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Chloride transport in fly ash and glass powder modified concretes – Influence of test methods on microstructure

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ABSTRACT

This paper discusses the influence of rapid chloride transport test methods on the microstructure and the measured chloride penetration resistance of concretes containing fly ash or fine glass powder as partial cement replacement materials. Rapid chloride permeability (RCP), non-steady-state migration (NSSM), and steady state conduction (SSC) tests are performed on plain and modified concretes. The glass powder modified concretes demonstrate similar or lower RCP values as compared to the fly ash modified concretes of the same cement replacement level whereas the steady state conductivities are lower for the fly ash modified mixtures. The NSSM coefficients are lower for the fly ash modified concretes even when the initial conductivities are similar to those of plain or glass powder modified concretes. Chloride binding under the conditions of NSSM test, that influence the microstructure and the transport parameter, is quantified using thermal analysis and XRD patterns as well as an electrical circuit model for the impedance response. The resistance of connected pores (R_c) extracted from the model adequately captures the changes in microstructure with time and with chloride transport. The changes in R_c between the start and finish of the NSSM test also indicate microstructural alteration in fly ash modified concretes.

1. Introduction

Moisture and ionic transport into concrete is a well studied topic because this dictates the service life of reinforced concrete structures [1–3]. Chloride ion penetration and subsequent reinforcement corrosion is critical for bridges and other transportation structures subjected to deicing salts, as well as structures in marine environment. The use of supplementary cementing materials (SCM) such as fly ash, ground granulated blast furnace slag, silica fume, and metakaolin have been found to be beneficial in resisting the ingress of chloride ions into concrete because of the microstructural densification imparted by the pozzolanic reaction or secondary hydration of these materials. Several other SCMs of local or regional origin are also being used in concrete to advance the cause of sustainability. Glass powder is one such material which is amorphous and has a high silica content, which are the primary requirements for a pozzolanic material. Hydration and strength development in glass powder modified cement pastes [4,5], and mechanical and durability properties of concrete containing glass powder [6–8] have been reported in earlier studies. In this study, the chloride penetration resistance of glass powder modified concretes is evaluated using a few rapid chloride transport test methods and the performance compared to those of fly ash modified concretes of identical cement replacement levels.

Transport experiments such as the conventional chloride diffusion test are typically time consuming. Hence three rapid test methods – rapid chloride permeability (RCP), non-steady-state migration (NSSM), and steady state conductivity (SSC) tests - are carried out on plain and modified concretes as part of this study. These tests are fairly well established (even though there are certain limitations with some of them, which are adequately reported) [9–13]. The influence of these test methods, specifically the concentration of either the catholyte chloride solution or the chloride solution used for specimen pre-conditioning, the duration of the transport test, and the chemical composition of the cement replacement materials (Class F fly ash and glass powder) that result in microstructural modifications and variations in the measured chloride transport parameters are discussed in detail in this paper. Electrical impedance spectroscopy along with equivalent circuit modeling and analytical methods such as thermal analysis and X-ray diffraction are used to quantify the physical and chemical changes that occur in the material microstructure as a result of the transport tests.

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2. Experimental program

2.1. Materials and mixture proportions

Type I ordinary Portland cement conforming to ASTM C 150 was used to proportion all the concrete mixtures in this study. A Class F fly ash (FA) conforming to ASTM C 618, and a fine glass powder (GP) which is a byproduct of industrial and highway safety glass bead manufacturing were used as partial cement replacement materials. The physical and chemical characteristics of the binding materials are shown in Table 1. The water-to-cementing materials ratio (w/cm) for all the mixtures was maintained at 0.40, and 10% or 20% of cement was replaced with either glass powder or fly ash by mass. Cylindrical specimens (100 mm diameter × 200 mm height) were cast and cured at 95% RH and 25 °C after demolding at 24 h.

Table 1
Chemical composition and physical characteristics of the materials used.

