Short Communication

Study on the Hydration Behavior of Portland Cement Partially Replaced with Mineral Additives via an Electrochemical Technique

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In this work, the effects of mineral admixtures, corn cob ash (CCA) and waste plastic fiber (WPF) fillers, on mechanical properties and hydration of Portland cement (PC) were investigated. The partial replacement of both WPF and CCA in PC accelerates the setting process as compared to control PC sample without additives. The addition of WPF decreased the compressive strength of PC and the strength of 42.1 MPa has been obtained in 4-weeks of curing time. CCA addition rises the strength and maximum value of 74 MPa has been found. The electrochemical results indicate that the values of charge-transfer resistance in the equivalent circuit model for PC increase with increasing hydration period. CCA replacement can affect the resistance value in the equivalent circuit. In the 4-weeks hydration time, CCA additives can decrease the resistance value and hydration degree of PC paste. The surface morphology of samples indicated that modified CCA-concrete had lower hydration products than the PC concrete, which was compatible with electrochemical results.

1. INTRODUCTION

Contemporary building composites, such as mortar and concrete, are still the major material produced in construction technology [1, 2]. Using sorptive clays and industrial byproduct as economical resources, which do not impair hydration of cement, in the production of new environmentally friendly cement binders can be a new challenge among engineers [3, 4]. Continuous waste processing, resulting from agricultural waste and manufacturing by-products, creates serious environmental problems in terms of management and treatment [5, 6]. The building industry has been recognized as one of the industries that absorbs the most materials such as fillers in concrete [7]. If these admixtures have pozzolanic properties, they provide technical benefits to the concrete and allow for greater amounts of cement replacement [8].

Several types of mineral admixtures such as fly ash and slag have been widely utilized to substitute Portland cement (PC) in structure of concretes [9, 10]. These admixtures, however, are not readily available in all regions, and even where they are, they are not always readily available [11-13]. Furthermore, there are several agricultural wastes that may be burned, and the causing ash utilized as replacement of PC. Among these hopeful agricultural wastes is corn cob that may be used in corn cob ash(CCA) [14]. It can be used as an admixture in concrete structure. There are many countries in the world that produce millions of tons of corn annually. High corn production can indicate the production of large amounts of corn cobs [15]. Thus, the combination of these wastes in concrete also helps to effectively manage this waste.

Reuse of waste plastic plays a significant role in sustainable management of solid waste. Waste plastic management assists to save natural resources that cannot be replenished, reduces the environment pollution and also aids in recycling and saves energy production processes [16]. Application of waste plastic fiber (WPF) to concrete and mortar is very common and numerous studies have been performed to assess the performance characteristics of the plastic concrete [17]. Choi et al. [18] showed experimental study to explore the effect of WPF as aggregate on concrete properties. Some investigations have used CCA or WPF as cement ingredients in concrete structures [19-22]. However, only a few studies have been conducted on the use of wastes as a binary cementitious material in concrete mixes. Furthermore, research on the use of WPF or CCA has only focused at compressive power, ignoring properties like cement hydration. Furthermore, none of the previous works on the utilization of both admixtures in the concrete have considered their hydration behavior by electrochemical technique. As a result, it is essential to evaluate the hydration process of concrete made from WPF and CCA. Therefore, in the present work, a comparative study was done on the effect of WPF and CCA as mineral additives on the hydration behavior, compressive strength and setting time of PC.

2. MATERIALS AND METHODS

In this study, PC along with CCA and basalt fibers WPF was utilized as the binder. Table 1 shows the chemical composition of PC and CCA. The used corn cob to prepare the CCA was achieved from the Dengfeng City Ludian Town Xingguang Abrasives Factory and grind to a smaller size before combusting at a temperature of around 650 °C for 15 hours. Then, the CCAs were sieved and only particles less than 70μm were utilized in this work.

Table 1. Chemical compositions of PC and CCA

	PC	CCA
Al_2O_3	4.32	6.38
SiO_2	18.17	67.29
Fe_2O_3	2.35	5.28
SO_3	2.84	1.12
CaO	60.34	10.83
Na_2O	0.17	0.39

Table 2 indicates five mixtures which were designed and prepared for this work. CCA and WPF were used as admixtures to replace the PC binder. The water to cement ratio (w/c) for all mixes was kept at 0.4.

