25 | 0.06 |
| LOI | 0.87 | 0.53 | 0.62 |

Table 2 exhibits the compositions of the different mixtures which were used in this research. In this study, the PC were replaced with different admixtures such as free-admixture, 10% FS, 10% FS and 10% BA, 10% FS and 20% BA, and 10% FS and 30% BA, which are indicated as PC, FS, F-10BA, F-20BA and F-30BA, respectively. The prepared cement mixtures were placed in cylinder molds with a diameter of 12cm and a height of 25cm at ambient temperature for 24 hours with a relative humidity of 90%. In order to investigate the replacement effect of BA and FS in PC on chloride diffusion, electrochemical tests were done on steel reinforced concretes in 3.5wt% NaCl media as aggressive ions in an immersion time of 28 days. A steel rebar with a diameter of 10mm and a length of 10cm was placed in the center of the cylinder. Table 3 shows the chemical compositions of steel.

**Table 2.** Mixture proportions for different concrete structures

| Admixtures | PC (wt%) | FS (wt%) | BA (wt%) |
|------------|----------|----------|----------|
| PC | 100 | 0.0 | 0.0 |
| FS | 90 | 10 | 0 |
| F-10BA | 80 | 10 | 10 |
| F-20BA | 70 | 10 | 20 |
| F-30BA | 60 | 10 | 30 |

**Table 3.** The chemical composition of commonly used steel rebar(wt%)

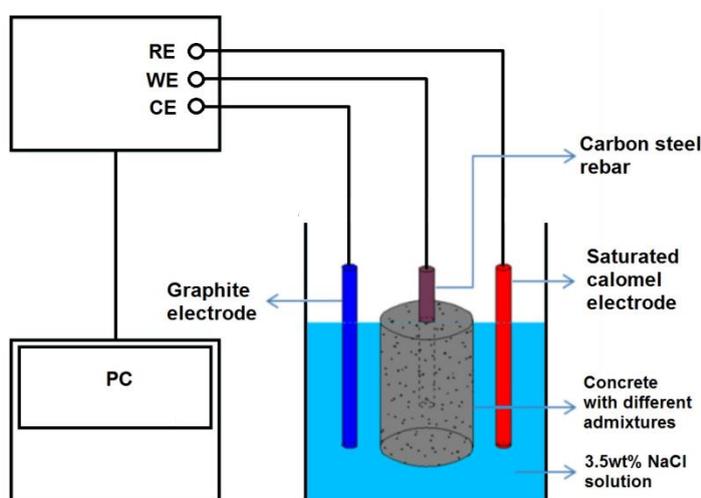| Carbon | Si | Cr | S | Ni | Mn | P | Fe |
|--------|------|------|-------|------|------|--------|----------|
| 0.16 | 0.26 | 0.14 | 0.018 | 0.11 | 0.47 | 0.0048 | Residual |



**Figure 1.** Schematic diagram of EIS technique

The steel rebars were inserted vertically into the middle of the cylinder mold to create a working electrode, and the concrete mix was transported in cylindrical molds. The chloride diffusion

phenomena in concrete systems were investigated using the EIS technique. Carbon steel reinforced concrete, saturated calomel, and graphite electrodes were used as working, reference, and counter electrodes, respectively. Figure 1 shows a schematic diagram of used EIS technique. The results were obtained after immersion in an aggressive medium of 3.5wt% NaCl. The EIS was performed at frequencies ranging from 0.01Hz to 0.1MHz. The surface morphology of the specimens was examined using a scanning electron microscope (SEM). All of the mixture specimens were also subjected to compressive strength checks four weeks after curing, which is the recommended minimum curing period for concrete structures. These experiments were carried out in accordance with ASTM C10911.

To assess the chloride migration depth, the test samples were taken out of the soaking tank at regular intervals during the immersion period in 3.5wt% NaCl solution. After splitting the prism on the compression-testing machine, the freshly split surfaces were sprayed with 0.10N $AgNO_3$ solution. The $AgNO_3$ solution reacts with the free-chloride existing in the hardened matrix to form a white AgCl precipitate, while $AgNO_3$ reacts with the hydroxides to form the brown AgO precipitate at greater depths where free-chlorides are absent. As a result, the depth of chloride movement is easily visible as the colour boundary changes.