Composition (% by mass)/ property	Cement	Fine glass powder (GP)	Fly ash (FA)
Silica (SiO_2)	20.2	72.5	50.24
Alumina (Al_2O_3)	4.7	0.4	28.78
Iron oxide (Fe_2O_3)	3	0.2	5.72
Calcium oxide (CaO)	61.9	9.7	5.86
Magnesium oxide (MgO)	2.6	3.3	1.74
Sodium oxide (Na_2O)	0.19	13.7	0.96[a]
Potassium oxide (K_2O)	0.82	0.1	
Sulfur trioxide (SO_3)	3.9	–	0.51
Loss on ignition	1.9	0.36	2.8
Median particle size (μm)	13	20	20
Density (kg/m^3)	3150	2490	2250

[a] Equivalent alkalis.

2.2. Test methods

Fifty millimeter thick slices were cut from the cylindrical concrete specimens for the rapid chloride permeability (RCP) test as per ASTM C 1202 and non-steady-state migration (NSSM) test as per NT Build 492 [14], where as 25 mm thick specimens were used for steady state chloride conduction (SSC) test based on the procedure outlined in [15]. The bulk electrical resistances of the specimens before and after the RCP and NSSM tests were obtained using Electrical Impedance Spectroscopy (EIS). RCP, NSSM, and EIS tests were performed on samples cured for 28, 56, or 90 days in saturated limewater, while the SSC test was conducted on samples cured for 28 or 90 days.

2.2.1. RCP and NSSM tests

The RCP test based on ASTM C 1202 provides an indication of the resistivity or conductivity of the concrete, which is in turn expressed as an index of the penetrability of chloride ions into concrete. The 50 mm thick specimens were conditioned by vacuum saturation, and enclosed in a cell flanked by reservoirs that contain 0.3 N NaOH solution on one side and 3% NaCl solution on the other. A 60 V potential difference was applied between the electrodes placed on both faces of the specimen, for a duration of 6 h. The total charge passed (in coulombs) at the end of 6 h of testing is reported as the RCP value. The RCP test basically measures the conductivity (or resistivity) of concrete, which depends on both the pore structure as well as the pore solution composition. The pore solution conductivity can change due to ohmic heating, and microstructural changes can be induced by electromigration under the conditions of this test. For concretes containing cement replacement materials, the chemical composition of the pore solution also changes either due to the consumption of calcium hydroxide (CH) during pozzolanic reaction, or the presence of ions contributed by the cement replacement materials, both of which changes its conductivity.

The NSSM test avoids some of the drawbacks of RCP test. In this test, the specimen pre-conditioning is carried out using saturated $Ca(OH)_2$ solution and the applied voltage and test duration depends on the measurement of initial current on application of a 30 V electrical potential. The catholyte and anolyte solutions used were 2 N NaCl (10%) and 0.3 N NaOH, respectively, and the test cell was the same as that used for the RCP test. The applied external electrical potential forces the chloride ions in the cell to migrate into the specimen. After a specified test duration (which depends on the initial current), the specimen was axially split and a 0.1 N silver nitrate solution sprayed on the freshly split sections. The chloride penetration depth was then measured from the visible white silver chloride precipitation. The NSSM coefficient, D_{nssm} (in m^2/s), was calculated using the average value of the penetration depths (x_d)

$$D_{\mathrm{nssm}} = \frac{RT}{zFE}\,\frac{x_d - \alpha\sqrt{x_d}}{t} \tag{1}$$

where

$$E = \frac{U-2}{L} \quad \text{and} \quad \alpha = 2\sqrt{\frac{RT}{zFE}} * erf^{-1}\left(1 - \frac{2C_d}{C_o}\right) \tag{2}$$

R is the molar gas constant (8.314 J/(K mol)), Z is the absolute value of ion valence (1, for chloride ions), F is the Faraday constant (96,485 J/(V mol)), U is the absolute value of the applied voltage, T is the average value of the initial and final temperatures in the anolyte solution (K), L is the thickness of the specimen (m), t is the test duration (s), C_d is the chloride concentration that causes the precipitation of silver chloride, and C_0 is chloride concentration in the catholyte solution.

