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Self-Healing of Cementitious Composites to Reduce High CO_2 Emissions

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Existing concrete structures worldwide are suffering from deterioration/distress. With ever-growing urban population and global warming, higher CO_2 concentrations in the atmosphere are likely to further weaken the chemical stability of concrete material, and it is very important to understand how its effects will impair the material. To help moderate the harmful effects of increased CO_2 concentrations, an experimental study was undertaken in which efforts were made to accelerate the capability of engineered cementitious composites (ECCs) with different pozzolanic materials (PMs) to self-heal its own damage (for example, cracks) in a CO_2-rich environment. Self-healing was assessed by electrical impedance (EI) and rapid chloride permeability tests (RCPTs) on 28-day-old specimens. Experimental findings show that self-healing in a CO_2-rich environment is more pronounced than it is in normal atmospheric conditions. The findings also show that PM type can be very decisive on self-healing performance in a CO_2-rich environment, depending on testing method. Results suggest that proper material design can lead to the development of environmentally friendly ECC options with superior mechanical and durability characteristics.

Keywords: carbonation; CO_2-rich environment; electrical properties; engineered cementitious composites (ECCs); self-healing.

INTRODUCTION

For the last several decades, growing attention has been placed on reducing the emission of greenhouse gases due to their detrimental effects on climate. Within this context, CO_2 emissions, which constitute three-fourths of total greenhouse gas emissions, seem to be primarily responsible for climate change.[1] Between the preindustrial period and 2010, the concentration of CO_2 in the atmosphere rose from 280 parts per million (ppm) to 390 ppm—an increase of 39%.[2] In this respect, the construction industry is in a critical position; production of one cubic meter of concrete results in CO_2 liberation of 0.2 tons (440.9 lb) on average.[3] For concretes produced with only portland cement as binder, this value ranges between 0.29 and 0.32 tons (639.3 and 705.5 lb) per cubic meter. Of the overall CO_2 emission made by the construction industry, 74 to 81% is generated by portland cement production.[4] One ton of portland cement generates 0.86 to 0.94 tons (1895.9 to 2072.3 lb) of CO_2, which makes the cement industry responsible for 5 to 8% of the total anthropogenic CO_2 in the atmosphere.[5]

Although concrete production is largely responsible for CO_2 emission, reinforced concrete structures suffer from its abundance in the atmosphere. When atmospheric CO_2 reacts with portlandite (one of the hydration products) to form calcite, the pH of the pore solution drops from approximately 13 to 9, which eventually destroys the passive layer protecting the reinforcement from corrosion. Researchers therefore anticipate that the service lives of reinforced concrete structures are reduced by 15 to 20 years due to carbonation-induced corrosion damage.[6] However, there have been a variety of studies concerning CO_2 emissions stemming from the construction industry and methods to effectively reduce it.[6,7] Although almost all of the studies focus on the detrimental effect of atmospheric CO_2, there may be a possible beneficial influence of increased CO_2 concentration, as CO_2 is one of the reactants required for intrinsic self-healing of cracks in cementitious composites. This article mainly concentrates on the contribution of increased CO_2 in the atmosphere on the intrinsic self-healing (autogenous self-healing) capability of cement-based materials favored by the formation of micro-sized cracks.

Deterioration of concrete structures is accelerated mainly by the crack formation in a direct or indirect manner as it facilitates the ingress of deleterious materials inside concrete. Although achieving crack-free concrete seems almost impossible, it has been well-documented that materials such as engineered cementitious composites (ECCs) can be regarded as crack-free due to their tight crack widths, even under extreme loading conditions. It has been shown in many occasions that ECCs with self-controlled multiple and micro-sized tight cracks have better or at least comparable transport properties to conventional sound concrete.[8] Not only does this property increase the service life, it can also reduce repair and/or maintenance costs by an intrinsic characteristic called self-healing.

Self-healing in cementitious materials is an attractive phenomenon that has drawn the recent attention of many researchers. Although pioneering techniques such as the use of hollow fibers, microencapsulation, expansive agents, and bacteria have been proposed to trigger the mechanism,[9] autogeneous self-healing, which is potentially intrinsic in cementitious materials seems, to be an easier and more robust alternative now.[9] Researchers have also determined that crack widths significantly affect intrinsic self-healing, because small cracks have a higher tendency to close via self-healing.[9] Given the high amounts of cementitious materials used in ECC production and its multiple tight microcracking (generally less than 100 μm [0.0039 in.])[10] pattern, the mate-

rial itself is a good example for autogenous self-healing. Numerous studies have revealed its superior self-healing capability, and those studies are growing in number.[10]

When the mechanism of intrinsic self-healing in ECC was investigated, two main triggers were mentioned in the literature: ongoing hydration and carbonation. Preformed cracks are filled with the hydration products in the former, while calcium carbonate precipitates as calcium hydroxide formed during the hydration of portland cement reacts with CO_2 in the atmosphere, or as the Ca^{2+} ions leached from hydration products react with carbonates or bicarbonates in the latter. Although carbonation reactions could be problematic for reinforced concrete in some cases, they can also be significantly beneficial in terms of capturing excessive CO_2 in the atmosphere and crack-plugging through self-healing. To examine this issue, a detailed experimental study was performed whose main purpose was to favor self-healing of ECC in a CO_2-abundant environment and to a limited extent to contribute the reduction for increased CO_2 levels in the atmosphere by chemically binding it. ECC mixtures were produced using different pozzolanic materials (PMs). Specimens with and without mechanical preloading were subjected to environmental conditioning where CO_2 levels were much higher than those in normal atmospheric conditions to simulate very polluted environments such as airport pavements or bridge decks. Self-healing performance of ECC materials was evaluated through electrical impedance (EI) and rapid chloride permeability test (RCPT) measurements.

RESEARCH SIGNIFICANCE

Emission of greenhouse gases is the leading contributor of global warming, which is one of the challenges facing mankind today. In this sense, the increased concentration of CO_2 in the atmosphere is of greater significance given its larger share in total released greenhouse gases and its negative effects on both environment and health. In addition, shortened service life of buildings due to corrosion damage is another detrimental influence of the CO_2 from the engineering point of view. However, structures constructed with engineered cementitious composites (ECCs) may possibly compensate this detrimental effect through self-healing. With this in mind, the present study's focus is placed on taking advantage of high CO_2 concentrations to be used for the intrinsic self-healing behavior of ECCs. It is believed that chemical binding of the CO_2 gas to self-heal the damage (that is, cracks) is likely to contribute to both prolonged sustainability and cleaner environments.