## 3. RESULTS AND DISCUSSION

The effect of mineral admixtures on the cementitious system's EIS was investigated, and the results are shown in Figure 2. Because of the addition of FS, the diameter of the semi-circle has grown in diameter. The micro-aggregate filling effect results in a more dense paste in terms of microstructure [20], preventing ions from migrating across the solid/liquid interface. From an electrochemical standpoint, the pozzolanic reactions of the mineral additives and the increasing replacement of the mineral admixtures content reduce the hydroxide in cementitious systems [21]. Snyder et al. [22] indicated that $OH^-$ was the most powerful conductive ion in cementitious materials' pore solution. Electro-migration will be reduced as the hydroxyl content decreases [23]. As a result of the decrease in OH, the radius of the Nyquist plot will increase. Figure 2 shows the same findings when the BA content is increased. The chloride ions diffusion of cement binary incorporated with FS and BA can be traced using Nyquist curves. However, it is essential to establish a relationship between the migration depth of Cl ions and the EIS parameters. The diffusion of chloride ions has the largest impact on the solid-liquid phase interface of cementitious materials [24].
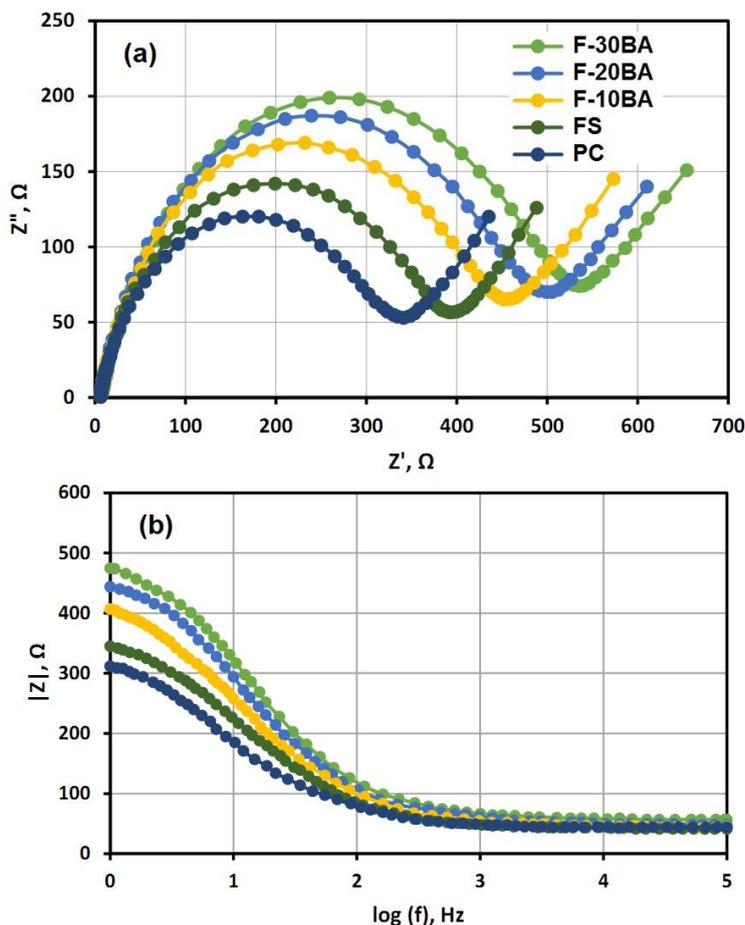
**Figure 2.** (a) Nyquist and (b) Bode plots of carbon steel reinforced concrete samples with different admixtures after 3 days immersion in 3.5wt% NaCl solution at room temperature

As shown in figure 2b, by the addition of FS and BA, the modulus-values were increased. The micro-aggregate filling effect results in a more dense paste in terms of microstructure which indicates that the chloride ions diffusion of cement binary incorporated with FS and BA can be decreased.