Table 2. Compositions of prepared mixes

Mixture	Cement (kg/m^3)	Water (kg/m^3)	CCA (kg/m^3)	Fine aggregates (kg/m^3)	Coarse aggregates (kg/m^3)	WPF (wt%)
PC	200	80	---	466	491	---
WPF	200	80	---	457	482	0.3
WPF-CCA	180	80	20	455	480	0.3
CCA	170	80	30	454	478	---

The samples for evaluation of compressive strength were prepared by 20cm cube steel molds. The samples were cast in three-layers, each layer tampered with 35 strokes of a pressure rod that was evenly distributed over the cross-section of the mold. The molds and their contents were maintained in a curing room at 25 °C and relative humidity more than 90% for one day. The cubes were de-molded after one day and the samples were transferred to a water bath which was kept at 27±2 °C in the cooking room. The compressive strength was calculated at curing age 1 day, 3 day, 1, 2 and 4 weeks using a compression machine by maximum testing capacity of 338,000 lbf.
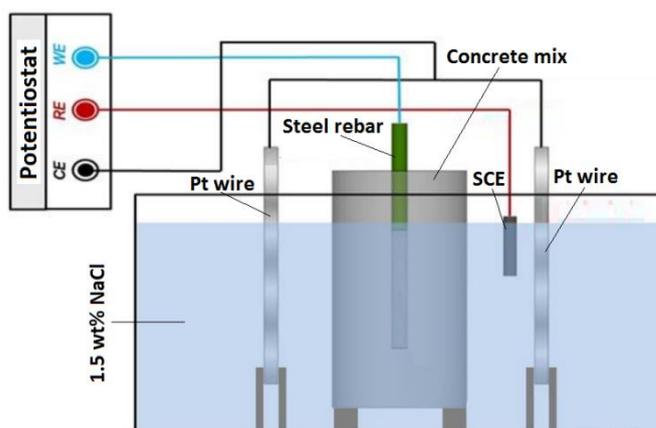
Figure 1. Schematic diagram of EIS experiment

For electrochemical tests, the concrete specimen was poured into cylindrical mold, 10 cm in diameter and a 30cm height for one day at 90% relative humidity and ambient temperature to do the hydration reactions. Figure 1 indicates a schematic diagram of the cells configured for the EIS experiment.

A steel rebar was positioned vertically in the cylinder center. In the present study, carbon steel with 6mm diameter was used to consider the hydration behavior of cement materials. The chemical

composition of utilized carbon steel was C (0.21wt%), Si (0.55wt%), Mn (1.52wt%), P (0.03wt%), S (0.024wt%) and Fe (residual).

The steel rebar was cleaned using SiC papers and then washed by the acetone and deionized water.

An electrochemical impedance spectroscopy (EIS) was utilized to evaluate the hydration behavior of blended cements. A conventional EIS system was used to measure which contains the steel rebar incorporated into the concrete samples as a working electrode, a saturated calomel electrode and a Pt wire as a reference and an auxiliary electrodes, respectively. The EIS measurements were performed at frequency range of 0.01Hz to 0.1MHz. Initial and final setting times of PC, CCA and WPF blended cement were considered consistent with IS: 4031 by a Vicat's needle. Scanning electron microscope (SEM, ZEISS Sigma 300) was used to evaluate the morphologies of hydration products.

3. RESULTS AND DISCUSSION

A reduction in concentration of OH^- and CaO can be observed in all PC samples including the CCA admixture with increased curing period. This can be related to the changes in their cement hydration process. In PC hydration process, C_2S and C_3S undergo hydration reactions to yield CH as revealed in following equations [23]:

$$2C_3S+6H\rightarrow3CSH+3CH \qquad (1)$$
$$2C_2S+4H\rightarrow2CSH +2CH \qquad (2)$$

The CSH appeared in above equations is commonly responsible for strength improvement in the cement structures. The rise in the amount of OH^- and CaO in PC can be associated to the CH production with continued curing. In contrast, the decrease in the amount of OH^- and CaO may be related to the CH consumption during the pozzolanic reactions in CCA-blended PCs. CCA have amorphous alumina and silica which reflects the properties of pozzolanic. In the pozzolanic reactions, the hydration of cement produces CH which reacts by alumina and silica existent in CCA as presented in following equations [24]:

$$3CH+S+H\rightarrow CSH \qquad (3)$$
$$A+H+CH\rightarrow CAH \qquad (4)$$

Increasing the curing period leads to higher CH consumption in pozzolanic reactions and thus a gradual decrease in the CH amount in the hydrated CCA-blended PC.
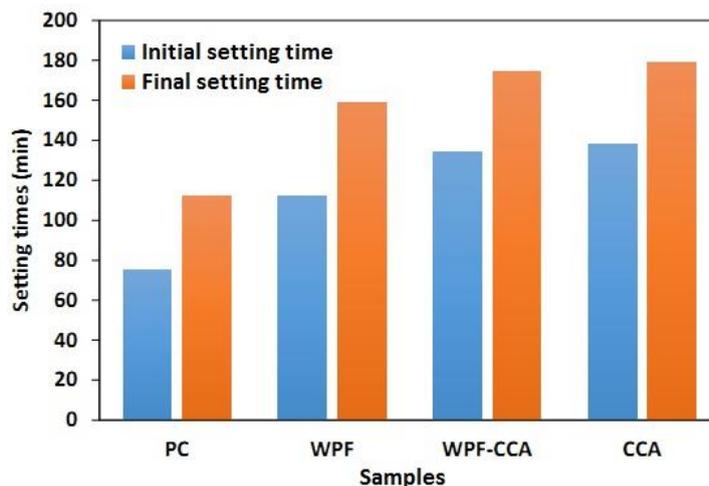
Figure 2. Initial and final STs of Portland cement replaced by various admixtures

Initial and final setting times (STs) of Portland cement replaced by various admixtures are revealed in Figure 2. PC samples displayed shorter initial and final STs than the blended PC samples. It can be associated with higher concentration of clinker phases (C_3A and C_3S) in PC samples than in the other PC samples blended with CCA and WPF. C_3S hardens quickly in the existence of water; therefore, it is responsible for the initial setting of cement. C_3A hydration produces a considerable amount of heat which rises the setting temperature causing a faster setting behavior of PC samples compared by blended cements. The STs of cement falls with an increase in temperature. Furthermore, the slow pozzolana reaction that occurs in CCA-blended PC samples result in slow hydration of cement and, therefore, increased STs [25]. It was found that both the initial and final STs of CCA-blended PC samples were enhanced by addition of CCA and WPF in the order PC < WPF< WPF-CCA < CCA. It can be related to the fact that CCA addition in blended PCs gradually decreased the amount of C3A and C3S components causing the slow STs of these samples.
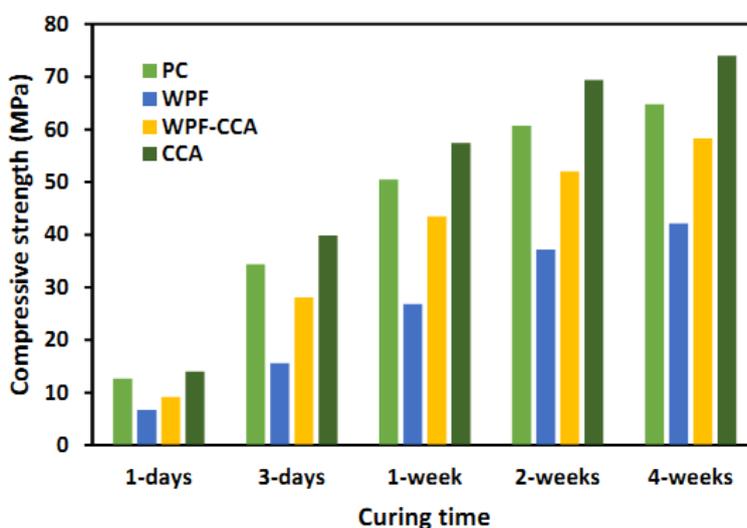
Figure 3. Compressive strength of the concrete samples incorporated with different admixtures along with the PC during 4 weeks curing times

Figure 3 shows the compressive strength of the concrete samples incorporated with different admixtures along with the PC during 4 weeks curing times. As shown in Fig. 3, the compressive strength was a function of time and rises with increase in curing time up to 4 weeks.