2.2.2. Chloride conduction test method

The chloride conduction test based on [15] was performed on 25 mm thick slices of concrete. The test set up is shown in Fig. 1. The specimens were heated in an oven at 50 °C for 7 days prior to the test. The specimens were then completely saturated in a 5 M NaCl solution under vacuum. The introduction of a highly conductive solution into the pores of the concrete negates the influence of the conductivity of the original pore solution. This ensures that the measured electrical conductivities of different specimens can be used as strong indicators of the pore structure. The specimen was placed in the conductivity cell and a 10 V electrical potential was applied between the carbon and steel electrodes placed in the electrolyte (5 M NaCl) in both the cells, and the current (i) measured. The potential across the specimen (V) was measured using copper–copper sulfate half cells. Since the pores in the concrete as well as the surrounding electrolyte have the same concentration (5 M NaCl), the conduction was considered to be under steady state. The steady state conductivity (σ_{ssc}) was then calculated as:

$$\sigma_{\mathrm{ssc}} = \frac{i \cdot t}{VA} \tag{3}$$

where t is the thickness of the specimen, and A is the specimen cross-sectional area.

2.2.3. Electrical impedance spectroscopy (EIS)

Electrical impedance spectroscopy (EIS) measurements were performed on the concrete specimens used for RCP and NSSM tests before and after these tests were performed. EIS spectra were obtained using a Solartron™ 1260 gain-phase analyzer. A frequency range of 1 Hz–10 MHz using a 250 mV AC signal was employed, with 10 measurements per decade. Based on the bulk resistance

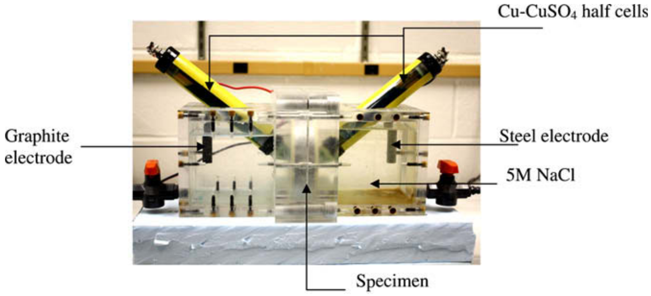

Fig. 1. Chloride conduction test set up used in this study.

(R_b), which is the meeting point of the bulk and electrode arcs in a Nyquist plot (plot of real vs. imaginary impedance), the effective specimen conductivity (σ_{eff}) can be determined as:

$$\sigma_{\text{eff}} = \frac{L}{R_b A} \tag{4}$$

where L is the length (50 mm), and A is the cross-sectional area of the specimens. In the specimen cells used for RCP and NSSM tests, there is a small gap (~2–5 mm) between the electrodes and the specimen, which is filled by the corresponding electrolyte. Since the specimen resistance is much larger than this electrolyte resistance, the influence of the presence of this gap on the measured bulk resistance of the specimen can be neglected.

3. Results, analysis, and discussions

3.1. Rapid chloride test parameters of glass powder and fly ash modified concretes

3.1.1. RCP values

Fig. 2a shows the RCP values of the plain and modified concrete specimens cured under saturated conditions for 28, 56, and 90 days. The RCP values decrease with increase in curing duration as expected for all the mixtures due to increasing hydration. At all ages, the plain concrete shows higher RCP values as compared to the modified mixtures of both replacement levels. Since the cement replacements by both glass powder and fly ash were carried out in this study on a mass basis, the modified concretes will have lower porosities at early ages because of the lower specific gravities of the replacement materials than the cement it replaces. Replacement of cement by glass powder or fly ash on an equivalent volume basis might have lead to different observations, especially at early ages. At later ages, the pozzolanic reaction of the replacement materials results in pore structure densification. The mixtures where 20% of cement was replaced by either glass powder or fly ash show slightly higher RCP values at 28 days of curing than the mixtures where 10% of cement was replaced, possibly because of the dominant effect of dilution at early ages. The pozzolanic reaction of the replacement materials might not be occurring at this age. After 56 and 90 days of curing, as a result of pozzolanic reaction and consequent pore structure densification, the mixtures with 20% cement replacement show lower RCP values than those with 10% cement replacement. It can be also observed from this figure that the glass powder modified mixtures show lower RCP values than the corresponding fly ash modified mixtures at 56 days. This could be taken as an indication of the faster pozzolanic reaction of glass powder as compared to that of fly ash, which has been quantified in [5]. After 90 days of curing, the RCP values of modified concretes of similar replacement levels are comparable. It is well known that the RCP test is basically an electrical conductivity or resistivity test, and the pore solution conductivity also influences the results of this test. The presence of a more conductive pore solution results in higher apparent RCP values even if the microstructure is identical. Based on previous studies [5], it was observed that the glass powder, which has a high Na_2O content, releases a small fraction of alkalis into the pore solution, thus increasing the conductivity of the pore solution. Even with such an increase, the RCP values of glass powder modified concretes are similar to or lower than that of fly ash modified concretes.

