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**SPECIAL ISSUE**  
**ON**  
**DURABLE CONCRETE STRUCTURES EXPOSED TO CHLORIDES**

# **ELECTRICAL RESISTANCE TO MONITOR CARBONATION AND CHLORIDE INGRESS**

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5

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10 He has published widely in the field of durability of concrete and its measurements using NDT  
11 and sensors.

12

## ABSTRACT

Electrical resistance (R) of concrete is sensitive to changes in the chemical phases and physical structure of hydrated cement paste, moisture content and the physical structure of concrete. Therefore, R is influenced by both carbonation and chloride ingress. However, in a structure, subjected to a combination of carbonation and chlorides, in which there are complex changes to both physical and chemical characteristics of hydration products, the use of electrical resistance measurements to assess the durability of concrete is still limited. In this investigation, four different combinations of carbon dioxide and chloride exposure regimes were used to examine the relationship between the electrical resistance, degree of carbonation and quantity of chlorides (or chloride content). It has been found that for concretes with a stabilized relative humidity, the electrical resistance is sensitive to cement hydration and variations in chloride content in both independent chloride exposure regime and combined chloride and carbonation regime. However, the relationship between electrical resistance and the degree of carbonation is not that pronounced for accelerated carbonation test regime for three months.

**Key words:** electrical resistance, chloride ingress, carbonation, relative humidity, combined carbonation and chloride ingress

## INTRODUCTION AND RESEARCH SIGNIFICANCE

The electrical resistance (R) is used nowadays to assess the durability of cement-based materials. Numerous sensors and monitoring systems have been developed to determine this property, such as the Anode Ladder (1), the Multi Ring Electrode (2) and the Covercrete Resistance Array (3). Due to the high sensitivity of electrical resistance to chemical and physical changes in pore structure of concrete, the electrical resistance is already used in structures to monitor the ingress of chloride ions (Cl<sup>-</sup>) in cover concrete (1-4). Despite numerous practical applications of this approach, interpretation of electrical resistance data to assess accurately chloride profile or chloride content is still a challenge because of the high level of background noises from other factors, e.g. hydration, temperature and moisture content (4).

Both the independent and combined effects of CO<sub>2</sub> and Cl<sup>-</sup> are frequently associated with the corrosion of reinforcement in structures exposed to the atmospheric and tidal zones in the marine environment (5, 6), in abutments of bridges or in concrete tunnel linings constructed in cold regions, where salt is used for melting ice in the winter (7). Results from existing studies have clearly shown that concrete exposed to CO<sub>2</sub> is less resistant to Cl<sup>-</sup> (8-10). This effect is complex and has not been fully considered in the above practical situations. Thus, there is a compelling need to propose an easy, rapid and reliable approach to identify the rate of Cl<sup>-</sup> ingress and carbonation under these combined conditions. Electrical resistance is one potential parameter which is sensitive enough to detect changes in moisture, ion concentration and microstructure. At the moment, the individual effect of these factors on electrical resistance

1 signals have been widely studied, which can be used to remove corresponding influences on  
2 the electrical resistance data. However, the effect of carbonation induced changes in  
3 microstructure and chemical compositions in concrete on the electrical resistance signals is still  
4 unclear, so as to validate whether it is possible to assess the ingress of  $\text{Cl}^-$  in concretes with a  
5 satisfactory degree under the combined carbonation and chloride ingress exposures.

6  
7 Against these backgrounds, a systematic investigation was carried out to clarify the influence  
8 of  $\text{Cl}^-$  and  $\text{CO}_2$  on electrical resistance in **cover concrete** with an aim of proposing a  
9 methodology to determine the chloride profile from resistance results. New analytical methods  
10 are offered, thus assisting the industry to more easily estimate the chloride profile from a  
11 coupled transport process and accordingly predict the service life. An explanation of the  
12 analytical procedure is also given, thus helping researchers who have queried the basis of this  
13 method.

## 15 **EXPERIMENTAL PROGRAMME**

### 16 **Materials and Test Specimens**

17 Details of the mixes used in this investigation were the same as those reported in a previous  
18 paper by the authors (8). As some readers may not have access to this paper, details relevant to  
19 this paper are given below.

1 **Table 1** gives detailed proportions of the concrete mixes used in this study. All the mixes were  
2 selected according to the British standard BS EN 206 (11) for designing concretes exposed to  
3 medium extents of carbonation (XC2 class), chloride induced reinforcement corrosion from  
4 deicing salts (XD2 class) and marine environment (XS2 class) for an expected service life of  
5 50 years. Therefore, they had a w/b of 0.55 and a total binder content of 320kg/m<sup>3</sup> (19.968  
6 lb/ft<sup>3</sup>). Three types of binders were used, viz. Portland cement (PC), Pulverised Fuel Ash (PFA)  
7 and microsilica (MS). Based on the w/b and type of binder used, the three mixes are denoted as  
8 0.55PC, 0.55PFA and 0.55PFA+MS. The slump of the fresh concretes was adjusted in the range  
9 of 50 to 90mm (1.95 to 3.51 in) (which is S2 class in the British standard BS EN 206) by using  
10 a polycarboxylate based superplasticiser.

11

12 Three types of concrete blocks were manufactured for carrying out different tests:

13 (i) Blocks of size 150x150x80mm (**Fig. 1a**) with four embedded PVC tubes of different lengths  
14 (10, 20, 30 and 40mm) (0.39, 0.78, 1.17, 1.56 in) were cast for monitoring the RH of concrete  
15 (**Fig. 1b**) during conditioning and carbonation. The details of experimental procedures were  
16 described by Russell *et al.* (12).

17 (ii) Blocks of size 150x150x80mm embedded with four pairs of electrodes at the depths of 5,  
18 15, 25 and 35mm (0.195, 0.585, 0.975, 1.365 in) were manufactured for monitoring the  
19 development of electrical resistance under the different exposures. The stainless steel electrodes  
20 had a length of about 200mm and wrapped with electric insulation tube, leaving a 10mm (0.39  
21 in) stripped part at the middle for testing the electrical resistance. The configuration of



1 electrodes is shown in **Fig. 2a**.

2 (iii) Blocks of size  $500 \times 500 \times 80 \text{mm}^3$  ( $19.5 \times 19.5 \times 3.12 \text{in}^3$ ) were cast for coring  $\Phi 75 \times 80 \text{mm}$   
3 ( $\Phi 2.925 \times 3.12 \text{in}$ ) cylindrical specimens. After each exposure regime, two replicate cylinders  
4 were used to determine the extent of carbonation and degree of chloride ingress using methods  
5 described below, and the average values are presented in the paper.

6

7 All specimens were covered with polythene sheet and placed in a room at a temperature of  
8  $20 \pm 2^\circ\text{C}$  ( $68 \pm 3.6^\circ\text{F}$ ) for 24 hours initial curing. The samples were then demoulded and were  
9 subjected to another period of 55 days of curing, which included water curing for 6 days with  
10 controlled temperature of  $20 \pm 1^\circ\text{C}$  ( $68 \pm 1.8^\circ\text{F}$ ) and storage in a room environment at  $20 \pm 1^\circ\text{C}$   
11 ( $68 \pm 1.8^\circ\text{F}$ ) and  $60 \pm 5\%$  RH for 49 days.

12

### 13 **Exposure Regimes and Test Methods**

14 The independent and combined carbonation and chloride ingress regimes are denoted as  $x\text{Cl}^-$ ,  
15  $y\text{CO}_2$ ,  $y\text{CO}_2 + x\text{Cl}^-$  and  $x\text{Cl}^- + y\text{CO}_2$ , where x and y indicate the duration of exposure to chlorides  
16 and carbon dioxide, respectively. For example,  $x\text{Cl}^-$  indicates that these samples were exposed  
17 to 'x' months of chloride ingress;  $y\text{CO}_2 + x\text{Cl}^-$  indicates that the concretes were exposed to a  
18 combined carbonation and chloride ingress exposure regime, starting with 'y' months of  
19 carbonation and a subsequent immersion in chloride solution for 'x' months. Furthermore, since  
20 the measured electrical resistances are also influenced by both the continuous hydration of  
21 cement and moisture/water content of the samples, control exposure regimes have also been

1 considered for assessing these two effects on the test results. Corresponding to the ‘xCl<sup>-</sup>’ and  
2 ‘yCO<sub>2</sub>’, the control regimes are respectively denoted as ‘xH<sub>2</sub>O’ and ‘yAir’ in this study. In all  
3 the designed regimes, maximum duration for the carbonation and chloride ingress processes  
4 was three months for practical reasons of completing the laboratory study within the project  
5 duration.