Figure 3 indicates that with addition of WPF, hydration reaction starts and formation of ettringite occurs for initial strength. Although, WPF blended cement sample shows reduction in strength in comparison with control cement (PC). This shows that WPF participated a little in the reaction hydration and acted as filler. Furthermore, blending of CCA with PC in WPF sample rises compressive strength as compared with WPF sample. Maximum strength of 74 MPa has been found for the CCA sample in 4 weeks which was about 14% higher than control cement (64.8 MPa). The enhancement of strength for the CCA samples can be attributed to pozzolanic reactions. This improvement in strength may be related to creation of secondary C-S-H gel through the pozzolanic activity of CCA [26, 27].
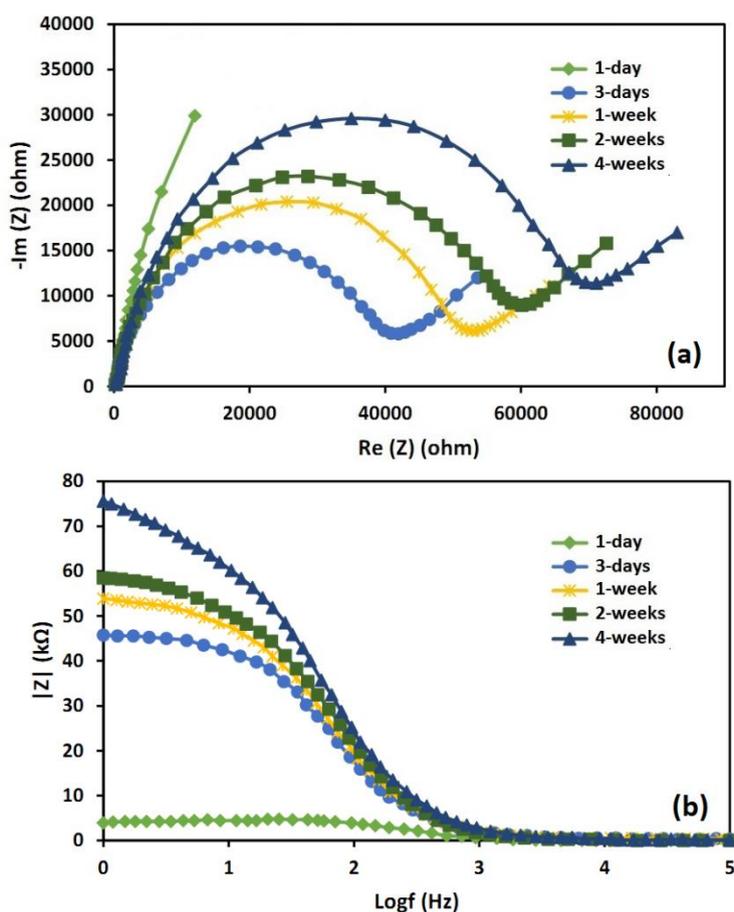
Figure 4. (a) Nyquist curves and (b) Bode plots of PC sample at different hydration period
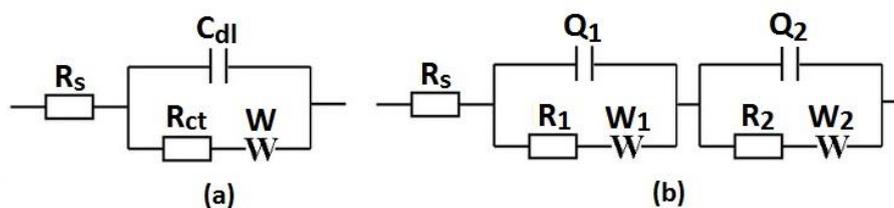
Figure 5. (a) Classical Randles model (b) An equivalent circuit for hydrated PC

Figure 4 exhibits the Nyquist curves of PC samples at different hydration periods. The standard equivalent circuit for EIS from cement-based materials may be considered as a special electrochemical system. Figure 5a indicates a classical Randles model. Rs and Cdl are the electrolyte resistance and the electric double-layer capacitance in the electrode/solution interface, respectively [28]. The electrochemical impedance done in the electrochemical method is Faraday impedance (Z_F). Since for the electrochemical reactions, the Faraday process primarily includes the charge-transfer and diffusion, thus the Faraday impedance is indicated by the impedance R_{ct} and the impedance (W) of the diffusion procedure [29]. Based on the PC characteristics, the equivalent circuit model for PC is designed as revealed in Figure 5, where R_s shows the pore solution resistance in PC. R_1, Q_1 and W_1 represent the resistance resulted from ion transfer processes in the cement, the capacitance of double-layer between the liquid/solid phases and the Warburg resistance resulted from ion diffusion processes in the cement, respectively. R_2, Q_2 and W_2 represent the resistance resulted from the charge-transfer process on the electrode surface, the capacitance of double-layer between electrode and cement and the Warburg resistance resulted from ion diffusion process on the electrode surface, respectively [30].