EXPERIMENTAL PROGRAM
Materials and mixture proportions

Pozzolanic materials (PMs) used in the production of ECC mixtures included Class F fly ash (FA) used in the production of F-ECC specimens, and ground-granulated blast-furnace slag (GGBFS) used in the production of S-ECC specimens. A separate mixture similar to F-ECC was manufactured by incorporating hydrated lime (CH) into the composition. In this mixture, CH was used in F-ECC by 5% of total weight of cementitious materials (F-ECC-5%-CH). In addition to different PM and CH, all mixtures also included general-use

Table 1—Chemical and physical properties of FA, GGBFS, OPC, and silica sand

Chemical composition	FA	GGBFS	OPC	Silica sand
CaO	3.48	35.09	61.43	0.02
SiO_2	60.78	37.55	20.77	99.79
Al_2O_3	21.68	10.55	5.55	0.06
Fe_2O_3	5.48	0.28	3.35	0.02
MgO	1.71	7.92	2.49	0.01
SO_3	0.34	2.95	2.49	—
K_2O	1.95	1.07	0.77	0.01
Na_2O	0.74	0.24	0.19	0.02
Loss on ignition	1.57	2.79	2.20	0.07
Physical properties				
Specific gravity	2.10	2.79	3.06	2.60
Blaine fineness, m^2/kg	269	425	325	—

CEM I 42.5R ordinary portland cement (OPC) (similar to ASTM Type I), silica sand with a maximum aggregate size of 0.4 mm (0.0157 in.), water, polycarboxylic-ether based high-range water-reducing admixture (HRWRA) with solid content of 40%, and polyvinyl alcohol (PVA) fibers. PVA fibers, which occupied 2% of the mixture volume, had a diameter of 39 μm (0.0015 in.), length of 8 mm (0.315 in.), nominal tensile strength of 1610 MPa (233.5 ksi), elastic modulus of 42.8 GPa (6207.6 ksi), maximum elongation of 6%, and specific gravity of 1.3. All mixtures were produced with the same water-cementitious materials (CM = OPC + FA or OPC + GGBFS) ratio (*w/cm*) of 0.27, and PM-to-OPC ratio (FA/OPC or GGBFS/OPC) of 1.2, by weight. The amount of HRWRA was not constant in the mixtures and was adjusted in accordance with desirable fresh mortar properties to favor fiber distribution. All mixing operations were conducted by using a 25 L (845.35 fl. oz) capacity planetary-type laboratory mixer. In the case of the F-ECC-5%-CH mixture, to ensure uniform dispersion of fine CH particles that are prone to flocculation, ultrasonication was applied to the mixture of hydrated lime, some part of the water, and some part of HRWRA for 10 minutes. This aqueous solution was then added to the OPC, FA, and sand mixture, and mixing was continued for 5 additional minutes in a mortar mixer after adding the rest of the water and HRWRA. PVA fibers were then added to the fresh mixture and mixed for 3 more minutes. The physical and chemical properties of FA, GGBFS, OPC, and silica sand are shown in Table 1. Table 2 shows the amount of ingredients used for producing different ECC mixtures.

Specimen preparation and initial preloading

Several Ø100 x 200 mm (4 x 8 in.) cylindrical specimens were cast from different ECC mixtures to be used in different self-healing evaluation tests (electrical impedance [EI] and rapid chloride permeability test [RCPT]). As seen from the schematic representation of specimen preparation in Fig. 1, after being kept at 50 ± 5% RH and 23 ± 2°C (73.4 ± 3.6°F) for 24 hours, all specimens were demolded and placed in isolated plastic bags at 95 ± 5% RH and 23 ± 2°C

(73.4 ± 3.6°F) for curing until the end of 28 days. After 28 days, Ø100 x 200 mm (4 x 8 in.) cylindrical specimens were cut into Ø100 x 50 mm (4 x 2 in.) cylinders to be used in different tests for self-healing evaluation. Specimens with the same dimensions (Ø100 x 50 mm [4 x 2 in.] cylinders) were used for all test methods. Taking the RCPT method (explained in the next section) into account, in accordance with ASTM C1202 (which uses Ø100 x 50 mm [4 x 2 in.] cylinders), specimen dimensions were reduced and identical specimens were used to make easier and clearer comments on the self-healing performance of ECC mixtures based on different test methods. Tests were conducted on the preloaded specimens subjected to initial preloading under splitting tensile loading to impart microcracks together with the same number of sound (intact) specimens. Because it was not easy to set a constant initial preloading level to obtain similar microcracking damage for different ECC mixtures with different ingredients, four Ø100 x 50 mm (4

x 2 in.) cylinders from each ECC mixture were failed under splitting tensile loading to determine average ultimate splitting tensile deformation capacities of different mixtures before initial preloading. Splitting tensile loading to failure, the specimens was applied using a closed-loop controlled material testing system at a loading rate of 0.005 mm/s (0.0002 in./s). To measure splitting tensile deformation, two linear variable displacement transducers (LVDTs) were fixed on the test setup. Splitting tensile stress-deformation graphs were drawn upon completion of testing, and deformation levels corresponding to maximum splitting tensile stress levels were defined as the ultimate splitting tensile deformation capacity. Ultimate splitting tensile deformation capacities of F-ECC, F-ECC-5%-CH, and S-ECC specimens were 1.73, 1.58, and 1.52 mm (0.068, 0.062, and 0.060 in.), respectively. Considering that the ultimate splitting tensile deformation levels for different ECC mixtures were very close to each other, a common initial preloading level (70% of ultimate splitting tensile deformation capacity) was agreed upon to introduce microcracks in all specimens. For all proposed test methods, four pieces of Ø100 x 50 mm (4 x 2 in.) cylinders from both sound and preloaded specimens were used to account for possible variations due to different crack characteristics and testing conditions. Photos representative of the crack characteristics of different ECC mixtures, taken after the application of initial preloading, are shown in Fig. 2(a). A higher number of smaller microcracks was observed in F-ECC specimens compared to other mixtures (Fig. 2(a)). The reduced fracture toughness values of Class F fly ash-bearing matrixes and the smooth surface characteristics of fly ash particles reduced the fiber-to-matrix chemical bond while increasing the interfacial frictional bond in favor of attaining high ductility by preventing fiber rupture. F-ECC-5%-CH and S-ECC specimens, on the other hand, had fewer

Table 2—Ingredients of different ECC mixtures

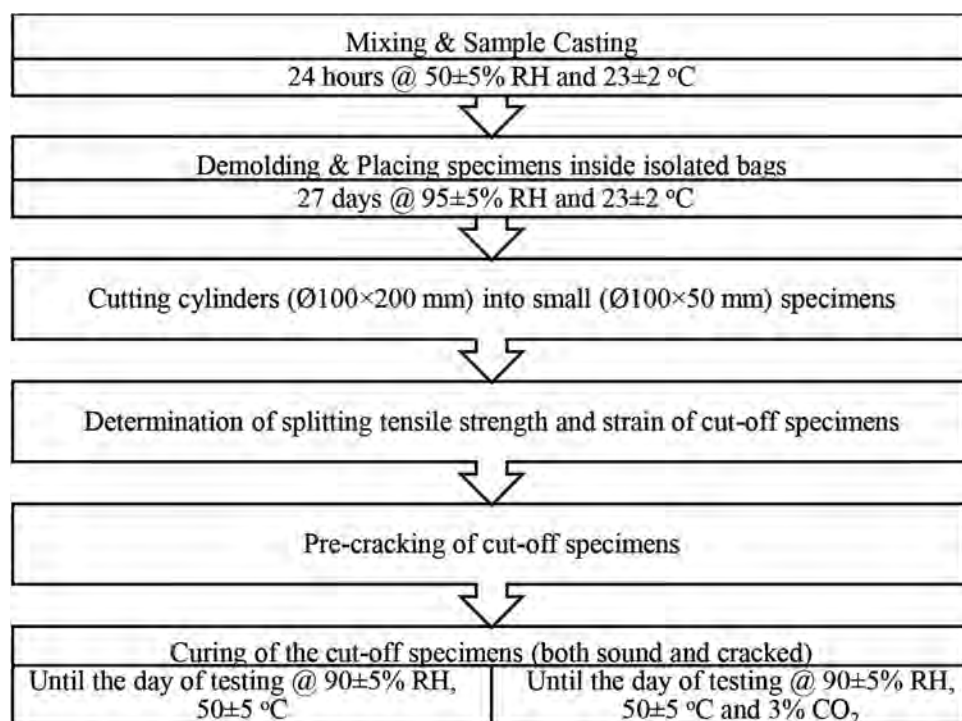| Ingredients, kg/m³	Mixture ID		
	F-ECC	F-ECC-5%-CH	S-ECC
OPC	566	566	593
FA	680	680	—
GGBFS	—	—	712
CH	—	62	—
Water	331	331	347
PVA	26	26	26
Sand	453	453	474
HRWRA	5.1	6.0	6.0

Note: 1 kg/m³ = 1.685 lb/yd³.