6  
7 As the ingress of Cl<sup>-</sup> and CO<sub>2</sub> in concretes and the measured electrical resistance values are  
8 strongly related to the moisture condition, i.e. water content, of the concretes, the test samples  
9 were conditioned to a constant RH value before the carbonation and the immersion in chloride  
10 solution. In both the individual and combined regimes, samples for the ‘CO<sub>2</sub>’ and ‘Air’ test  
11 regimes were conditioned to a consistent internal relative humidity (RH) of 65 ±2% before the  
12 exposure, and those for ‘Cl<sup>-</sup>’ and ‘H<sub>2</sub>O’ test regimes were conditioned to a fully water saturated  
13 state in advance. It has been established previously that the internal RH could be relied on for  
14 interpreting results on the effect of moisture content (8) and hence, no separate measurement of  
15 the moisture content was carried out. Details for the RH conditioning procedure have also been  
16 reported in the previous paper (8). The entire curing and conditioning processes lasted for a  
17 duration of approximately 4 months, which was then followed by the carbonation or chloride  
18 ingress exposure regimes.

19  
20 For the carbonation process, the carbonation chamber was kept at 20±1°C (68±1.8°F), 5±0.1%  
21 CO<sub>2</sub> and 65±2% RH, and the corresponding control ‘Air’ exposure was at an environment of

1 20±1°C (68 ±1.8°F) and 65±2% RH. For the chloride exposure, sodium chloride solution  
2 (165g/l (1.252lb/ft<sup>3</sup>)), as defined in NT Build 443 (13) and corresponding to the chloride content  
3 of some marine conditions, was used at a temperature of 20±1°C (68±1.8°F) and the  
4 environment for the control 'H<sub>2</sub>O' exposure was a water tank containing tap water at a  
5 temperature of 20 ±1°C (68 ±1.8°F).

6  
7 During all the test regimes, two cylindrical samples of each mix were taken out every two weeks  
8 for assessing the degree of carbonation and chloride ingress. Powder samples were extracted  
9 by progressively profile grinding from the exposure surface in layers up to a depth of  
10 approximately 30mm. In the region that was close to the exposure surface (0-5mm) (0-0.195in),  
11 the degree of carbonation and the chloride concentration were relatively high and changes in  
12 degree of carbonation and chloride ingress were obvious. Therefore, powder samples were  
13 extracted every 1mm (0.039in) to determine the extent of the ingress. At the inner depths  
14 (beyond 5mm (0.195in)), the degree of carbonation as well as the chloride concentration had  
15 relevantly smaller difference and hence dust samples were collected from 2mm (0.078in) to  
16 3mm (0.117in) deep layer of concrete. The exact location of the depth at which the powder  
17 samples were collected was measured by using a Vernier caliper.

18  
19 The powder samples were analysed for the acid soluble chloride content in accordance with  
20 RILEM TC 178-TMC recommendations (14). Meanwhile, the pH of solution that was obtained  
21 by digesting the powder samples in deionized water was determined, which was used to indicate

1 the alkalinity of concretes, referred to as the apparent pH (15). For this purpose,  $1\pm 0.001\text{g}$   
2 ( $0.0268\pm 0.00000268\text{lb}$ ) of powder sample from each layer was digested with 20ml ( $0.00122\text{in}^3$ )  
3 of deionized water. By further analysis of the results, the amount of consumed  $\text{OH}^-$  at different  
4 depths of the samples was ascertained using Eq. 1, where the  $\text{pH}_0$  and the  $\text{pH}_x$  are the apparent  
5 pH results measured before and after the exposure.

$$6 \quad \text{Consumed } \text{OH}^- = \text{Initial } \text{OH}^- - \text{Remaining } \text{OH}^- = 10^{\text{pH}_0-14} - 10^{\text{pH}_x-14} \quad (\text{Eq. 1})$$

7 The samples for measuring the electrical resistance were taken out from the exposure regimes  
8 (chloride as well as carbonation) at every 7 days and measurements were carried out using a  
9 handheld LCR meter. During measurements, alternating current with a frequency of 1kHz was  
10 selected and the cathode and anode of the meter were connected with the stripped part of the  
11 electrodes (as shown in **Fig. 2b**).

12  
13 For the chloride exposure samples, free water on the surface of test specimens and electrodes  
14 was wiped with tissue paper before carrying out measurements. Once the measurements were  
15 completed, the test samples were put back immediately for continuing with the exposure. In the  
16 case of samples exposed to carbon dioxide, in addition to the weekly determination of the  
17 electrical resistivity, the RH at the four different depths from the exposure surface of concretes  
18 (**Fig. 1**) was measured at every two weeks with a digital RH meter.

19

## PRESENTATION AND DISCUSSION OF RESULTS

### Methodology of interpreting the resistance data from chloride exposure tests

Figure 3a - 3c show the changes in the as-measured electrical resistance (R) for the three tested concretes under the '3H<sub>2</sub>O' regime, while Fig. 3d is the normalized resistance, i.e. R<sub>t</sub>/R<sub>0</sub>, where R<sub>t</sub> and R<sub>0</sub> indicate the R values measured using the electrodes at different exposure duration t and before the exposure respectively, for the 0.55PC mix. The data in these figures will be discussed in the next section.

As highlighted in the introduction, R values are affected by the degree of hydration and internal environmental conditions of the concrete, viz. temperature and relative humidity, which could vary at different depths from the exposure surface. By normalizing the resistance, the effect of depth on the resistance variation can easily be identified. In Fig. 3d, obviously there is no effect of depth on the resistance variation with time, which would confirm that the degree of hydration and internal environmental conditions at different electrode depths were similar across the tested depths.

Another parameter that will be used for the interpretation of data is the ratio of change in resistance between R<sub>t</sub> and R<sub>0</sub> to R<sub>0</sub>, ΔR (Eq.2):

$$\Delta R = \frac{R_t - R_0}{R_0} \quad (\text{Eq. 2})$$

This ratio indicates the change in resistance with time of a sample subjected to a specific

1 exposure,  $R_t$ , compared to the resistance of a control (non-exposed sample),  $R_o$ , expressed as a  
2 ratio with respect to the latter. So  $\Delta R$  gives the influence of exposure on change in resistance  
3 with time, for a specific depth in the concrete.

4  
5 **Figure 3d** also indicates that for the '3H<sub>2</sub>O' regime (i.e. under the water saturated condition),  
6 the normalized R of the concrete at the 35mm (1.365in) depth can be used to assess the effects  
7 of cement hydration across the whole depth of the concrete specimen. It can also be expected  
8 that when there is the chloride ingress the difference of  $\Delta R$  between the electrode at any depth  
9 of the exposed sample and that at 35mm (1.365in) of the control, non-exposed sample, can be  
10 used to quantify the influence of ingress Cl<sup>-</sup> on the R value at that specific depth (16, 17),  
11 expressed using Eq.3:

$$12 \quad \Delta R_d = \Delta R_i - \Delta R_{ref} \quad (\text{Eq. 3})$$

13 where  $\Delta R_d$  indicates the difference of normalized R value at a specific depth;  $\Delta R_i$  represents  
14 the normalized R value for the specific electrode embedded at the depth of  $i$  mm for the sample  
15 exposed to the test condition;  $\Delta R_{ref}$  represents the normalized R value of the reference electrode,  
16 *i.e.* the 35mm (1.365in) electrode, for the control sample not exposed to the test condition.

17

### 18 **Influence of the 3Cl<sup>-</sup> regime on electrical resistance**

19 **Figures 3a - 3c** show that in each concrete, prior to the three months immersion in water, the R  
20 values were mostly in the range of 2 to 7 k $\Omega$  (in the 0.55PFA+MS, the 35mm (1.365in) value

1 was slightly higher than the other three depths). The PFA and PFA+MS concretes had a higher  
2 R than the PC concrete, indicative of the denser pore structure of these concretes caused by the  
3 two supplementary cementitious materials (18). For the three concrete mixes in **Fig. 3**, the  
4 measured R values at different depths increased gradually with the duration of water immersion,  
5 which can be considered to be due to the continuous hydration of the cementitious materials  
6 (16). The difference in slope for the R values at 35mm (1.365in) depth gives an indication of  
7 the effect of degree of continuous hydration **during the immersion**, the order of which is  
8 PFA+MS > PFA > PC.

9  
10 **Figures 4a - 4c** present the changes in R values for the concretes immersed in the NaCl solution.  
11 Compared with the results of the three concrete mixes tested in the 3H<sub>2</sub>O regime (**Fig. 3a - 3c**),  
12 the initial R values of the corresponding three concretes here are very close. However, the R  
13 values of the concretes immersed in the chloride solution gradually decreased as the immersion  
14 duration increased (**Fig. 4**), primarily due to the increase of mobilized Cl<sup>-</sup> in the samples as  
15 reported by others (17-19). The decrease in R values measured with the first tier of electrodes  
16 nearer to the surface was evident, particularly for concrete mixes containing supplementary  
17 cementitious materials (**Figs. 4b and 4c**), which is considered to be due to the relatively higher  
18 content of Cl<sup>-</sup>, and associated higher chloride binding by hydrated cement phases, at the near-  
19 surface layer (18, 19).