In addition to the microstructure modification, another explanation for the lower RCP values of glass powder modified concretes possibly lies in the viscosity of the pore solution. The release of alkali ions results in an increase in the viscosity of the pore solution [16], thereby, hindering the transport of chloride ions, consequently reducing the RCP values. Since only a small fraction of alkalis are released into the pore solution, the pore solution viscosity increase is not expected to be very high. If it is assumed that the increase in RCP values contributed by the small increase in conductivity of the pore solution is compensated by the slightly increased viscosity affecting ionic movements, then the microstructural contribution towards the later age RCP values of glass powder and fly ash modified concretes can be considered to be similar.

3.1.2. Non-steady-state migration coefficients

Fig. 2b shows the non-steady-state migration coefficients (D_{nssm}) for plain and modified concretes at all the chosen ages. The general trend in D_{nssm} values is similar to that of the RCP values, with lower values at later ages and for modified mixtures. The behavior of the 10% glass powder modified concrete is quite similar to that of the plain concrete. The later age (56 and 90 days) D_{nssm} values of 20% glass powder modified concrete are lower than those of plain concrete, indicating microstructure densification because of the pozzolanic reaction. The fly ash modified concretes show lower D_{nssm} values than the plain concrete at all ages, and the glass powder modified concretes at early ages. At later ages, D_{nssm} values for fly ash modified concretes are lower than, or comparable to those of glass powder modified concretes. If it can be considered, as was done using RCP test results, that the fly ash and glass powder modified mixtures have similar microstructural features such as porosity, then one reason for the reduction in D_{nssm} values of fly ash modified mixtures could be attributed to chloride binding by the aluminate phases during the transport test. As can be seen from Table 1, fly ash contains a higher proportion of alumina, and a 20% replacement of cement, for example, increases the aluminate phase content in fly ash modified concretes, which can bind the chloride ions to form Friedel's salt ($3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10\ H_2O$) [17–19]. Since the NSSM test was carried out for a longer duration of time (24 h, as opposed to 6 h for the RCP test), and with a higher concentration of the NaCl solution in the catholyte (10%, as opposed to 3% for RCP test), more chloride binding is likely to occur during the NSSM test. The glass powder has lower alumina content than the cement it replaces, and hence no additional binding can be expected. The reduced D_{nssm} values for 20% glass powder modified concretes at later ages can then be attributed largely to the densified microstructure.

3.1.3. Steady state conductivities

The pre-conditioning procedure for the steady state conduction test involved vacuum saturation of the 25 mm thick specimens in 5 M NaCl solution. Thus the pore structure is saturated with a high conductivity NaCl solution, eliminating the effects of pore solution conductivity on the measured results (assuming that the saturating solution penetrates the entire 25 mm thick specimen). The application of only a 10 V potential eliminates heating effects also. However, the exposure of specimens to a high concentration of NaCl before the test can result in the formation of a certain amount of chloride binding products if the mixture contains substantial