Fig. 1—Schematic description of sample preparation procedure and curing regimes.
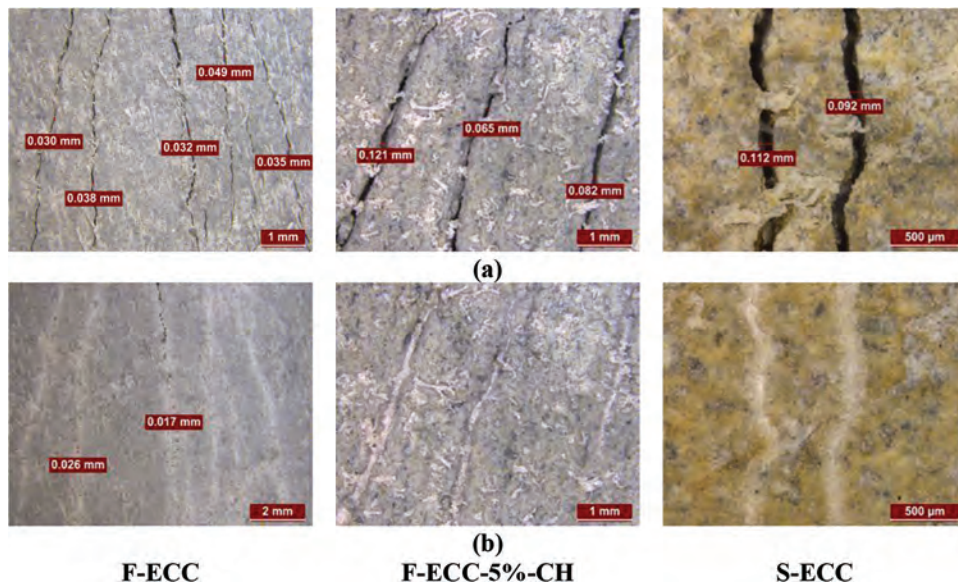
Fig. 2—Crack characteristics of ECC specimens: (a) after initial preloading; and (b) 45 days of CO_2-rich curing.

microcracks with increased widths, although this was more pronounced for S-ECC specimens, as seen in Fig. 2(a). After the application of initial preloading on the 28th day, reference measurements from sound and preloaded specimens were recorded using different test methods. Two curing cabinets having 120 L (4057.68 fl. oz) capacities, both capable of applying between 20 to 95% and both having –10 to 60°C (14 to 140°F) temperature ranges were used for curing. Additionally, one of the cabinets used enabled adjusting the CO_2 concentration up to 20%. One was set at a controlled environment of 90 ± 5% RH and 50 ± 5°C (122 ± 9°F), and the other to 90 ± 5% RH, 50 ± 5°C (122 ± 9°F) and 3% CO_2. The same number of specimens was placed in both curing cabinets. After the first 28 days, self-healing tests were repeated every 15 days until the end of 90 days. One might think that the selected RH is relatively high for carbonation to occur. However, it must be stated that self-healing is more evident in completely and/or partially wet conditions.[11] Moreover, in most of the cases in our daily lives, structures are not in direct contact with the water, which means that moisture that is to be used for self-healing mechanism needs to find its own way through the microcracks to seal them. Although the selected humidity level is relatively high and can be regarded as almost fully water-saturated condition, there is an obvious difference between submerging in water and letting the surface of specimens to be exposed to external moisture without very high osmotic pressure. Along these lines, a high RH level was selected to favor carbonation and self-healing processes simultaneously. Similarly, 50 ± 5°C (122 ± 9°F) was selected, given the fact that self-healing kinetics is faster at high temperatures, as concluded by Reinhardt and Jooss.[12] There is a consensus between the results of carbonation tests conducted at CO_2 concentrations that are natural and/or below 4%, which indicates that this type of accelerated test can be used to interpret probable long-term carbonation effect.[13] Overall, the selected temperature, relative humidity, and CO_2 levels were agreed upon because hot and humid environments are very common

in different climatic zones, especially during the summer seasons and so as not to compromise the natural self-healing process by staying inside the acceptable limits for carbonation reactions.

Testing for self-healing assessment

One of the test methods used for the evaluation of self-healing behavior of ECC was direct electrical impedance (EI) measurement. EI testing used a standard concrete resistivity meter with uniaxial configuration; the typical test setup related to this configuration can be found elsewhere.[14] For this test, Ø100 x 50 mm (4 x 2 in.) cylindrical ECC specimens were positioned between a set of plate electrodes, with their 100 mm (4 in.) sawn circular surfaces positioned vertically upward (Fig. 3). Ø150 x 10 mm (6 x 0.4 in.) water-saturated sponges were used to provide adequate electrical contact between specimen surfaces and plate electrodes (Fig. 3(a)). Special care was taken to select similar sponge-to-surface contact area characteristics (without very large pores and/ or visible microcracks) for all specimens from different mixtures so as not to affect EI measurements. Individual sponges were saturated with the same amount of water for each instance of measurement. Each saturated sponge also underwent EI testing before the tests began, and no associated results were recorded from any of the sponges. Therefore, EI results taken directly from the resistivity meter were used, as they did not require correction due to the individual impedance measurements of the sponges. The concrete resistivity meter used in the study used alternating current (AC) impedance technique. The device was very fast (able to give results in less than 5 seconds), had frequency options ranging from 1 Hz to 30 kHz, and was able to detect the phase angle between 0 and 180 degrees. Despite the wide range of available frequency options, the working frequency throughout the study was set at 1 kHz to avoid polarization effect with the application of AC.[15] A line was drawn at the center of the sawn-smooth surfaces of Ø100 x 50 mm (4 x 2 in.) cylinders, and measurements for both sound and
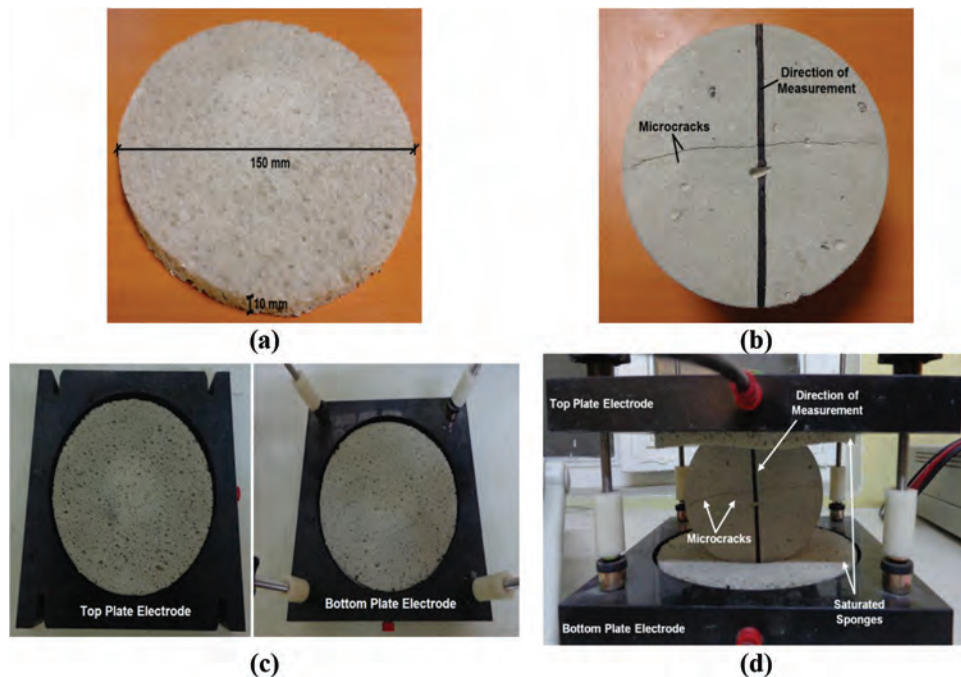
Fig. 3—(a) Water-saturated sponge; (b) preloaded cylindrical specimen; (c) top and bottom plate electrodes with saturated sponges; and (d) electrical impedance testing. (Note: 1 mm = 0.0394 in.)