## 1 Relationship between $\Delta R_d$ and chloride concentration for 3Cl<sup>-</sup> regime

2 During the ingress of Cl<sup>-</sup> into concrete, the R value starts changing only when Cl<sup>-</sup> arrives at the  
3 sensitive test depth (STD) of electrodes. According to a Finite Element study by Rajabipour *et*  
4 *al.* (20), the STD of a pair of electrodes in a homogeneous material is  $-0.6 \sim +0.6d_{\text{elec}}$ , where the  
5 ‘ $d_{\text{elec}}$ ’ refers to the distance between the two electrodes, *i.e.* 10mm in this study. The ‘+’ means  
6 depth above the electrodes and the ‘-’ indicates depth below the electrodes. As R changes with  
7 the increase in Cl<sup>-</sup> content, it can be expected that there is a corresponding influence on STD.  
8 From **Fig. 4d**, for a concrete subjected to chloride immersion, the ratio of R values before and  
9 after the chloride ingress is approximately 0.5 and, hence, based on the analysis by Rajabipour  
10 *et al.* (20), the STD of electrodes changes slightly to the range of  $-0.5 \sim +0.6d_{\text{elec}}$ . **Table 2**  
11 summaries the STD of the embedded electrodes in this study.

12  
13 The ingress of Cl<sup>-</sup> during the three months of immersion in NaCl solution and its distribution  
14 in the three concretes were reported in a previous paper (8). With the Cl<sup>-</sup> distribution profiles,  
15 the content of Cl<sup>-</sup> ( $Q_{\text{Cl}^-}$ ) that led to changes in the R values can be determined by integrating the  
16 area under the Cl<sup>-</sup> distribution profiles at the corresponding STD, as illustrated in **Fig. 5**.  
17 Therefore, to establish the usefulness of electrical resistance measurements, the  $\Delta R_d$  from Eq.  
18 3 can be compared with  $Q_{\text{Cl}^-}$ , as shown in **Fig. 6** for the 3Cl<sup>-</sup> exposure regime.

19  
20 As the grinding bits used for extracting powder samples to determine the ingress of Cl<sup>-</sup> and  
21 degree of carbonation were of a length of about 30mm (1.17in), the content of Cl<sup>-</sup> and OH<sup>-</sup>



1 beyond this depth was not available. Further, the R value from electrodes at a depth of 35mm  
2 (1.365in) did not present any obvious change in this study. Therefore, the relationship between  
3 the R value and the ingress of  $\text{Cl}^-$  was established in **Fig. 6** based on R values obtained from  
4 electrodes at the depths of 5mm (0.195in), 15mm (0.585in) and 25mm (0.975in).

5

6 Results in **Fig. 6** indicate that generally  $\Delta R_d$  decreased with an increase in  $Q_{\text{Cl}^-}$  in all the three  
7 concrete mixes, but no general relationship can be established for the three mixes together.  
8 Furthermore,  $Q_{\text{Cl}^-}$  and  $\Delta R_d$  corresponding to the top layer, *i.e.* 0-5mm (0.195in), varied  
9 significantly. This is because most of the  $\text{Cl}^-$  ingress was at this layer, resulting in an increase  
10 in the  $Q_{\text{Cl}^-}$  value and a correspondingly decrease in  $\Delta R_d$ . At the inner depths of concretes, e.g.  
11 0.55PC 15mm (0.585in) and 25mm (0.975in) and 0.55PFA 25mm (0.975in),  $Q_{\text{Cl}^-}$  increased  
12 during the three months of immersion, but the variation in R was not obvious. This indicates  
13 that R did not decrease instantly when the chloride ions entered the STD of the electrodes. It  
14 might be due to the effect of chloride binding by hydration products (21), which will not  
15 contribute to the electrical current flow during the electrical resistance test. In addition to this,  
16 for the 0.55PFA+MS 15mm (0.585in) result,  $Q_{\text{Cl}^-}$  was relatively stable, while the  $\Delta R_d$  value  
17 changed significantly, which is an unexpected phenomenon that requires further investigation.  
18 Based on the different trends obtained, it can be inferred that the electrical resistance related  
19 parameter,  $\Delta R_d$ , cannot satisfactorily identify the amount of  $\text{Cl}^-$  ingress into the three concretes  
20 in the  $3\text{Cl}^-$  regime.

21

1 **Influence of the 3CO<sub>2</sub> regime on electrical resistance**

2 **Figure 7** shows changes in R values for the three concrete mixes when exposed to 3 months in  
3 the ‘Air’ environment (i.e. 20°C (68°F), 65% RH). The as-measured data (**Figs. 7a - 7c**),  
4 especially for those at inner depths, indicate that the samples were in a relatively stable  
5 condition. It can also be seen that R values from the 5mm (0.195in) electrode were relatively  
6 higher than that for electrodes from other depths. The higher R value for the surface was also  
7 observed by McCarter *et al.* (19) and this is due to a combination of different factors, including  
8 the wall effect during the manufacture of the specimens, where the proportion of coarse  
9 aggregate, mortar and cement paste in the surface area is different from that of the inner concrete.  
10 In addition, during curing and conditioning of the test specimens, the moisture in the near-  
11 surface region might have evaporated, leading to a modest level of carbonation, both of which  
12 could lead to a higher resistance at the 0-5mm (0.195in) region.

13

14 **Figures 7a - 7c** also show that the R values for the 5mm (0.195in) deep electrodes increased  
15 with the exposure duration. When the concrete blocks were exposed to the ‘Air’ environment  
16 at 20°C (68°F), 65% RH, it is highly likely that there was the slow release of moisture from the  
17 near surface region as well as mild carbonation, both of which are known to increase the  
18 resistance. When R values at the 5mm (0.195in) depth for the three concrete mixes are  
19 compared, 0.55PFA had the highest change in resistance, followed by 0.55PFA+MS and the  
20 0.55PC coming last. That is, the combined effect of drying out and mild carbonation is the  
21 highest for the PFA concretes.

1 At the inner depths (15-35mm (0.585-1.365in)), the R values for the PFA and PFA+MS were  
2 higher than that of the PC, similar to the data in **Figs. 3 and 4**, which is believed to be caused  
3 by the refinement of pore structure by PFA and MS (8, 12). Based on the trends observed in  
4 **Fig. 7**, it can be concluded that the R values from the 35mm electrode are able to exclude the  
5 effect of exposure to air, which is similar to what was deduced from the 3H<sub>2</sub>O regime.

6

7 The normalized R values in **Fig. 7d** continually increased during the test duration, meaning that  
8 there was continuous hydration of PC in the 0.55PC concrete. Results for both 0.55PFA and  
9 0.55PFA+MS (not presented here) were similar to that for 0.55PC.

10

11 **Figure 8** shows the changes in R values during the three months of exposure to CO<sub>2</sub>; **Figs. 8a**  
12 **- 8c** presenting the as-measured data and **Fig. 8d** showing the normalized electrical resistance  
13 ratio for the 0.55PC concrete. In **Fig. 8** two different trends can be seen for the change in R  
14 value with time for the electrode at 5mm (0.195in) depth, one for the 0.55PC concrete (**Fig. 8a**)  
15 and the other for the two concretes containing supplementary cementitious materials (**Fig. 8b**  
16 and 8c). In the case of 0.55PC concrete, the R value for the 5mm (0.195in) electrode increased  
17 initially and then continually decreased. However, there was a sharp decrease in R value for  
18 both 0.55PFA and 0.55PFA+MS concretes. These variations can be explained by relating the  
19 electrical resistance changes to the degree of carbonation.

20

21 As reported in a previous paper (8), the degree of carbonation in the three concretes followed a

1 descending order of 0.55PFA > 0.55PFA+MS > 0.55PC. Further, for each concrete block, the  
2 degree of carbonation at the surface layer (0-5mm (0-0.195in) depth) was relatively higher than  
3 that at inner depths (>5mm (0.195in)). Combining these findings from (8) with the changes in  
4 R values in **Figs. 8a - 8c**, it can be deduced that the R values decreased sharply for concretes  
5 which were carbonated extensively, whilst the PC concrete which carbonated the least had an  
6 increase in R value initially, followed by a gradual decrease with exposure time. Basheer *et al.*  
7 (22) found a similar trend in R values during their accelerated carbonation, *viz.* R increased at  
8 the initial stage of carbonation, which was followed by a slight decrease with further exposure  
9 to CO<sub>2</sub>. They also detected an increase in RH with increased carbonation. Therefore, they  
10 assigned the increase in R value to the pore refinement (densification of pores) due to  
11 carbonation and the gradual decrease to the increase in RH value with the progress of  
12 carbonation.

13

14 The significant decrease in R value for both 0.55PFA and 0.55PFA+MS concretes is considered  
15 to be due to the presence of carbonation induced cracks in the 0-5mm (0-0.195in) region.  
16 Further gradual decrease in R values for these two cases in the 0-5mm (0-0.195in) region is due  
17 to an increase in RH from 55% to 75% (values measured from the RH samples).