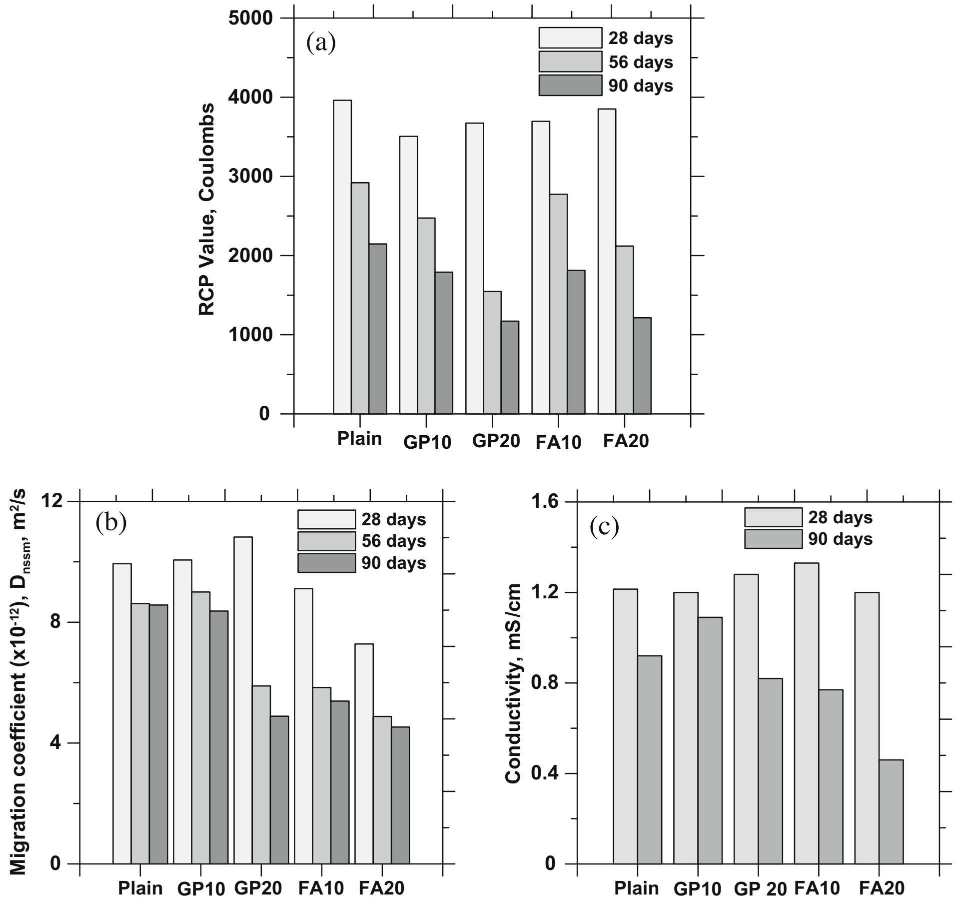

Fig. 2. (a) RCP charge values, (b) non-steady-state migration coefficient (D_{nssm}) from NSSM tests, and (c) conductivity from chloride conduction test at different times.

amount of aluminates. Fig. 2c shows the conductivity of specimens determined after 28 and 90 days of curing. At early ages, the conductivity values of all modified mixtures are similar to that of the plain concrete. Since this test provides an indication of the material microstructure because pore solution conductivity effects are avoided, the direct inference could be that the microstructures at the early age are similar for plain and modified concretes. However, as described earlier, dilution effect is dominant at early ages, and the pozzolanic reaction of glass powder begins earlier than that of the fly ash, which should have resulted in higher conductivity values for fly ash modified concretes. But, chloride binding and the formation of Friedel's salt might have resulted in a lowering of the 28-day conductivity values of fly ash modified concretes.

At later ages, the distinction between the conductivity of fly ash and glass powder modified concretes is highly noticeable, with the fly ash modified concretes showing 30–50% lower conductivities than the glass powder modified concretes of similar cement replacement level. The results presented could lead to the conclusion that fly ash modified concretes have a much denser microstructure than the glass powder modified concretes, which is not the case as is evident from the results of RCP or migration tests even after considering the effects of pore solution, presented earlier in this paper. Also, compressive strength tests after 90 days of curing on glass powder and fly ash modified concretes with similar cement replacement levels showed a strength difference of only about 5% within each other. The reduced conductivity of fly ash modified concretes can thus be attributed to the formation of chloride binding products (Friedel's salt) that alters the pore structure. In the later sections of this paper, Friedel's salt formation has been quantified using X-ray diffraction (XRD) spectra and thermal analysis. Electrical impedance test results and equivalent circuit modeling have also been used as indirect estimators of the above.