Figure3 shows an equivalent circuit model to fit EIS records. $R_s$ indicates the solution resistance. $R_1$ and $Q_1$ represent resistance and capacitance of the concrete samples, respectively. $R_2$ and $Q_2$ show the charge-transfer resistance and double-layer capacitance of steels, respectively [25]. The value of $R_1$ is critical since it determines the resistance to ion migration into the cement inner structure, which is inversely proportional to the number of hydrated electrons into the cement internal structures and the content of OH ions in the concrete [26, 27]. As a result, the R1 value is sufficient to assess chloride migration in concrete structures.
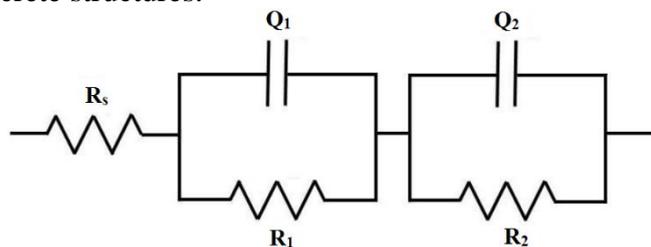


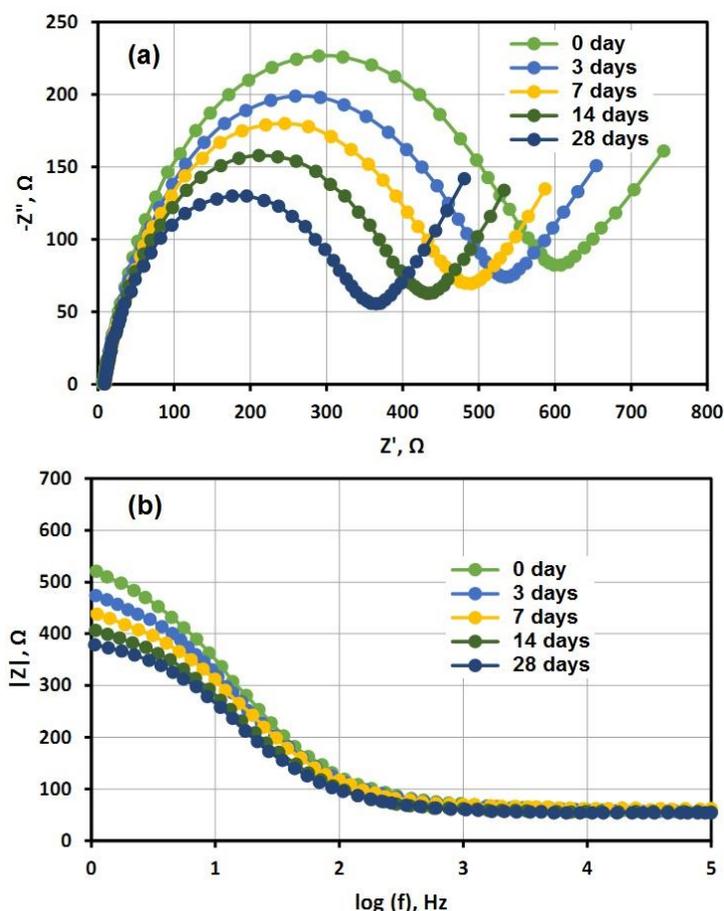**Figure 3.** An equivalent circuit model

**Figure 4.** (a) Nyquist and (b) Bode plots of carbon steel reinforced F-30BA concrete sample after different diffusion in 3.5wt% NaCl solution at room temperature

The Nyquist plots measured after different diffusion times for F-30BA sample are given in Figure 4a. These plots indicate that the semi-circle diameter falls systematically by the migration procedure of Cl ions. The decrease is due to an increase in the chloride ion content in the paste as the EIS test progresses. The bode plot represented in Figure 4b displays that migration time leads to the rise in the modulus-value. Table 4 shows the $R_1$ value derived from data fitting findings.