18

### 19 **Relationship between $\Delta R_d$ and degree of carbonation for 3CO<sub>2</sub> regime**

20 As seen in **Fig. 8d**, the R ratio during and prior to the carbonation varied in the range of 0.1 to  
21 3.5 and this can affect the STD of electrodes to a limited extent according to Rajabipour *et al.*'s

1 results (20). Therefore, for establishing the relationship between R and degree of carbonation,  
2 the STD was assumed to be the same as that for the chloride ingress study, as given in **Table 2**.

3 Following the similar methodology as presented previously, the correlation between degree of  
4 carbonation (revealed by amount of consumed  $\text{OH}^-$  (8) ) and  $\Delta R_d$  in the tested three concretes  
5 can be determined obtained and **Fig. 9** shows the results. Clearly, there is no strong relationship  
6 between the two parameters, which should be due to the inter-related influence of  
7 microstructure modifications and RH changes during the carbonation on the  $\Delta R_d$ . Therefore, no  
8 further analysis on this relationship was carried out.

#### 10 **Relationship between $\Delta R_d$ and chloride concentration for the $3\text{Cl}^-+3\text{CO}_2$ regime**

11 The measured electrical resistances for the three types of concrete for the  $3\text{Cl}^-+3\text{CO}_2$  regime  
12 were analysed by following the procedures described in previous sections and the relationship  
13 between the change in normalized R values,  $\Delta R_d$ , and the amount of  $\text{Cl}^-$  in the STD,  $Q_{\text{Cl}^-}$ , was  
14 established for the three types of concretes (**Fig. 10**). The data in **Fig. 10** are for the  $3\text{CO}_2$  part  
15 of the exposure regime, but still analyzing for establishing the relationship between  $\text{Cl}^-$   
16 distribution and the electrical resistance variations. Clearly, the two parameters are linearly  
17 related for all three concrete mixes and the value of  $\Delta R_d$  decreases with an increase in  $Q_{\text{Cl}^-}$ . This  
18 confirms that R values could reveal the distribution and content of  $\text{Cl}^-$  in concretes during the  
19  $\text{CO}_2$  stage of the  $3\text{Cl}^-+3\text{CO}_2$  exposure regime, much better than the relationship obtained in  
20 **Fig. 6** between the two parameters for the  $3\text{Cl}^-$  regime. The concretes were in a relative dry  
21 condition (RH between 50% and 70%) during the three months of exposure to  $\text{CO}_2$ .

1

## 2 **Relationship between $\Delta R_d$ and chloride concentration for the $3CO_2+3Cl^-$ regime**

3 **Figure 11** shows the relationship between  $\Delta R_d$  and  $Q_{Cl^-}$  in the STD during the chloride ingress  
4 stage of the  $3CO_2+3Cl^-$  regime. It can be seen that the  $\Delta R_d$  decreased with an increase in  $Q_{Cl^-}$   
5 and once again the relationship between the two parameters is linear. Therefore, it can be  
6 concluded that the R value is capable of identifying the ingress of  $Cl^-$  in concretes when exposed  
7 to the  $3CO_2+3Cl^-$  regime.

8

## 9 **The possibility of using electrical resistance to assess ingress of $Cl^-$ in concretes**

10 Based on the previous analyses of the relationship between  $\Delta R_d$  of electrodes and  $Q_{Cl^-}$  after  
11 exposing to various combinations of regimes (**Figs. 6, 10 and 11**), it is clear that the two  
12 parameters followed approximately a linear relationship, although the coefficient of regression  
13 ( $R^2$ ) for some of the datasets is not very high. The coefficients of regression analysis for all the  
14 cases reported in this paper are summarized in **Table 3**, together with the initial as-measured R  
15 value (in  $k\Omega$ ) at the 35mm (1.365in) depth for the control specimens before subjecting to any  
16 of the exposures. It can be found that the relationship is the best for the ' $3Cl^-+3CO_2$ ' regime,  
17 followed by the ' $3CO_2+3Cl^-$ ' regime, whilst that for the ' $3Cl^-$ ' regime was relatively poor. This  
18 does not follow the as-measure R values of concretes prior to the exposure, which means that  
19 the influence of RH and degree of densification of the concretes during the exposure need to be  
20 studied further.

21

1 **Figure 12** shows all the data obtained from the three chloride exposure regimes, viz.  $3\text{Cl}^-+3\text{CO}_2$ ,  
2  $3\text{CO}_2+3\text{Cl}^-$  and  $3\text{Cl}^-$ , and the two parameters show a relatively strong linear relationship. It  
3 may be noted that the regression analysis was carried out for the 0.55PFA+MS concrete (**Fig.**  
4 **12c**) after discarding the data from the 5mm deep electrodes for the  $3\text{Cl}^-$  regime (**Fig. 6c**) due  
5 to the absence of any specific trend for this data set. Although microcracks were present at the  
6 near surface layer of the concretes for the  $3\text{CO}_2+3\text{Cl}^-$  exposure, results in **Fig. 12** show that  
7 these cracks did not have any influence on the relationship between  $Q_{\text{Cl}^-}$  and  $\Delta R_d$ .

## 9 CONCLUSIONS

10 Based on the results obtained in this study, the following conclusions have been drawn:

- 11 1. During the exposure of concrete to individual and combined carbonation and chloride  
12 ingress regimes, once RH of concretes is maintained without significant variation, the  
13 electrical resistance at various depths of concretes can effectively reflect the influence of:  
14 (a) the continuous hydration of cement during the exposure; (b) variation in  $\text{Cl}^-$  contents in  
15 concretes; (c) the combined effect of chlorides and carbonation of concretes.
- 16 2. The change in normalized electrical resistance,  $\Delta R_d$  decreased linearly with an increase in  
17 the content of  $\text{Cl}^-$  in the sensitive test depth of the corresponding electrode,  $Q_{\text{Cl}^-}$  and this  
18 relationship was different for the three concrete mixes.
- 19 3. The relationship between  $\Delta R_d$  and the extent of carbonation in the sensitive test depth of the  
20 corresponding electrode,  $Q_{\text{OH}^-}$  was very poor, which was related to the complex interactive  
21 effects of pore modification and change in RH due to carbonation. Therefore, electrical  
22 resistance cannot be used to assess either the onset or the degree of carbonation.

1 4. Monitoring the resistance profile within the concrete cover allows the assessment of the  
2 variation of chloride contents in concrete under the combined CO<sub>2</sub> and chloride exposure  
3 conditions, provided the influences of hydration, temperature and moisture on resistance  
4 are removed. According to the results obtained, the resistance alone, however, is not  
5 sensitive enough to assess the carbonation process even without the influence from these  
6 factors.

7 It should be highlighted that the conclusions obtained are based on the specific exposure  
8 regimes, which did not fully cover all practical situations. It means that further study is required  
9 to verify the proposed approach under different combinations of environmental conditions.

10 Another aspect that requires the attention is that the observations were collected from a  
11 relatively short duration of exposure and, therefore, a long-term experiment should be carried  
12 out to further assess the link between the Cl<sup>-</sup> content and resistance at different ages and  
13 combinations of exposure regimes. Finally, a field study would be very valuable to establish  
14 the reliability of the laboratory-based research for establishing a reliable, rapid and easy  
15 technique for monitoring concrete durability.

#### 17 **ACKNOWLEDGEMENT**

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19 Physical Sciences Research Council (EP/G042594/1), the National Nature Science Foundation  
20 of China (Project number: 51520105012, 51678368, 51878102) and the Chinese Scholarship  
21 Council.



## 1 REFERENCES

- 2 1. A. Husain, S.K. Al-Bahar, and S.A.A. Salam, Performance indicator of the atmospheric  
3 corrosion monitor and concrete corrosion sensors in Kuwait field research station, *Smart*  
4 *Struct. Syst.*, 17(6), 2016, 981-994.
- 5 2. R. du Plooy, S.P. Lopes, G. Villain, and X. Derobert, Development of a multi-ring  
6 resistivity cell and multi-electrode resistivity probe for investigation of cover concrete  
7 condition, *NDT & E International*, 54, 2013, 27-36.
- 8 3. W.J. McCarter, G. Starrs, S. Kandasami, R. Jones, and M. Chrisp, Electrode Configurations  
9 for Resistivity Measurements on Concrete, *ACI Materials Journal*, 106(3), 2009, 258-264.
- 10 4. W.J. McCarter, G. Starrs, A. Adamson, T.M. Chrisp, P.A.M. Basheer, S. Nanukuttan, S.  
11 Srinivasan, and C. Green, Influence of Different European Cements on the Hydration of  
12 Cover-Zone Concrete during the Curing and Post-curing Periods, *Journal of Materials in*  
13 *Civil Engineering*, 25(9), 2013, 1335-1343.
- 14 5. P. Castro, E.I. Moreno, and J. Genesca, Influence of marine micro-climates on carbonation  
15 of reinforced concrete buildings, *Cement and Concrete Research*, 30, 2000, 1565-1571.
- 16 6. T.U. Mohammed, H. Hamada, and T. Yamaji, Concrete after 30 years of exposure - Part II:  
17 Chloride ingress and corrosion of steel bars, *ACI Materials Journal*, 101(1), 2004, 13-18.
- 18 7. R.R. Avelano and N.F. Ortega, Characterization of concrete cracking due to corrosion of  
19 reinforcements in different environments, *Construction and Building Materials*, 25(2),  
20 2011, 630-637.