The Bode plots of the carbon steel rebar at different hydration periods are shown in Figure 4b. At high frequencies, |Z| vs. Logf plot shows a slope near to zero reflecting the mortar resistance such as pore solution and bulk material [31]. At mid frequencies, the phase angle near to 70 indicates the capacitive activities at the rebar/concrete interface. At low frequencies, |Z| vs. Logf plots show a slope decreasing to 0° that is attributed to the resistance of the charge-transfer processes [32].

As shown in figure 4, once the hydration time is one day, there is not any semicircle at the high-frequency, and the complete Nyquist plot is a straight line. Thus, the EIS curve (1-day) is quite varied from a classical Randles model (Inset figure 4). Compared with the classical Randles model, the equivalent circuit (1-day) has a big parallel resistance; the capacitors and resistors may be connected in series from the initial hydration, the slurry interface is not completed, thus the liquid/solid interface resistance is relatively low. The chemical reaction of the PC system proceeds very rapidly, and the main factor in controlling system change is the diffusion process. Once the hydration time is 3-days, an incomplete semicircle seems at high-frequency, which shows that the SO_2^{-4} and OH^- in the system constantly contribute to the hydration reactions and produce the hydrated phase. With continued hydration reactions, the Nyquist plot of the PC samples indicate the classical Nyquist plot, and the reaction is controlled by diffusion and kinetic processes. By continuing the hydration reactions, the moisture in PC matrix contributes in the hydration reactions, the charge-transfer resistance slowly rises, the curve shifts toward the right, and forms a capillary networks in the PC. ZSimp Win software was utilized to study and process the Nyquist plots of the PC at different hydration times. The charge-transfer resistance in the cement (R_{ct}) can be found using the software. These findings are indicated in Figure 5. As revealed, once the PC is hydrated for 1-day, the R_{ct} value is very small which shows that the PC has a low hydration degree. Furthermore, during 1-day hydrated time, there are a few hydration products in the PC and the liquid phase of the cement environment is more stable. By increasing hydration time, the R_{ct} values increases which displays that the free water amount in pore solution was slowly consumed, and the content of solid hydrated products rises; the solid product resistance is much greater than that of the cement liquid phase, thus the ion-transfer resistance increases by curing time. Furthermore, a fast increase in Rct shows that the hydration reactions are intense during the initial stage and came with lots of electron hydration.
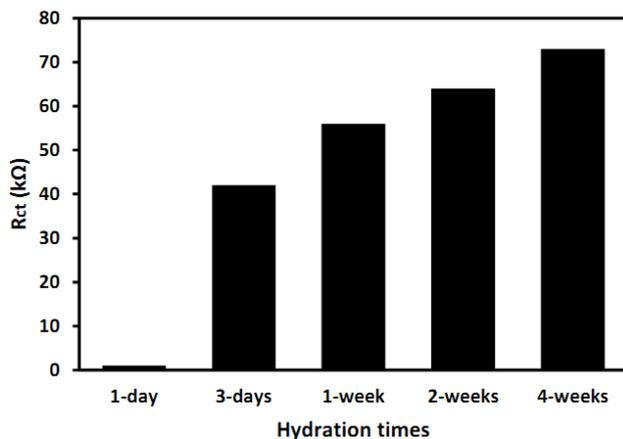
Figure 6. Relationship between R_{ct} values and hydration times
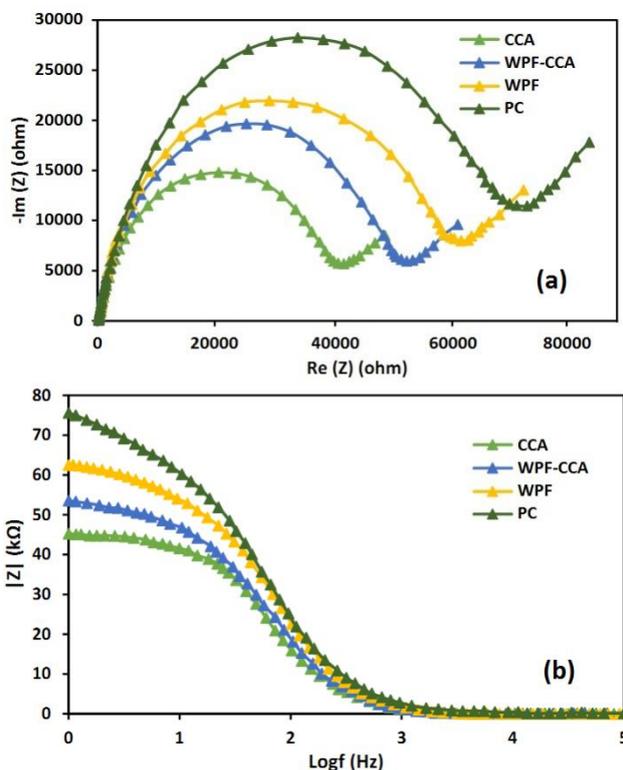
Figure 7. (a) Nyquist (b) Bode plots for concrete samples with various admixtures at 4-weeks hydration times