**Table 4.** The $R_1$ values attained from the plot fitting with circuit model for different concrete structures at various migration times

| Admixtures | 0 day | 3 days | 7 days | 14 days | 28 days |
|---|---|---|---|---|---|
| PC | 449 Ω | 362Ω | 304 Ω | 195 Ω | 35 Ω |
| FS | 491 Ω | 412Ω | 373 Ω | 260 Ω | 108 Ω |
| F-10BA | 539 Ω | 481Ω | 446 Ω | 365 Ω | 188 Ω |
| F-20BA | 586 Ω | 538Ω | 503 Ω | 437 Ω | 257 Ω |
| F-30BA | 613 Ω | 585Ω | 533 Ω | 465 Ω | 335 Ω |

The $R_1$ resistance to ion transfer phase in cementitious materials decreases with migration time. As a result, after chloride ion ingress, the $R_1$ value has been used to evaluate the EIS of cement mixed with BA or/and FS. Table 4 reveals that the value of $R_1$ decreases as migration time increases, resulting in an equation that is a function of Cl ion migration depth and $R_1$[24]:

$$D \sim \sqrt{(R_1(0) - R_1(t))} \qquad (1)$$

Where D represents migration depth of chloride ions, $R_1(0)$ shows the value of R1 at beginning time of Cl ion diffusion (0 day), and $R_1(t)$ indicates to the value of $R_1$ after t-days migration. Eq. (1) can be used to calculate the depth migration of chloride ions in the following diffusion time of chloride ions.
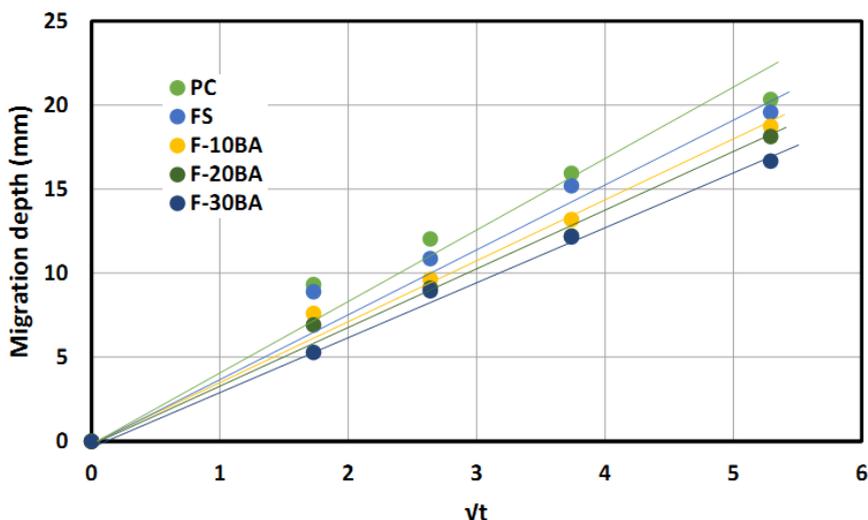


**Figure 5.** The measured migration depth of Cl ions and the fitting lines for blended samples with FS or/and BA.

The estimated depth assumed by equation (1) and measured depth migration of Cl ions depth for blended samples with FS or/and BA are compared in Figure 5. The EIS technique is capable of predicting the migration depth of chloride ions into cementitious materials with various replacements of FS or/and BA, based on the findings and discussion which are comparable to previous reports [28-31].