- 1 8. Y. Wang, P.A.M. Basheer, S. Nanukuttan, and Y. Bai, Influence of combined carbonation  
2 and chloride ingress regimes on rate of ingress and redistribution of chlorides in concretes,  
3 *Construction and Building Materials*, 140, 2017, 170-183.
- 4 9. M. Moreno, W. Morris, M.G. Alvarez, and G.S. Duffó, Corrosion of reinforcing steel in  
5 simulated concrete pore solutions Effect of carbonation and chloride content, *Corrosion*  
6 *Science*, 46(11), 2004, 2681-2699.
- 7 10. S. Pakawat and T. Uomoto, Effect of cyclic exposure of carbonation and chloride on  
8 corrosion of reinforcing steel in concrete, *Seisan Kenkyu*, 57(2), 2005, 29-32.
- 9 11. British Standard Institution, BS EN 206-1 Concrete. Specification, performance,  
10 production and conformity, London, 2000.
- 11 12. D. Russell, P.A.M. Basheer, G.I.B. Rankin, and A.E. Long, Effect of relative humidity and  
12 air permeability on prediction of the rate of carbonation of concrete, *Proceedings of the*  
13 *Institution of Civil Engineers: Structures and Buildings*, 146(3), 2001, 319-326.
- 14 13. Nordtest method, NT BUILD 443 Concrete, hardened Accelerated chloride penetration,  
15 *NORDTEST*, Espoo, Finland, 1995.
- 16 14. Ø. Vennesland, M.A. Climent, and C. Andrade, Recommendation of RILEM TC 178-TMC,  
17 Testing and modelling chloride penetration in concrete: Analysis of total chloride content  
18 in concrete, *Materials and Structures*, 46(3), 2002, 337-344.
- 19 15. D. McPolin, P. Basheer, A. Long, K. Grattan, and T. Sun, New test method to obtain pH  
20 profiles due to carbonation of concretes containing supplementary cementitious materials,  
21 *Journal of Materials in Civil Engineering*, 19(11), 2007, 936-946.

- 1 16. T.M. Chrisp, W.J. McCarter, G. Starrs, P.A.M. Basheer, and J. Blewett, Depth-related  
2 variation in conductivity to study cover-zone concrete during wetting and drying, *Cement  
3 and Concrete Composite*, 24(5), 2002, 415-426.
- 4 17. F. Rajabipour, W. Weiss, and D. Abraham, In-situ electrical conductivity measurements to  
5 assess moisture and ionic transport in concrete, *International RILEM Symposium on  
6 Advances in Concrete through Science and Engineering*, 2004.
- 7 18. P.A.M. Basheer, P.R.V. Gilleece, A.E. Long, and W.J. McCarter, Monitoring electrical  
8 resistance of concretes containing alternative cementitious materials to assess their  
9 resistance to chloride penetration, *Cement and Concrete Composites*, 24(5), 2002, 437-449.
- 10 19. W.J. McCarter, T.M. Chrisp, G. Starrs, P.A.M. Basheer, and J. Blewett, Field monitoring of  
11 electrical conductivity of cover-zone concrete, *Cement and Concrete Composites*, 27(7-8),  
12 2005, 809-817.
- 13 20. F. Rajabipour, J. Weiss, J.D. Shane, T.O. Mason, and S.P. Shah, Procedure to interpret  
14 electrical conductivity measurements in cover concrete during rewetting, *Journal of  
15 Materials in Civil Engineering*, 17(5), 2005, 586-594.
- 16 21. L.P. Tang and L.O. Nilsson, Chloride binding capacity and binding isotherms of OPC pastes  
17 and mortars, *Cement and Concrete Research*, 23(2), 1993, 247-253.
- 18 22. P.A.M. Basheer, D. Russell, R. Andrews, and W.J. McCarter, Monitoring internal changes  
19 in concrete during carbonation and chloride ingress using a covercrete electrode array.  
20 *Structural Faults and Repair-06*, Edinburgh, Engineering Technic Press, 2006, June, CD  
21 Rom.

## TABLES AND FIGURES

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19 **Fig.12** Relationship between Q<sub>Cl<sup>-</sup></sub> and ΔR<sub>d</sub> for the three chloride related exposure regimes  
20 together

1

**Table 1.** Mix proportions used

Mixes	w/b	Quantities (kg/m <sup>3</sup> )							
		PC	PFA	MS	Sand	10mm- Agg	20mm- Agg	Super- plasticiser	Water
0.55PC	0.55	320	0	0	683	663	663	1.60	176
0.55PFA	0.55	224	96	0	677	658	658	1.68	176
0.55PFA+MS	0.55	272	32	16	679	659	659	2.18	176

2

(Note: 1 kg/m<sup>3</sup>= 0.0624 lb/ft<sup>3</sup>; 1mm= 0.039 in. The background Cl<sup>-</sup> concentration in the three concretes was 1.0%, 0.8% and 0.7% by mass of concrete, respectively.)

3

4

5

**Table 2.** Sensitive Test Depth (STD) of the embedded electrodes

Electrode location	Sensitive test depth
5mm	0-11mm
15mm	10-21mm
25mm	20-31mm
35mm	30-41mm

6

(Note: 1mm= 0.039 in.)

7

8

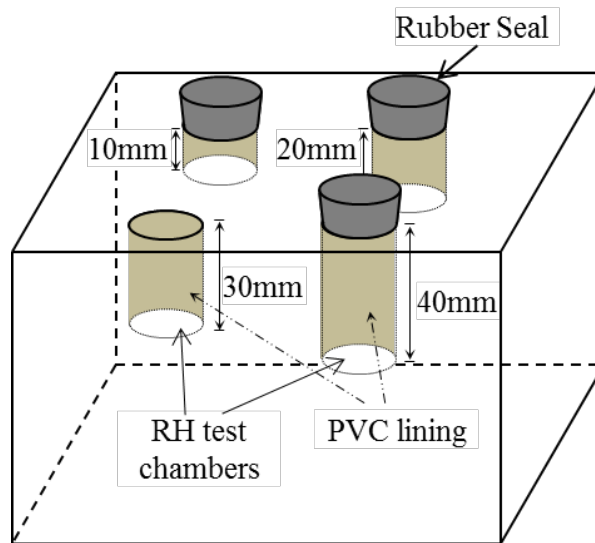
**Table 3.** Coefficient of regression and as-measured R values for the concretes exposed to various chloride exposure regimes

9

Exposure conditions	0.55PC		0.55PFA		0.55PFA+MS	
	R <sub>0,35mm</sub> (kΩ)	R <sup>2</sup>	R <sub>0,35mm</sub> (kΩ)	R <sup>2</sup>	R <sub>0,35mm</sub> (kΩ)	R <sup>2</sup>
3Cl <sup>-</sup>	2.0	0.75	3.4	0.66	5.7	0.51
3Cl <sup>-</sup> +3CO <sub>2</sub>	21.2	0.71	50.6	0.84	39.7	0.86
3CO <sub>2</sub> +3Cl <sup>-</sup>	3.0	0.59	8.7	0.81	12.5	0.91
All data	-	0.59	-	0.64	/	0.87*

\* Results from the 5mm electrodes of 3Cl<sup>-</sup> regime were excluded.

10



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(a) Schematic diagram of test samples for RH measurements



3

4

(b) Measurement of RH in concrete with an RH meter

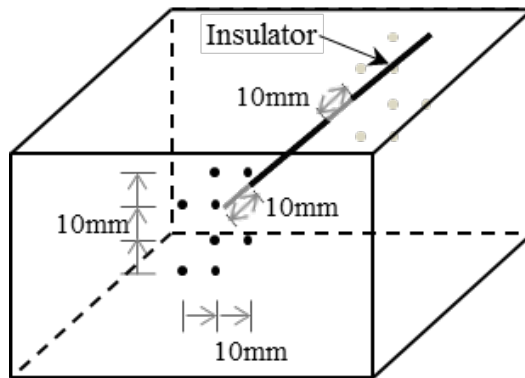
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**Fig. 1.** Test specimen details and setup for measuring the RH distribution in concretes

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(a) Schematic diagram of test samples for testing the electrical resistance