preloaded specimens were always recorded along this line to prevent confusion during repeated EI measurements. In preloaded specimens, microcracks were created directly perpendicular to the previously specified lines on each specimen to increase the chance of current travelling through the specimens to meet and catch the changes in EI results with the mechanically introduced damage (Fig. 3(b)). This EI measurement technique resulted in values with slight variations; two successive measurements were enough to complete testing for a specific specimen of a known age.

The moisture state of specimens at the moment of EI testing is very important, because EI results are closely related to this parameter. Excessive moisture in microcracks can affect the precision of self-healing evaluation, especially in preloaded specimens. To address this concern, specimens were removed from different curing cabinets at specified curing ages, then placed in a controlled environment of $50 \pm 5\%$ RH, $23 \pm 2°C$ ($73.4 \pm 3.6°F$) to dry out for 1 day. Drying duration and environmental conditions were determined based on the fact that they were enough for all specimens from different ECC mixtures to reach a constant weight at room temperature (the difference between any two successive weight measurements was less than 0.5% of the lowest value obtained).

Sponges, which supplied the electrical contact between the plate electrodes and specimens, were saturated with a reasonable amount of water, and tests were performed quickly so the water did not have time to enter pores and/or microcracks during testing. Due to the proposed configuration for EI measurement, it was difficult to calculate the area where the electrical current was traveling. Hence, only impedance measurements are presented, although these values can also be correlated with the resistivity measurements, because the same geometry was used for all specimens.

Rapid chloride permeability tests (RCPTs) were performed in accordance with ASTM C1202.[16] Although it would have been better to use the same specimens for all testing methods to better compare the results from different self-healing evaluation tests, this was not possible due to chloride ion ingress during RCP testing, which could dramatically influence the reliability of EI testing. Hence, a separate set of sound and preloaded ECC specimens was prepared for exclusive use in RCP testing. Tests were performed on water-saturated specimens, as mandated by ASTM C1202, to indirectly determine electrical resistivity through chloride ion permeability. Results were recorded in terms of electrical charge passed from the specimens in Coulomb (C).

EXPERIMENTAL RESULTS AND DISCUSSION

The main purpose of this study was to observe the self-healing capability of ECC mixtures subjected to CO_2-rich environment using different test methods (RCPT and EI). Among the test methods explained, RCPT is the one that is most commonly used for the self-healing assessment of ECC.[11,17,18] On the other hand, direct electrical measurements (EI) have quite recently begun to be used for this purpose.[19] The self-healing performance of each ECC mixture was individually analyzed, which will be further detailed in forthcoming sections.

ECC mixtures containing Class F fly ash (F-ECC)

Results of F-ECC specimens obtained from RCP and EI test methods are shown in Table 3 for sound and preloaded specimens cured in cabinets with and without CO_2 exposure until the end of 90 days beyond the first 28 days of curing. Data displayed in Table 3 are the average of results from four different specimens. In the RCPT results (chloride ion permeability) of sound F-ECC specimens, average results

Table 3—RCPT and EI test results of different ECC mixtures

Test method	Mixture ID	Curing age, days	With CO$_2$		Without CO$_2$	
			Sound	Preloaded	Sound	Preloaded
Rapid chloride permeability, C	F-ECC	28	915	1906	910	2116
		28 + 15	131	367	205	693
		28 + 30	99	341	105	498
		28 + 45	91	356	76	411
		28 + 60	80	278	62	374
		28 + 75	78	262	60	360
		28 + 90	58	247	42	332
	F-ECC-5%-CH	28	940	2150	1071	2384
		28 + 15	133	683	145	881
		28 + 30	122	458	124	528
		28 + 45	104	386	98	419
		28 + 60	80	325	100	398
		28 + 75	91	303	91	372
		28 + 90	64	256	61	345
	S-ECC	28	621	1367	611	1720
		28 + 15	322	605	323	954
		28 + 30	239	496	230	721
		28 + 45	173	394	165	559
		28 + 60	167	358	156	479
		28 + 75	150	321	135	441
		28 + 90	128	289	119	361
Electrical impedance, kΩ	F-ECC	28	8.41	11.7	7.50	9.60
		28 + 15	51.5	55.8	56.1	85.6
		28 + 30	73.1	81.5	85.2	125
		28 + 45	104	118	122	186
		28 + 60	125	136	149	226
		28 + 75	129	141	157	239
		28 + 90	145	157	167	260
	F-ECC-5%-CH	28	7.18	10.9	7.36	11.1
		28 + 15	40.9	49.3	46.9	84.3
		28 + 30	57.1	68.1	67.7	132
		28 + 45	92.2	92.7	87.4	181
		28 + 60	91.7	97.3	108	183
		28 + 75	99.7	110	119	189
		28 + 90	113	138	145	204
	S-ECC	28	12.3	24.1	11.5	23.1
		28 + 15	28.1	38.4	26.5	62.2
		28 + 30	35.2	53.1	34.9	95.1
		28 + 45	50.4	114.8	51.3	110.8
		28 + 60	51.6	127.0	55.3	119.2
		28 + 75	54.4	136.5	58.5	125.5
		28 + 90	68.9	160.8	70.5	155.5

were less than 1000 C, which is regarded as "very low" according to ASTM C1202. Application of initial preloading caused dramatic increments in RCPT results of 28-day-old sound F-ECC specimens. For example, average 28-day-old RCPT results of specimens to be further cured with and without CO$_2$ exposure increased by 108% and 133% (from 915 to 1906 C and from 910 to 2116 C), respectively, after initial preloading. This result, obtained with the application of preloading, was anticipated given the mechanical introduction of microcracks to specimens where the electrical

current can more easily be transferred during RCPT. Despite the highly escalated RCPT results of sound specimens upon exposure to initial preloading, even the highest average result (2116 C) was in the range of moderate chloride ion permeability level, in accordance with ASTM C1202. It must be noted that preloading caused almost complete failure of the sound specimens (70% of their splitting tensile deformation capacities), and that even under such conditions, average chloride ion permeability results of the F-ECC specimens stayed within acceptable limits. As also concluded in several other studies, although severe microcracking has limited influence on transport properties of ECC mixtures, crack characteristics (especially crack width) are of great importance.[11,20]

Further curing of both sound and preloaded F-ECC specimens in different cabinets caused RCPT results to be considerably lower than the 28-day results. Although the effect of further curing is shown in Table 3, an additional figure (Fig. 4) was created to more clearly show the percentage changes in RCPT results of F-ECC specimens. It clearly demonstrates that, regardless of preloading and environmental conditioning, the first 15 days of further curing were very effective in lowering the RCPT results of F-ECC specimens, which suggests self-healing occurrence in microcracks. For example, the lowest average percentage reduction recorded from F-ECC specimens cured under atmospheric conditions without excessive CO_2 concentration).