Figure 6 depicts the compressive strength of the specimens. It can be calculated if the F-30BA mix has a greater strength at each exposure period by comparing the different replacement admixtures. The high $Al_2O_3$ content of BA could explain the increased strength [32]. It reacts in both pozzolanic and hydraulic methods, resulting in a denser and more porous structure[33]. The F-30BA mixture was also shown to have a higher strength than the other samples. Furthermore, for each percentage of BA replacements, concrete with the BA had higher primary strength. Both admixtures had a final strength that was higher than the PC specimen.
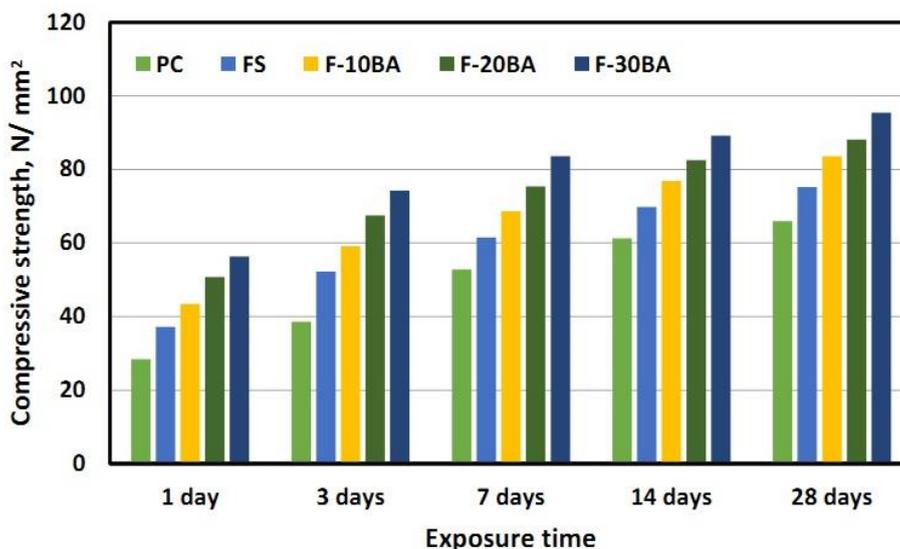
**Figure 6.** Compressive strength of samples with different admixtures at various curing times
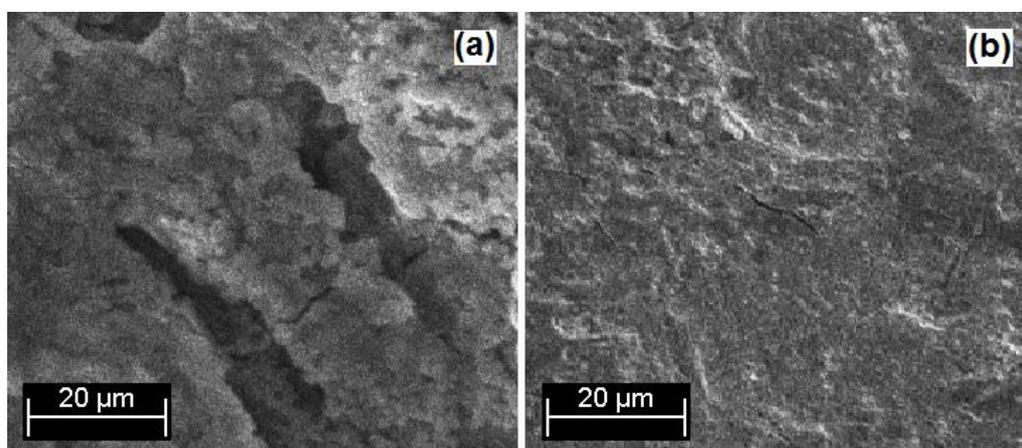


**Figure 7.** SEM images of carbon steel rebar in different concrete samples (a) PC, (b) F-30BA after 14 days immersed in 3.5wt% NaCl media

Figure 7 indicates the SEM image of carbon steel rebar in different concrete samples after 14 days immersed in 3.5wt% NaCl media. The surface of steel rebar in the F-30BA sample shows low corrosion products and minimum pits, indicating the mild pitting corrosion shaped on the steel surface, which is in line with electrochemical research findings. It may be linked to a reduction in the permeability of aggressive and chloride ions in reinforced concrete specimens.By inserting FS and BA admixtures, the big pores in the cement paste may be converted to smaller pores, resulting in a shift in the cement paste's structure. Because of the reduction in permeability of chloride ions and water, partial replacement of BAs in Cement paste resulted in a reduction in chloride migration and improved the resistance to corrosion of steel rebar.