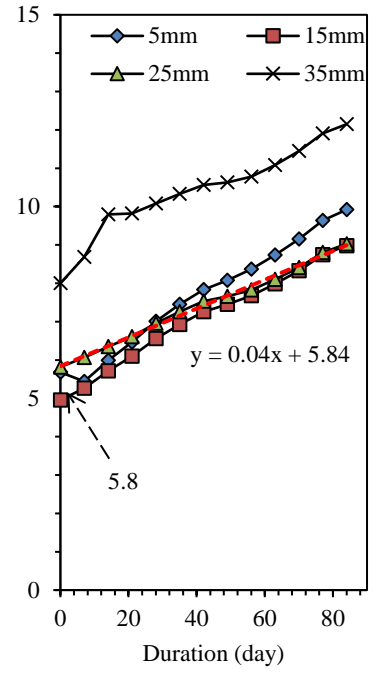
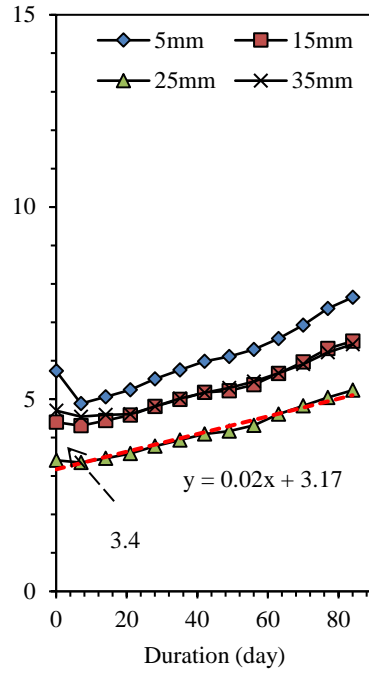
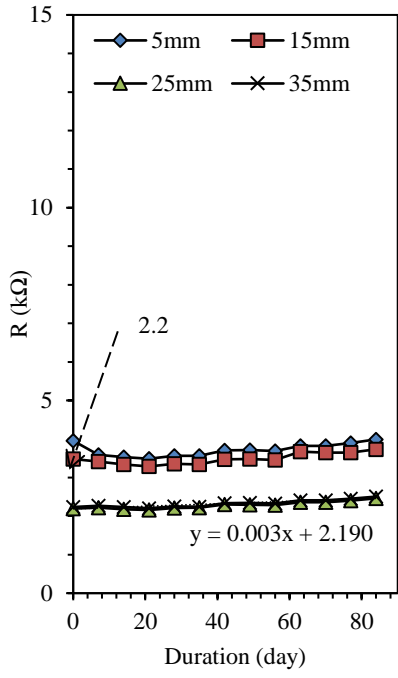
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(b) Measurement of the electrical resistance with a LCR meter

7

**Fig. 2.** Test specimen and setup for measuring the electrical resistance



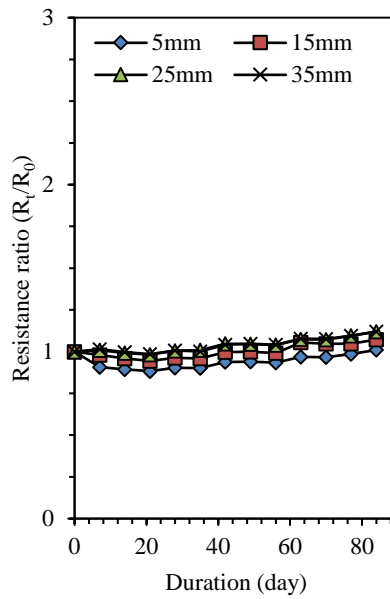
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(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

2



(d) Normalised R for 0.55PC

3

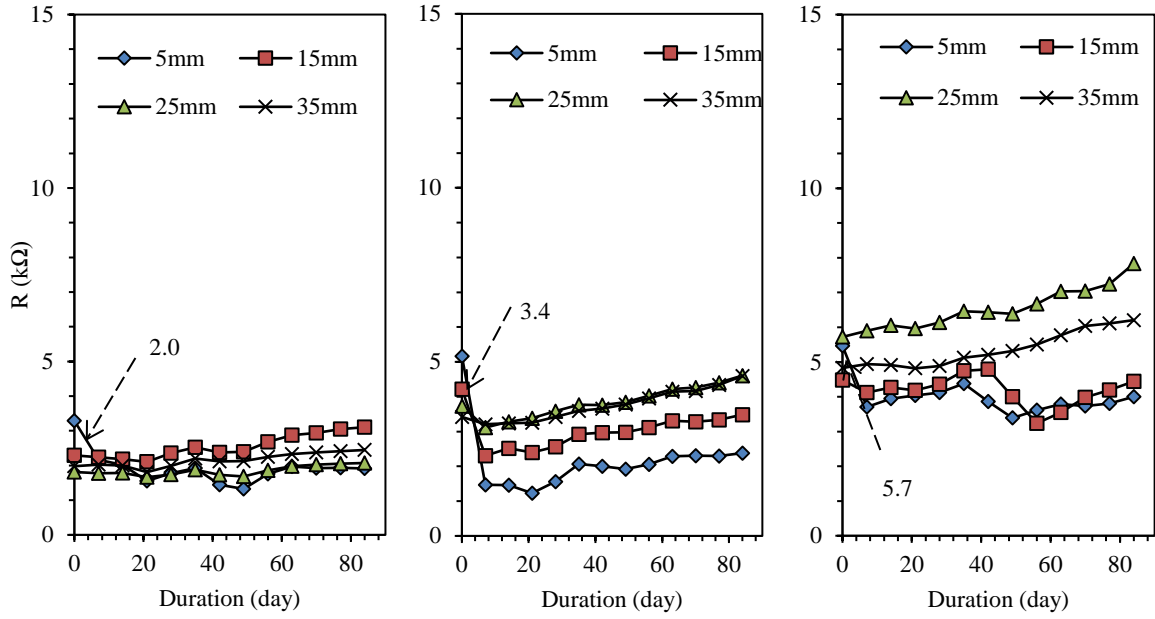
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**Fig. 3.** Electrical resistance, R within the near-surface concrete under the 3H<sub>2</sub>O regime

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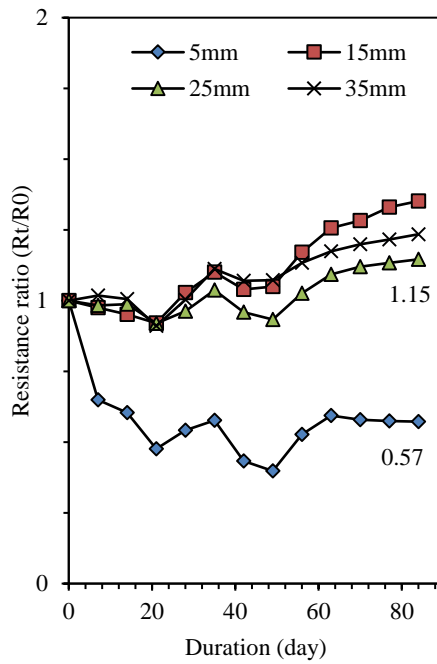
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2

(a) values for 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS



3

4

(d) Normalised R for 0.55PC

5

**Fig. 4.** Electrical resistance, R within the near-surface concrete under the 3Cl<sup>-</sup> regime

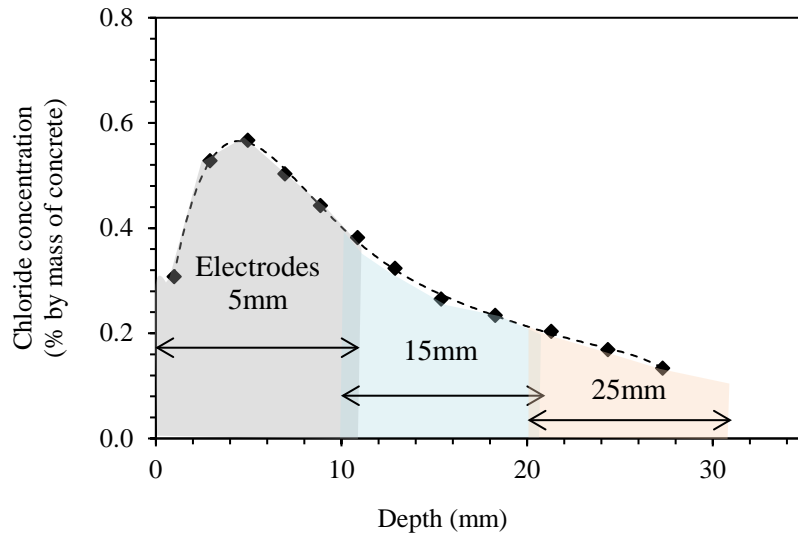
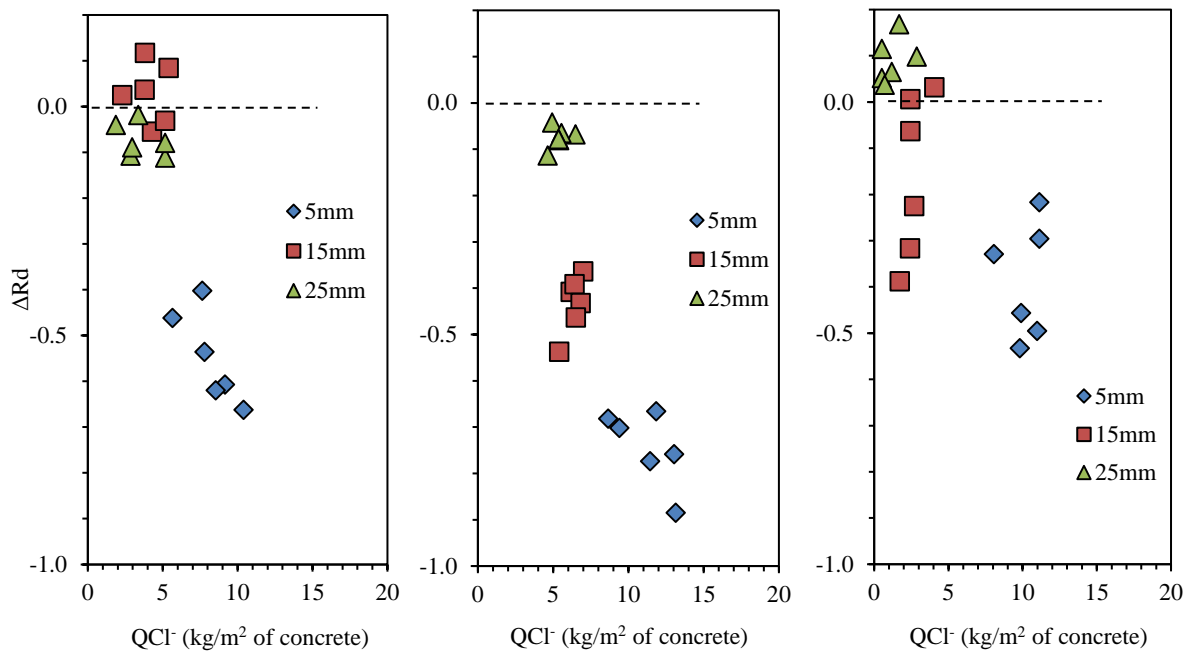