Beyond the first 15 days of further curing, especially after 28 + 30 days, environmental conditioning was significantly less influential, probably due to slow exhaustion of unhydrated cementitious materials and plugging of cracks, so that minimal reductions in chloride ion permeability values were observable. However, it is worth pointing out that after only 15 days of further curing, even the highest RCPT results were reduced to a very low chloride ion permeability level (less than 1000 C), as set by ASTM C1202. When the effect of environmental conditioning on RCPT results of F-ECC specimens is evaluated, it can be stated that subjecting sound F-ECC specimens to atmospheric or high CO_2 conditions did not make the expected difference in values; the results obtained in both environments were close to each other (Table 3). In the case of preloaded specimens, on the other hand, chloride ion permeability results of specimens further cured under high CO_2 always exhibited lower results than those cured under atmospheric CO_2 conditions. This can more easily be understood by looking at Fig. 4, which shows sharper drops in RCPT results when specimens were subjected to a high-CO_2 environment after the first 28 days of initial aging, although the behavior started to lose its intensity at later ages (especially beyond 28 + 30 days). Overall, these results suggest the improved self-healing capability of F-ECC specimens in terms of RCPT results in the presence of high CO_2 concentrations. Although calcite precipitation was not reported to be the main final self-healing product of F-ECC specimens in partially and/or fully saturated conditions with atmospheric CO_2 exposure,[11,21] the self-healing performance of preloaded F-ECC specimens subjected to a high-CO_2 environment at earlier ages was attributed to
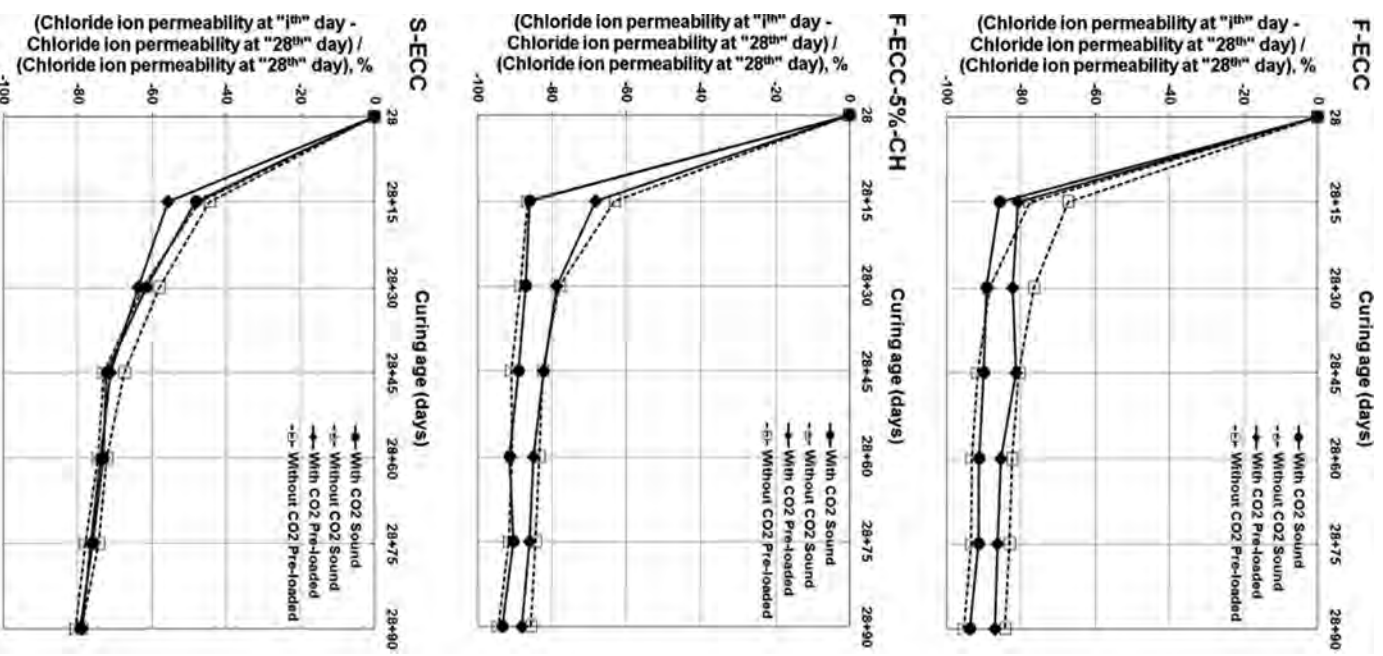

Fig. 4—Percentage changes in chloride ion permeability results of specimens from different ECC mixtures with further curing.

the enhanced calcite precipitation (Fig. 2(b)) because it has been reported that fly ash use increases the carbonation of concrete material.[22]

When the EI results of F-ECC specimens are assessed, it is evident that initial preloading was influential and caused increments in the values. This finding is not surprising, given the fact that electrical current cannot travel through empty cracks, and the cracks themselves act like resistors against the current. Continuous increments were visible in the EI measurements of all specimens with additional curing in different environmental cabinets. To illustrate this situation
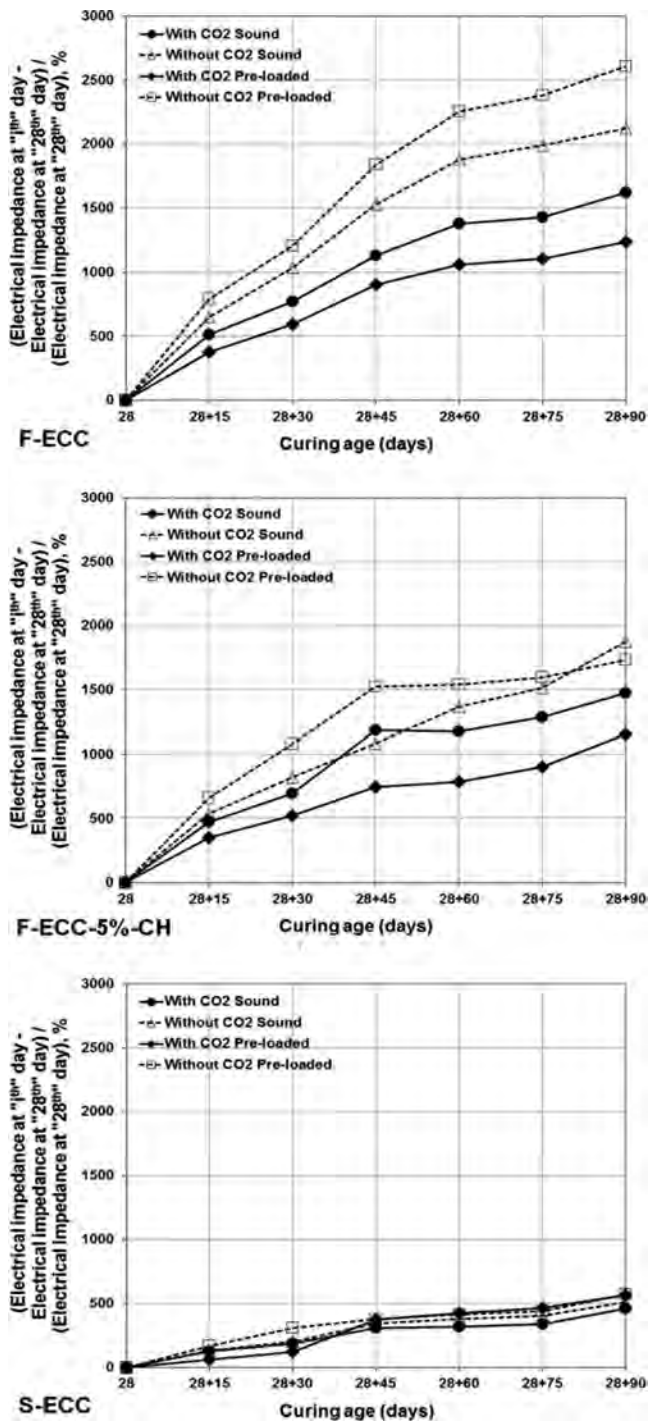
Fig. 5—Percentage changes in electrical impedance results of specimens from different ECC mixtures with further curing.