Depths of chloride migration were measured for the concrete samples during the 28 day soaking test were utilized to measure the coefficient of chloride migration (K, mm per week). The K magnitudes were predicted by the experimental relationship (eq. (2)) between the chloride migration depth (X) and immersion duration in salty solution (t) as suggested by Bakker [34].

$$X= a+K\sqrt{t} \quad (2)$$

The depth of chloride migration through concrete samples containing FS or/and BA also improved with time. After 28 days of immersion in NaCl solution, the migration depth of Cl ions into the F-30BA concrete sample containing BA was lower than the PC concrete sample. The migration depths of chloride ions measured for concrete samples containing FS and BA for 28 days immersion in NaCl solution were then utilized to estimate K value as stated before.
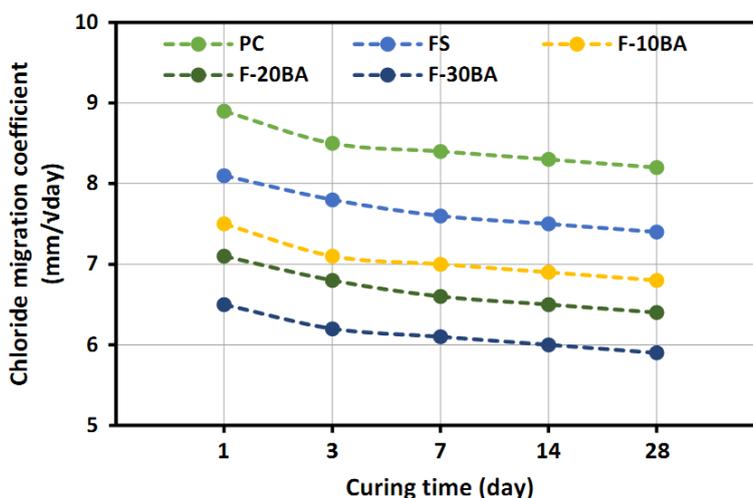


**Figure 8.** The relationship between pre-curing period and K for the concrete samples containing FS and BA

Figure 8 indicates the relationship between pre-curing period and K for the concrete samples containing FS and BA. As shown, it is clear that the resistance to chloride migration increases with rising pre-curing time for a given BA addition to the concrete mixes. Increased BA concentration in concrete mixture increased significantly the resistance to chloride migration, which is clarified by increased pore refining and filler activity attributable to BA. The K magnitudes were lower for the concrete mixture containing 30% BA compared to the other samples. The above findings indicate that concrete containing BA has a higher resistance to chloride migration, which is compatible with EIS results.

## 4. CONCLUSIONS

Chloride-induced reinforcement corrosion has long been recognized as a serious problem in reinforced concrete structures around the world. The diffusion of chloride ions in concrete systems containing FS and BA admixtures was investigated using soaking and EIS techniques in this study. Increasing the amount of FS and BA, according to the EIS results, increases resistance to chloride ion migration. After 28 days of curing, the use of 30% BA helped to improve the concrete's compressive strength. The F-30BA sample had an important impact on the migration and diffusion of chloride ions in concrete structures containing FS and BA additives, according to the soaking findings. The surface morphology of steel rebar revealed a small amount of corrosion substance and minor pits on the surface of the steel in the F-30BA sample, which was consistent with the findings of the soaking and EIS experiments.