3.2. Conductivity and its relationship to chloride transport parameters

The conductivities of the plain and modified concrete specimens determined from the electrical impedance tests before the RCP test, and their relationship to the RCP values are shown in Fig. 3a. It is clearly seen that the initial conductivities of the concretes (conductivities before subjecting the specimens to RCP test) are linearly related to the RCP values. This provides a convenient method of predicting the RCP values based on initial conductivity, an approach which has been proposed by others also [9,12,20]. This relationship also proves that the RCP test is just a conductivity or resistivity test. It can be observed that the 20% glass powder modified mixture has the lowest conductivity at later ages, indicating a denser pore structure. As discussed earlier, the increased alkalinity caused by the dissolution of Na_2O from glass powder should have increased the conductivity, but the fact that it is not observed points to microstructure refinement.

Fig. 3b shows the relationship between the initial conductivity from EIS before the NSSM tests and the D_{nssm} values. Two distinct linear relationships, which are essentially parallel to each other, can be observed in this figure: one for the plain and glass powder modified concretes, and the other for fly ash modified concretes. For a given value of initial conductivity, it can be seen that the D_{nssm} values of fly ash modified concretes are lower than those of plain or glass powder modified concretes. This could be attributed to the increased chloride binding in mixtures containing fly ash (because of the net higher aluminate content when fly ash

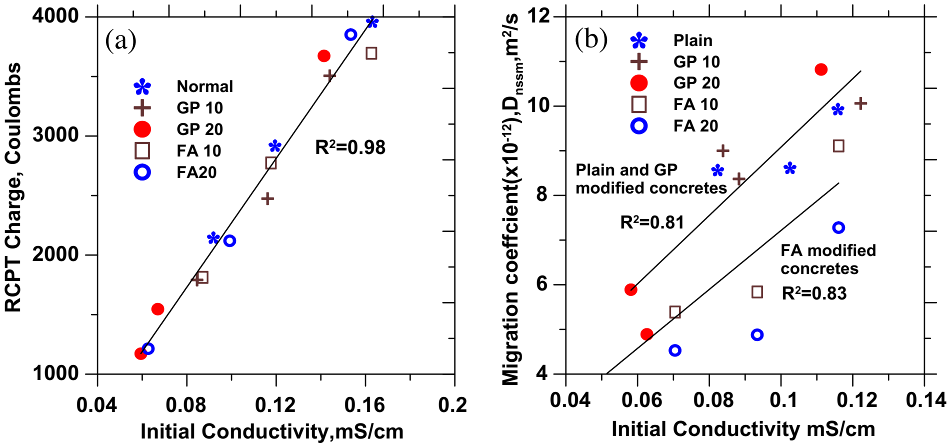

Fig. 3. Relationship between initial conductivity and: (a) RCP values, and (b) non-steady-state migration coefficient.

partially replaces cement), thus effectively reducing the migration coefficient due to reduction in pore sizes and increase in tortuosity caused because of the blocking of pore channels by the formation of chloride binding products.

3.3. Ascertaining the effect of chloride binding on transport: EIS, TGA and XRD studies

3.3.1. Electrical Impedance Spectra before and after RCP and NSSM tests

The use of electrical impedance spectroscopy (EIS) to identify the changes in the material microstructure, especially during cement hydration is well reported [21,22]. Impedance spectra of concretes subjected to chloride ingress have also been investigated [23–27]. In this section, electrical impedance spectra of plain concretes as well as concretes modified with either 20% glass powder or fly ash before and after the RCP and NSSM tests are discussed.

Fig. 4a shows the Nyquist plots (plots of real impedance vs. imaginary impedance) of plain and modified concretes cured for 90 days, before and after the RCP test. The solid symbols correspond to the spectra before the test, and the hollow symbols correspond to the spectra after the test. The glass powder modified concrete shows the highest resistance and the plain concrete the lowest, the reasons for which have been elucidated earlier. The trends are the same before and after the RCP tests. Both the modified mixtures show higher resistances than the plain concretes, which can be attributed to microstructure refinement. From the figure in the inset, it can be observed that the bulk resistance (R_b) values (the real impedance value for which the imaginary impedance is closest to zero) for all the specimens after the RCP test are lower than the R_b values before the test. This decrease could be attributed to the penetration of chloride ions into the concrete, which reduces the overall electrical resistance of the material. The increase in the temperature of the specimens due to the higher applied potential might also result in lower resistances after the test.