more clearly, Fig. 5 was constructed to show the percentage changes in EI measurements of F-ECC specimens with respect to 28-day results. For example, while the 28-day average EI result of sound F-ECC specimens cured without excessive CO_2 exposure was 7.5 kΩ, the average value increased tremendously by 2127%, reaching to 167 kΩ after 90 days of further curing. Similar behaviors occurred in all F-ECC specimens subjected to a CO_2-rich environment. Although EI results of preloaded F-ECC specimens were expected to decrease due to partial and/or complete sealing of microcracks with the self-healing effect, this

did not occur. This behavior in preloaded specimens was attributed to several parameters, including porosity, pore solution chemistry, and tortuosity of pore network.[14] With initial preloading of sound specimens, EI results increased because it was not possible for the electrical current to travel through empty space. It is accepted that the possibility for self-healing increases with the introduction of microcracks,[23] because additional space is created for the newly formed self-healing products. Considering that under normal atmospheric conditions, the final self-healing product of Class F fly ash-bearing ECC specimens is mainly further C-S-H gels,[11] pozzolanic reactions have a very high likelihood of contributing to increased EI results at late curing ages, rather than decreasing them with the crack-sealing effect. Consumption of CH favoring secondary C-S-H gel formation, which depleted the number of associated OH^- ions with very high ionic conductivity (198 cm^2 equiv^{-1} Ω^{-1} in an aqueous medium at 22°C [77°F])[24] in preloaded F-ECC specimens, appears to have overshadowed the crack healing effect by leaving a highly resistant pore solution. To reduce increased EI results after the creation of microcracks, healing should bring the damaged specimen back to a nearly sound situation. If this does not happen, self-healing in microcracks contributes to partial sealing, which can significantly increase the tortuosity pore/crack network and EI measurements at later ages.

Raw EI data in Table 3 and percentage changes in Fig. 5 show that CO_2-rich environment plays a significant role in lowering EI results of F-ECC specimens. For sound specimens after 28 + 90 days, EI values were 145 and 167 kΩ for specimens cured with and without excessive CO_2, respectively. For preloaded specimens, the differences became even more distinctive; results for preloaded specimens of the same age were 157 and 260 kΩ, respectively. Observed behaviors in environments with high CO_2 concentration also correspond closely with RCPT results. Lower EI measurements recorded from both sound and preloaded specimens cured under a CO_2-rich environment could have occurred because high concentrations caused CO_2 gas to more easily penetrate into specimens (especially preloaded ones), further binding the CH to form calcium carbonate. With anticipated further binding of CH in the presence of higher CO_2 concentrations, the amount of associated OH^- ions was expected to decrease, leading to increased EI results. However, this was not observed. Several researchers have reported that there are three zones in carbonated concrete: a completely carbonated zone; a semi-carbonated zone; and a noncarbonated zone.[25] While the pH levels of the noncarbonated zone were reported to be 12.5 to 12.9, the same values were 8.3 to 8.6 for the completely carbonated zone. For semi-carbonated zones, pH values ranged from 8.3 to 12.6.[25] In addition to causing faster direct formation in the presence of a CO_2-rich environment, leaching can also contribute to the formation of calcium carbonate. As explained by Jooss,[26] calcium carbonate formation is a process that depends on various factors to meet up. Carbonic acid (H_2CO_3)—a product of water from the permeating medium and CO_2 from the air—changes into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. The distribution of all carbonate species is

dependent on the pH value of the pore solution; while a pH value of approximately 8.3 is needed for CO_3^{2-} ions to be present in the system, the number of HCO_3^- ions reaches its maximum at the same pH value. As pH value continues to rise to approximately 10.3, the concentration of CO_3^{2-} ions starts to exceed HCO_3^- ions and accordingly, for pH values of more than 12.3, only CO_3^{2-} would be present in the solution. With the ingress of CO_2-incorporating water into concrete material, Ca^{2+} ions leach away from both CH and C-S-H gels to form calcium carbonate by combining with different carbonate species. As concluded by the aforementioned studies, even in a completely carbonated state, the lowest pH value of concrete was reported to be approximately 8.3. Leaching of CO_3^{2-} and HCO_3^- ions is therefore possible, even in a completely carbonated state. By taking the relatively high ionic conductivities of CO_3^{2-} (72 cm^2 equiv^{-1} Ω^{-1}) and HCO_3^- (44.5 cm^2 equiv^{-1} Ω^{-1}) ions along with the leached-away Ca^{2+} (59.5 cm^2 equiv^{-1} Ω^{-1}) ions[24] into account, the lower EI measurements recorded in sound and preloaded F-ECC specimens under CO_2-rich environments may be explained.

ECC mixtures containing fly ash and hydrated lime (F-ECC-5%-CH)

Table 3 shows chloride ion permeability test results of sound and preloaded F-ECC-5%-CH specimens obtained through the RCPT method for different curing conditions. Percentage changes in RCPT results upon further curing are shown in Fig. 4. Twenty-eight-day average RCPT results of sound F-ECC-5%-CH specimens were 940 and 1071 C for specimens to be cured with and without high-CO_2 exposure, respectively. In comparing the 28-day values of F-ECC and F-ECC-5%-CH specimens, RCPT results of sound F-ECC specimens were lower. Although additional CH was expected to lower the chloride ion permeability results compared to F-ECC specimens, due to secondary hydration reactions and filler effect, this did not occur. It should be noted that RCPT is an electrochemical method influenced by the chemical state of pore solution in addition to matrix properties. Under normal circumstances, ionic content of the pore solution is one of the major factors affecting RCPT results with lower alkali (K$^+$ and Na$^+$) and hydroxyl (OH$^-$) ions, leading to lower results.[27] Hence, the controversial results obtained from the F-ECC-5%-CH specimens could be due to higher alkalinity of the pore solution with the addition of CH into the mixtures.