Fig. 5. Illustration of  $Q_{Cl^-}$  in the STD of electrodes (0.55PC,  $3Cl^-+1CO_2$  regime)

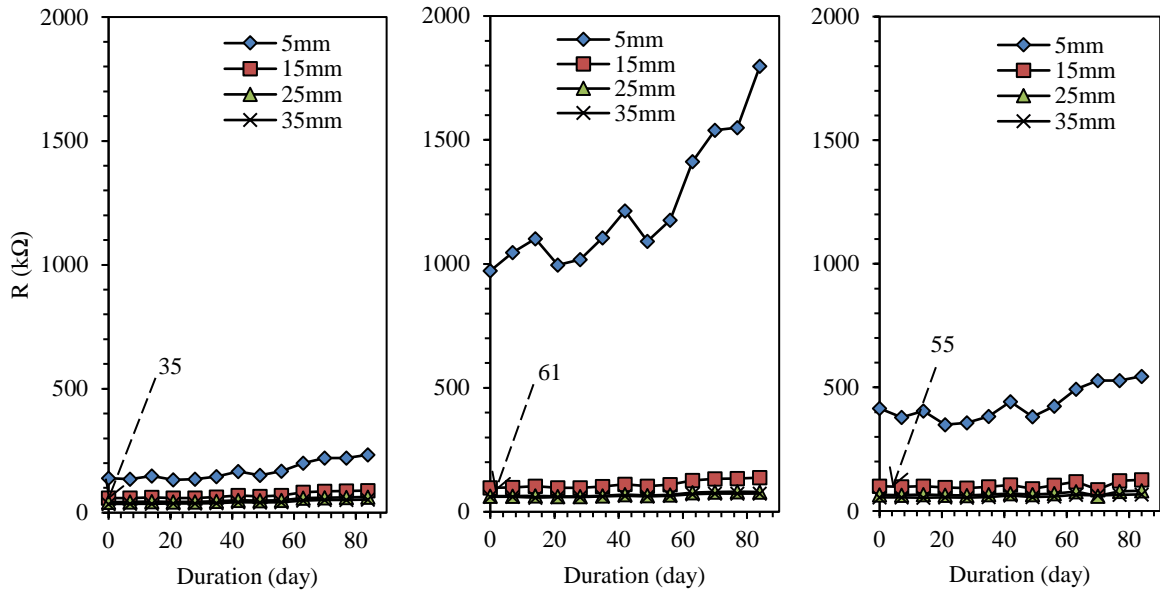


(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

Fig. 6. Relationship between  $Q_{Cl^-}$  and  $\Delta R_d$  for the three types of concrete in the  $3Cl^-$  regime



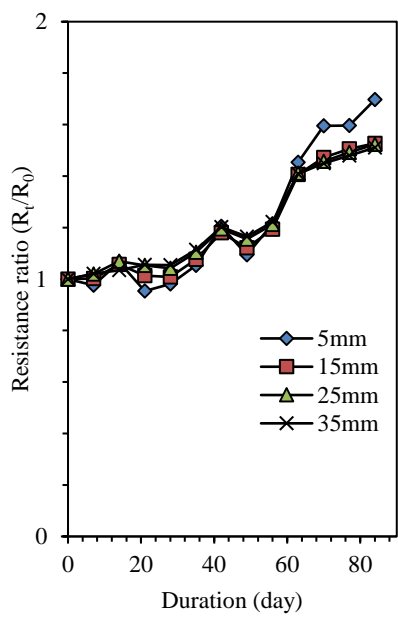
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(b) 0.55PFA

(c) 0.55PFA+MS



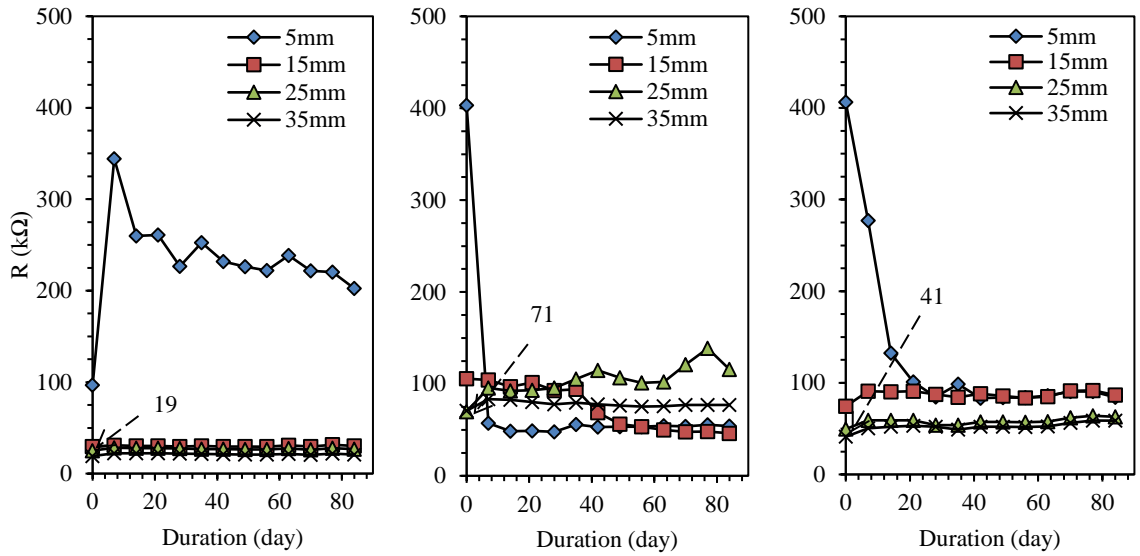
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(d) Normalised R of 0.55PC

**Fig. 7.** Electrical resistance, R within the near-surface concrete under the 3Air regime

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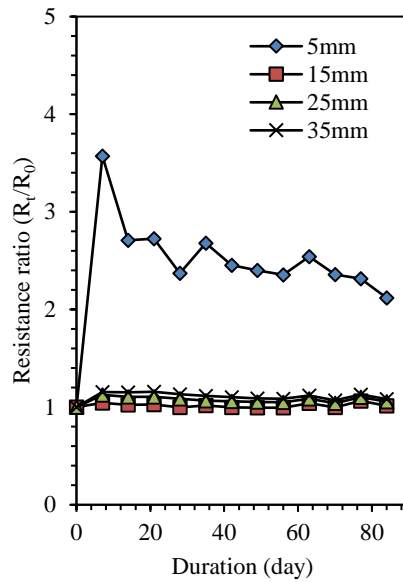
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(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