## References

1.      S. Karthick, S. Muralidharan, H.-S. Lee, S.-J. Kwon and V. Saraswathy, *Cement and Concrete Composites*, 100(2019)74.
2.      M.Z.Y. Ting, K.S. Wong, M.E. Rahman and S.J. Meheron, *Journal of Cleaner Production*, 29(2020)123383.
3.      J.Z. Du Fengyin, Z. Tiejun and D. Xueyan, *International Journal of Electrochemical Science*, 13(2018)7076.
4.      V.P. Kumar and D.R. Prasad, *Journal of Building Pathology and Rehabilitation*, 4(2019)1.
5.      A. Afshar, S. Jahandari, H. Rasekh, M. Shariati, A. Afshar and A. Shokrgozar, *Construction and Building Materials*, 262(2020)120034.
6.      S. Kakooei, H.M. Akil, M. Jamshidi and J. Rouhi, *Construction and Building Materials*, 27(2012)73.
7.      P. Azarsa, R. Gupta and A. Biparva, *Cement and Concrete Composites*, 99(2019)17.
8.      M. Kylasnath and R. Abraham, *International Research Journal of Advanced Engineering and Science*, 2(2020)170.
9.      S.A. Mangi, M.H.W. Ibrahim, N. Jamaluddin, M.F. Arshad and R.P. Jaya, *Engineering Science and Technology, an International Journal*, 22(2019)515.
10.     P. Tang, W. Chen, D. Xuan, Y. Zuo and C.S. Poon, *Journal of Cleaner Production*, 258(2020)120675.
11.     K. Muthusamy, M.H. Rasid, G.A. Jokhio, A.M.A. Budiea, M.W. Hussin and J. Mirza, *Construction and Building Materials*, 236(2020)117507.
12.     N. Singh, M. Mithulraj and S. Arya, *Resources, Conservation and Recycling*, 138(2018)257.
13.     L. Mengasini, M. Mavroulidou and M.J. Gunn, *Sustainable Chemistry and Pharmacy*, 20(2021)100380
14.     M. Alexander and H. Beushausen, *Cement and Concrete Research*, 122(2019)17.
15.     W. Zhao, J. Zhao, S. Zhang and J. Yang, *International Journal of Electrochemical Science*, 14(2019)8039.
16.     S.-h. Shi and Y.-Q. Xiong, *International Journal of Electrochemical Science*, 16(2021)1.
17.     M. Balonis, G. Sant and O.B. Isgor, *Cement and Concrete Composites*, 101(2019)15.
18.     J. Wang and E. Liu, *Magazine of Concrete Research*, 72(2020)1016.
19.     C.M. Tibbetts, J.M. Paris, C.C. Ferraro, K.A. Riding and T.G. Townsend, *Cement and Concrete Composites*, 107(2020)103491.

*Int. J. Electrochem. Sci.,* 16 **(2021)** Article ID: 210814

11

20.    N. Chousidis, I. Ioannou, E. Rakanta, C. Koutsodontis and G. Batis, *Construction and Building Materials*, 126(2016)86.
21.    P. Garcés, L. Andión, E. Zornoza, M. Bonilla and J. Payá, *Cement and Concrete Composites*, 32(2010)204.
22.    K.A. Snyder, X. Feng, B. Keen and T.O. Mason, *Cement and Concrete Research*, 33(2003)793.
23.    A. Ech-chebab, A. Ejbouh, M. Galai, S. Hassi, K. Berrami and M.E. Touhami, *Journal of Bio- and Tribo-Corrosion*, 7(2021)1.
24.    J.-z. Liu, M.-f. Ba, Y.-g. Du, Z.-m. He and J.-b. Chen, *Construction and Building Materials*, 122(2016)619.
25.    S.B. Aoun, M. Bouklah, K. Khaled and B. Hammouti, *International Journal of Electrochemical Science*, 11(2016)7343.
26.    K.A. Snyder, X. Feng, B. Keen and T. Mason, *Cem. Concr. Res.*, 33(2003)793.
27.    Q. Qiu, Z. Gu, J. Xiang, C. Huang and B. Dong, *ACI Mater. J.*, 114(2017)605.
28.    B. Dong, Z. Gu, Q. Qiu, Y. Liu, W. Ding, F. Xing and S. Hong, *Construction and Building Materials*, 161(2018)577.
29.    B.-q. Dong, Q.-w. Qiu, J.-q. Xiang, C.-j. Huang, F. Xing, N.-x. Han and Y.-y. Lu, *Construction and Building Materials*, 54(2014)558.
30.    B. Dong, Q. Qiu, Z. Gu, J. Xiang, C. Huang, Y. Fang, F. Xing and W. Liu, *Cement and Concrete Composites*, 65(2016)118.
31.    B. Dong, Y. Wu, X. Teng, Z. Zhuang, Z. Gu, J. Zhang, F. Xing and S. Hong, *Construction and Building Materials*, 211(2019)261.
32.    A. Dhawan, N. Gupta, R. Goyal and K. Saxena, *Materials Today: Proceedings*, 44(2021)17.
33.    T. Klathae, N. Tanawuttiphong, W. Tangchirapat, P. Chindaprasirt, P. Sukontasukkul and C. Jaturapitakkul, *Construction and Building Materials*, 258(2020)119443.
34.    P. Schissel, *Report of the technical committee 60-CSC RILEM*, 76(1988)1.