Similar to F-ECC specimens, the application of initial preloading to F-ECC-5%-CH sound specimens markedly increased chloride ion permeability results. However, with the initial preloading of sound specimens, the rate of increments in RCPT results was higher in F-ECC-5%-CH specimens than F-ECC. The difference was associated with the higher matrix fracture toughness values and enhanced fiber-to-matrix chemical bonding, which contribute to fiber breakage upon loading instead of pullout, resulting in fewer microcracks with wider widths (Fig. 2(a)) and increased chloride ion permeability results for the F-ECC-5%-CH mixture.[18]

With the further conditioning of all F-ECC-5%-CH specimens, RCPT results went down drastically regardless of environmental conditioning. Figure 4 also shows that the first 15 days of curing was very efficient in lowering values for both sound and preloaded specimens further cured in different cabinets. Although it looks like sound specimens were better compared to preloaded ones in terms of decrement rates in RCPT results, it is notable that the reductions in individual chloride ion permeability results were much more pronounced for preloaded specimens, suggesting the occurrence of self-healing. For example, for specimens subjected to 3% of CO_2 exposure between the ages of 28 and 28 + 90 days, the reduction in average RCPT results of sound specimens was 876 C (= 940 – 64) and 1894 C (= 2150 – 256) in preloaded specimens. The same was also true for specimens cured without excessive CO_2 exposure. It appears that microcrack generation triggered crack healing and reduced RCPT results further, enhancing matrix maturity with further curing. As in the F-ECC specimens, 15 days of moist curing was more than adequate for all severely deteriorated F-ECC-5%-CH specimens to be regarded as "harmless" in terms of chloride ion permeability according to ASTM C1202.

RCPT results recorded for specimens kept in a CO_2-rich cabinet were usually lower than those kept in atmospheric conditions (Table 3). A clearer comparison displaying this behavior can be made, especially for preloaded specimens, as seen from Fig. 4. The behavior observed in the preloaded specimens suggests superior self-healing occurrence was attained with high-CO_2 concentration. The occurrence of calcium carbonate precipitates with a high CO_2 environment and the slow diminishment of CH and related alkalis in the pore solution may be responsible for the enhanced self-healing capability, especially in preloaded specimens (Fig. 2(b)). Overall, because crack widths were generally larger than the preloaded F-ECC specimens (Fig. 2(a)),[18] the preloaded F-ECC-5%-CH specimens attained better self-healing performance in terms of RCPT results.

Average EI results of sound F-ECC-5%-CH specimens ranged from 7.18 to 7.36 kΩ after the initial 28 days of curing (Table 3). EI results increased upon initial preloading, with 28-day results for preloaded specimens in the 10.9 to 11.1 kΩ range (the reason for preloaded specimens exhibiting higher EI results was explained previously). EI results from both sound and pre-loaded specimens showed an increasing trend with further curing, most probably due to further hydration, lower porosity and pore size, and reduced pore solution. Percentage changes in EI measurements of F-ECC-5%-CH specimens are shown in Fig. 5. When a comparison is made between the figure belonging to F-ECC-5%-CH and F-ECC specimens, it can be seen that EI increment rates with time were higher for specimens with CH addition. To put it differently, inclusion of hydrated lime into F-ECC specimens caused drops in individual EI results, which can be seen in Table 3. This behavior could be related to the effect of individual OH$^-$ ions from CH particles increasing the conductivity of the pore solution. As previously explained, increased pH values due to high alkalinity of pore solution (high OH$^-$ concentration) could also be decisive in lowering the EI results of F-ECC-5%-CH specimens by helping the leaching of Ca^{2+} ions and the formation of highly conductive carbonate species for calcium carbonate precipitation. Although CH addition was expected to increase EI measure-

ments by enhancing the matrix properties through further hydration, filler effect, and pore restriction, the electrical properties of ECC specimens appear to be affected more by the changes in pore solution chemistry.

Unlike the RCPT results, the effect of curing in high-CO_2-concentrated environment was more evident in EI results of F-ECC-5%-CH specimens. Figure 5 shows that the rate of increments in EI values of specimens cured with high amounts of CO_2 was lower than those cured without suggesting improved self-healing. This behavior, in which specimens cured with high CO_2 had a more conductive chemical state, is also observable from data in Table 3. As discussed, electrical measurements of a concrete-like material are affected not only by the changes in pore characteristics, maturity, and mechanical properties, but also to a great extent by the ionic state of specimens at the time of testing. In light of this information, it can be stated that due to the high CH concentration of F-ECC-5%-CH specimens, pH values may get higher, which can accelerate the disassociation of CO_3^{2-} and HCO_3^- ions. With the easier diffusion of CO_2 into specimens at high concentrations, carbonation reactions could be more widespread over the specimens and disassociation of various carbonate species could get faster, leading to less electrical resistivity (EI herein).

ECC mixtures containing ground-granulated blast-furnace slag (S-ECC)

Twenty-eight-day RCPT results of S-ECC specimens are provided as raw data in Table 3. As seen, the results were in the 611 to 621 C range, meaning that 28 days of initial curing was more than enough for sound S-ECC specimens to exhibit chloride ion permeability results regarded as "very low" by ASTM C1202. Compared to sound specimens of other ECC mixtures, the lowest RCPT values were obtained from S-ECC specimens. This difference can be attributed to the fact that significantly finer slag particles with self-cementing capability contributed more to hydration reactions than Class F fly ash particles, forming a denser microstructure with disconnected pore structure and lower porosity.[11] Because sound S-ECC specimens were preloaded for microcrack generation, RCPT results escalated suddenly, as in other ECC mixtures. However, sharper increments were noted in average chloride ion permeability results of sound S-ECC specimens. For example, the percentage increments in RCPT results of sound S-ECC specimens, which were to be further cured without excessive CO_2, with initial preloading, were 182% (from 611 C to 1720 C), while the same values for F-ECC and F-ECC-5%-CH mixtures were 133% (from 910 C to 2116 C) and 123% (from 1071 C to 2384 C), respectively. A greater rate of increment in RCPT results of S-ECC specimens was associated with the tendency of slag particles to increase PVA fiber/matrix interface chemical bonding and matrix fracture toughness while reducing interface frictional bond, causing lower ductility and wider crack widths (Fig. 2(a)). In addition, because the sound S-ECC specimens had already reached very low chloride ion permeability levels at the end of 28 days, relative increments in the results with the application of initial preloading was

higher, although the differences in individual results did not show high variations compared to other ECC mixtures.

Percentage changes in RCPT results of S-ECC specimens with 28 days of further curing are shown in Fig. 4. The same decreasing trend in RCPT measurements occurred in S-ECC specimens as in F-ECC and F-ECC-5%-CH, as seen from Fig. 4. However, as also illustrated in Fig. 4, the drop in chloride ion permeability results during the first testing ages was more gradual compared to other ECC mixtures. This may be attributed to the self-cementing capability of slag particles in addition to the possible reactions of alkali hydroxides in portland cement with slag prior to CH formation inside the cementitious matrix.[28] This early reaction of slag with respect to fly ash may provide a denser matrix with disconnected pores at early ages, which results in better RCPT results at 28 days. Less room remains for further development of the matrix, which may result in a more gradual drop in RCPT results.