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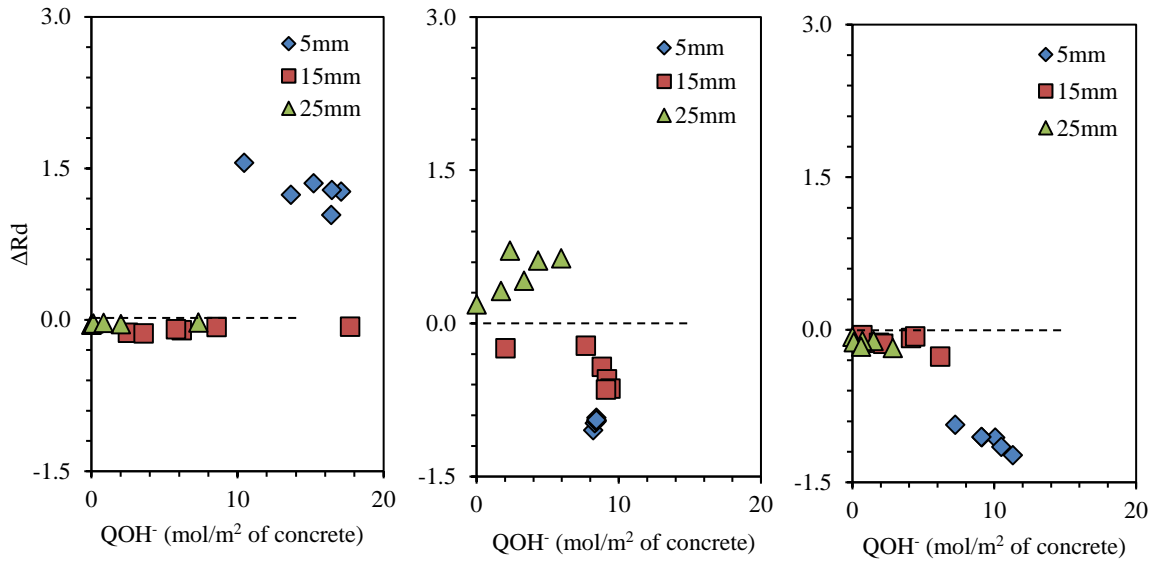
(d) Normalised R of 0.55PC

4

**Fig. 8.** Electrical resistance, R within the near-surface concrete under the 3CO<sub>2</sub> regime

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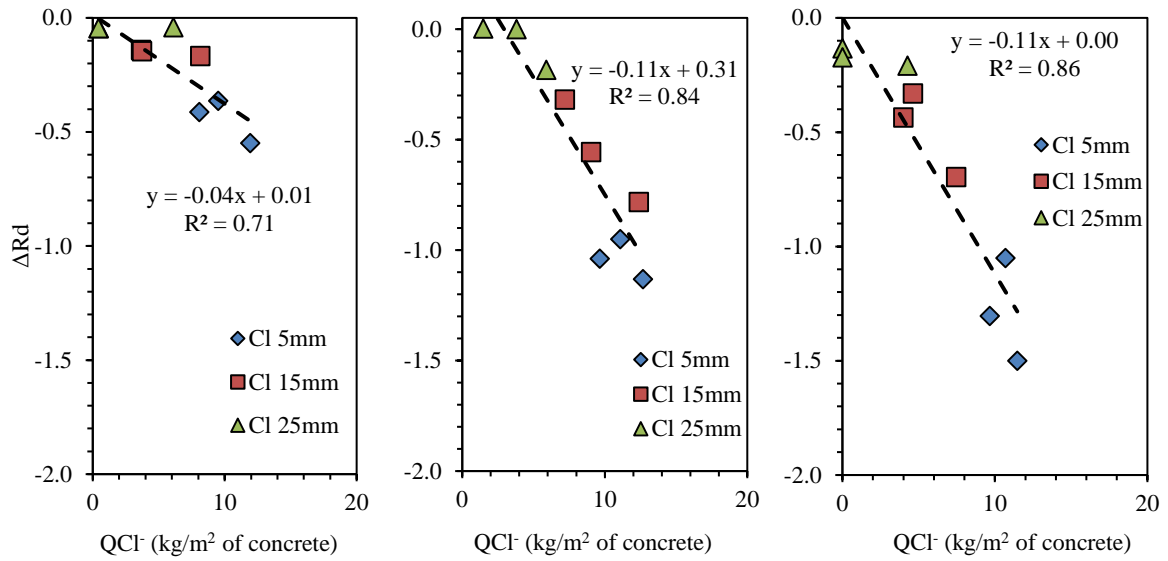


(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

**Fig. 9.** Relationship between  $Q_{OH^-}$  and  $\Delta R_d$  for the three types of concrete in the  $3CO_2$  regime

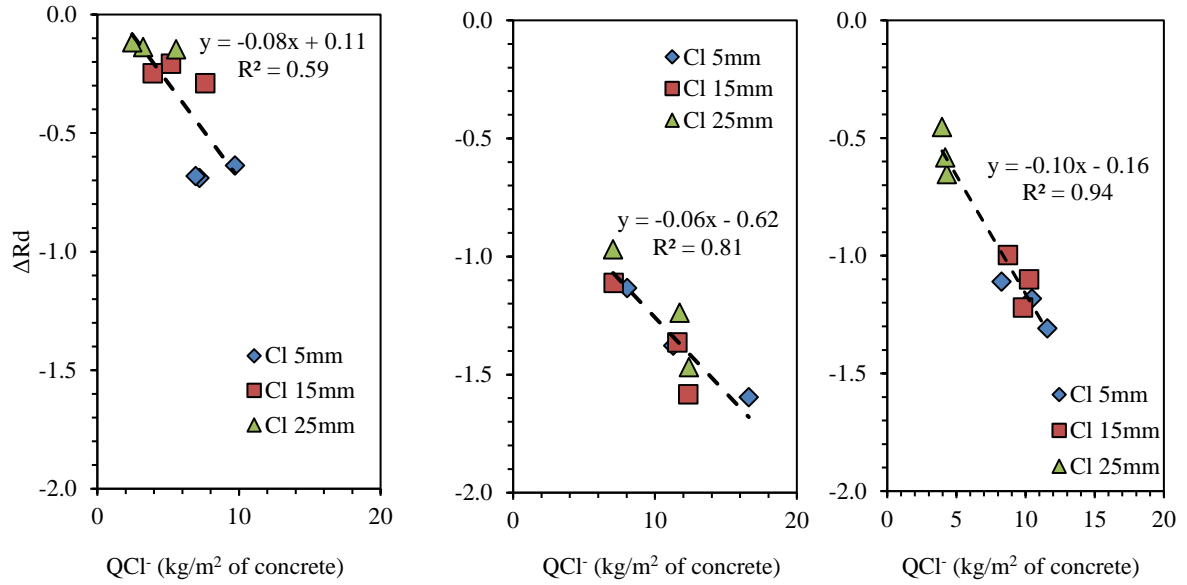


(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

**Fig. 10.** Relationship between  $Q_{Cl^-}$  and  $\Delta R_d$  for the  $3Cl+3CO_2$  regime



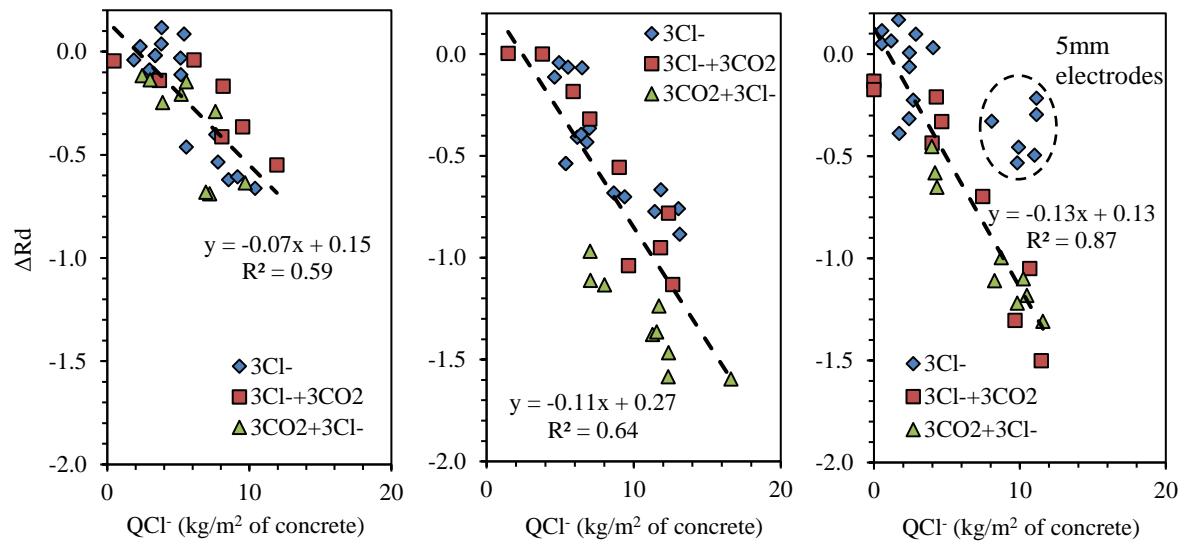
1  
2  
3

(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

**Fig. 11** Relationship between  $Q_{Cl^-}$  and  $\Delta R_d$  for the  $3CO_2+3Cl^-$  regime



4  
5  
6

(a) 0.55PC

(b) 0.55PFA

(c) 0.55PFA+MS

**Fig. 12** Relationship between  $Q_{Cl^-}$  and  $\Delta R_d$  for the three chloride related exposure regimes together