Figure 7 reveals the Nyquist plots for concrete samples with various admixtures at 4-weeks hydration times. The semicircle radius reduces at high-frequency by the addition of CCA. It may be attributed to the wrapped main active substance by a water-layer during initial and medium-term hydration which reduced its activity [33]. Consequently, the CCA does not contribute in the hydration process, and the amount of reacted cement falls. Once the hydration reaction starts, the reactions (OH^- and Ca^{2+}) decrease with the addition of CCA. Thus, Rct value decreases because of the reducing

amount of chemically bound-water and rising pore connectivity [34]. The compressive strength of CCA sample at 4-weeks hydration time had a higher value compared to the other samples, likely because the CCAs are not involved in initial hydration and helps only as a filler. Thus, the evolution of microstructural can happen by the PC. After curing, CCA particles are dispersed into the PC paste and secondary hydrations start, making a hard hydration gel layer and combining efficiently by the cement paste which improves compressive strength and R_{ct} value of the CCA samples [35]. Figure 7b shows the Bode plots of the specimens with different admixtures after 4-weeks hydration times. As shown, by addition of admixtures, the impedance values are reduced. It can be attributed to the wrapped main active substance by a water-layer during initial and medium-term hydration which reduced its activity.
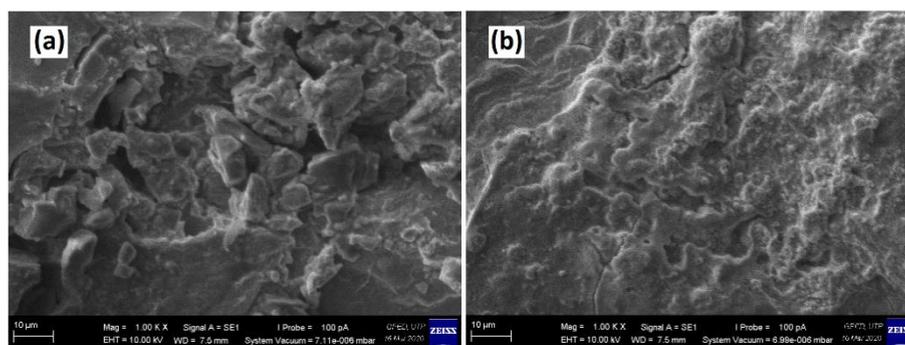
Figure 8. SEM images of the PC (a) without CCA and (b) with CCA admixture after 4-weeks hydration

In order to indicate the presence of CCA into the microstructures of PC, SEM characterizations were done on PC with and without CCA at 4-weeks hydration. As shown in Figure 8, the surface morphology of modified CCA concrete samples indicated lower hydration products than the PC concrete, which is compatible with electrochemical results.

4. CONCLUSIONS

The effects of mineral admixtures, CCA and WPF fillers, on mechanical properties and hydration of PC were investigated. The partial replacement of both WPF and CCA in PC accelerates the setting process as compared to controlling PC samples without additives. The addition of WPF decreased the compressive strength of PC and the strength of 42.1 MPa has been obtained in 4-weeks of curing time. CCA addition rises the strength and maximum value of 74 MPa has been found. The EIS results indicate that the values of charge-transfer resistance in the equivalent circuit model for PC increase with increasing hydration period. CCA replacement can affect the resistance value in the equivalent circuit. In the 4-weeks hydration time, CCA additives can decrease the resistance value and hydration degree of PC paste. It may be attributed to the wrapped main active substance by a water-layer during initial and medium-term hydrations which reduced its activity. The surface morphology of

samples indicated that modified CCA-concrete had lower hydration products than the PC concrete which was compatible with electrochemical results.

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