In terms of the effect of a CO_2-rich environment on RCPT results of S-ECC specimens, Fig. 4 shows no significant changes in percentage for values from sound specimens cured under different environments. Increased tightness of S-ECC matrixes as a result of higher packing and enhanced reactivity could be responsible for the prevention of CO_2 diffusion into the sound specimens, minimizing its influence. For preloaded specimens, on the other hand, RCPT results showed sharper decrements for those cured under a CO_2-rich environment. As Fig. 4 makes clear, the tangent of the curve for preloaded specimens with high CO_2 exposure was sharper, especially for the first 15 days of additional curing, which suggests superior self-healing behavior. However, percentage changes started to get closer with time. Enhancement in the case of CO_2-rich environment can be attributed to accelerated calcite formation due to carbonation that filled up the cracks at early ages (Fig. 2(b)).

EI measurements of S-ECC specimens are shown in Table 3. Average 28-day results of sound S-ECC specimens were 12.3 kΩ and 11.5 kΩ for specimens to be further cured with and without CO_2 exposure, respectively. When checked against the sound specimens of other ECC mixtures, these values were higher. This finding was attributed to the reduced overall porosity and pore size provided with the use of slag particles in ECC systems, in addition to the disassociated system of pores. Lower total alkali amounts in GGBFS could also be responsible for the higher EI results of sound S-ECC specimens compared to other ECC mixtures (Table 1).[19] Another interesting point related to the EI results of S-ECC specimens was that the increments in the values were very high compared to other mixtures with the application of preloading. In the sound S-ECC specimens to be further cured without excessive CO_2 exposure, average EI results of 11.5 kΩ increased to 23.1 kΩ with initial preloading, and the same behavior occurred in sound specimens to be further cured with CO_2. The reactions of different ECC mixtures to initial preloading in terms of changes in EI measurements can be explained by the different crack characteristics. As can also be seen from Fig. 2(a), S-ECC specimens exhibited a smaller number of cracks with higher average crack widths compared to spec-

imens from other mixtures. Therefore, it can be concluded that crack widths are more decisive on EI measurements than crack numbers, which supports the conclusions reached by Yıldırım et al.[19] It should be kept in mind that the low connectivity and tortuosity of the pore network in the preloaded situation could also be one of the reasons for higher EI results of S-ECC specimens. Another possible reason could be the PVA fibers bridging opposite crack lips. Although PVA fibers are nonconductive, they are covered with fragments of conductive cementitious matrix, which may be pulled out with initial preloading or might be the result of microspalling at the crack faces. Given the higher fracture toughness and fiber-to-matrix chemical bonding of S-ECC, there is a higher likelihood for fiber breakage instead of pullout under loading. The higher chance of fiber rupture reduces the possibility for fiber bridging and possible carriage of electrical current over microcracks, leading to higher EI results.

With further environmental curing under different conditions, EI results of S-ECC specimens increased continuously (Table 3). As Fig. 5 makes apparent, percentage changes in EI results of both sound and preloaded S-ECC specimens with further curing were lower than those of F-ECC and F-ECC-5%-CH mixtures. Taking the average EI results of sound specimens from different ECC mixtures to be kept with high CO_2 concentration as an example, EI results increased by 460% (from 12.3 to 68.9 kΩ) from 28 to 28 + 90 day for S-ECC specimens, while the same increment rates for F-ECC and F-ECC-5%-CH specimens were 1624% (from 8.41 to 145 kΩ) and 1473% (from 7.18 to 113 kΩ), respectively. Similar behavior was observed in the overall results from different sound and preloaded specimens. This shows that for sound S-ECC specimens in particular, a relatively high maturity level was reached after 28 days of initial curing. Beyond this period, minimal changes occurred, having only a slight effect on EI results compared to other ECC mixtures. The probable reasons for further increments in EI measurements of S-ECC specimens with additional curing have already been discussed in this paper and elsewhere.[19]

Both the percentage changes in Fig. 5 and the raw data in Table 3 make it clear that CO_2-rich curing was not as effective for S-ECC specimens as it was for the other ECC mixtures in terms of EI measurements. This might be due to considerably lower gas permeability characteristics and relatively high tightness[29] obstructing easy, uniform travel of CO_2 gas into the specimens. One distinctive point related to the effects of environmental conditions on EI measurements of S-ECC specimens was that the individual EI results of preloaded specimens cured under a high-CO_2 environment were higher than those cured under a normal atmospheric environment. The behavior manifested by the preloaded S-ECC specimens was opposite to that observed in F-ECC and F-ECC-5%-CH mixtures. This finding correlates with the enhanced improvements in the cementitious matrixes of preloaded S-ECC specimen microstructure with GGBFS use in a high-CO_2 environment. Although leaching of different conductive carbonate species (which would decrease the EI measurements of pre-loaded S-ECC specimens) was also

expected during calcium carbonate precipitation in microcracks, the superior performance of GGBFS-incorporating cementitious matrixes appears to have increased EI results by lowering pore size, overall porosity, and increasing compressive strength, pore and/or crack tortuosity, which counteracted the anticipated high conductivity.

CONCLUSIONS

This study presents the results of an experimental investigation into the effects of high CO_2 concentration (3%) on the self-healing behavior of ECC mixtures incorporating Class F fly ash (F-ECC), hydrated lime with Class F fly ash (F-ECC-5%-CH), and GGBFS (S-ECC). The self-healing ability of 28-day-old sound and preloaded ECC specimens from different mixtures was assessed via rapid chloride permeability test (RCPT) and direct electrical impedance (EI) measurements. The following conclusions were drawn:

1. Microcracking caused marked escalations in RCPT results of sound ECC specimens. However, the values from both sound and preloaded specimens decreased continuously upon further curing, with considerably larger reductions in the first 15 days of additional curing. Fifteen days of moist curing was more than adequate for all almost-failed ECC specimens to show "very low" chloride ion permeability levels in accordance with ASTM C1202. Although there were natural variations in the RCPT results, conditioning under a CO_2-rich environment favored the reduced RCPT results, especially in F-ECC specimens, which implies better self-healing performance under such conditions.

2. As a relatively new test technique, EI showed itself worthy for assessing self-healing in ECC; results were very consistent. Application of initial preloading increased the EI results of sound ECC specimens regardless of the type of PM selected due to the introduction of microcracks, over which no electrical current can travel. Further curing in different curing cabinets continuously increased EI results of sound and preloaded specimens from different mixtures. This increasing trend appears to be related to pore restriction, consumption of conductive pore media, and increased pore/crack tortuosity. Comparably higher results obtained for preloaded specimens with respect to the sound ones suggest that EI testing is able to capture self-healing occurrence adequately.

3. Sound S-ECC specimens showed relatively lower EI results than F-ECC and F-ECC-5%-CH mixtures, especially at later ages, most probably due to high fineness and reactivity of individual slag particles. For all specimens subjected to high-CO_2 environments, lower EI results were obtained compared to those further cured under normal atmospheric conditions. This is reported to be attributable to changes in the ionic states of different ECC mixtures, which mainly occurred due to the calcination and further hydration capabilities of specimens, along with the formation of different final self-healing products with different formation mechanisms and natures. The only specimen group that did not follow the aforementioned behavior was preloaded S-ECC (higher EI results were obtained for those cured with high CO_2 than those

cured without), which was attributed to the superior performance of GGBFS in enhancing matrix properties.

4. This paper details, for the first time, the positive effects of high CO_2 concentrations on the self-healing capability of cementitious composites, and it can be regarded as a starting point for further study. For upcoming studies, it would be interesting to observe whether the damage introduced due to carbonation or accelerated self-healing behavior in a CO_2-rich environment would outperform one another.

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