The Nyquist plots before and after the NSSM tests for 90 days cured plain and modified concretes are shown in Fig. 4b. In this case also, the glass powder and fly ash modified concretes show higher resistances than the plain concrete. Since the specimens were vacuum saturated in calcium hydroxide solution before the start of the test, the influence of changes in pore solution conductivity on the measured resistances is considerably reduced in this case. The glass powder modified concrete shows a higher R_b value, once again establishing the efficiency of glass powder in pore structure refinement. Contrary to the observations in Fig. 4a where

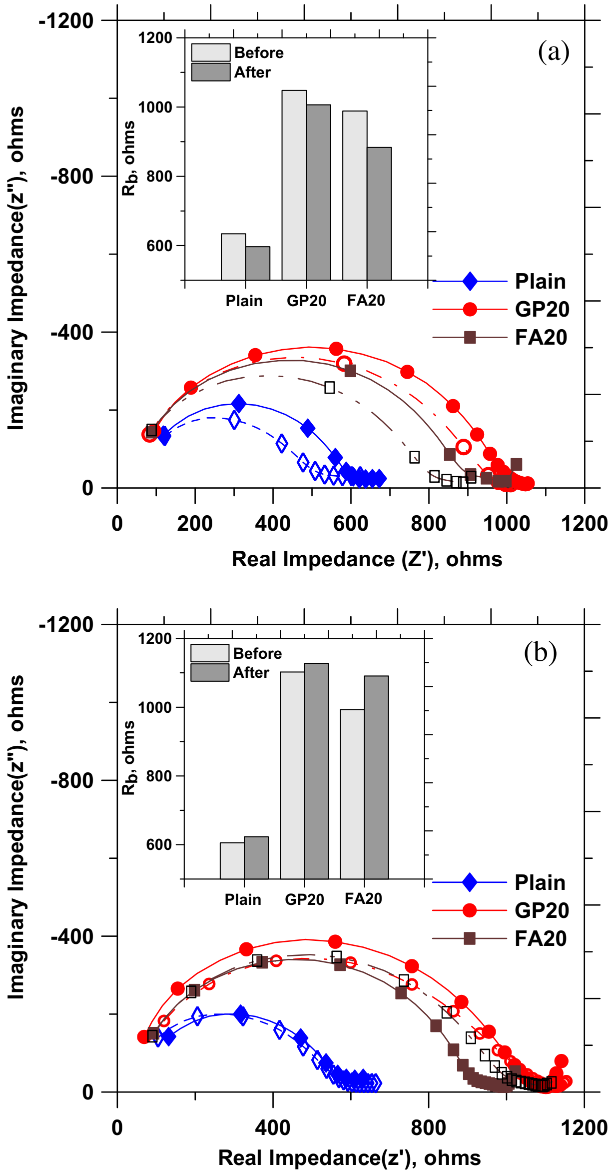

Fig. 4. Electrical impedance spectra for plain and modified concretes before and after: (a) RCP test, and (b) NSSM test. The figures in the inset show the bulk resistances (R_b) before and after the respective transport test.

the bulk resistances are seen to decrease after the RCP test, the R_b values increase for all the specimens after the NSSM test as shown in the figure in the inset. The bulk resistances can be expected to drop early on in the testing period because of the increase in the conductivity caused by penetrating chloride ions. However, the NSSM tests are carried out for a longer duration, which might result in the binding of some of the chloride ions with the aluminate phases in the hydrated cement paste. The formation of Friedel's salt after migration testing, also observed in [25], results in a reduction of pore sizes and increase in tortuosity, thus increasing the electrical resistance after an initial decrease. Also, the chloride binding products block the smaller pores closer to the surface exposed to chloride ions [13], resulting in a reduction in further ingress of chloride ions. While the R_b values before and after the NSSM test are very close to each other for the glass powder modified concretes, the difference in the R_b values is found to be the highest for the fly ash modified concrete after the test, suggesting an increased influence of chloride binding on the measured resistance. The following section examines this with the help of thermal analysis and X-ray diffraction patterns.

3.3.2. Thermal analysis and XRD studies to identify chloride binding

In order to confirm the formation of increased amounts of chloride binding products as evidenced in electrical impedance tests, plain and modified cement paste specimens having the same w/cm as the concretes were prepared and subjected to NSSM test after curing for 90 days. Thermogravimetric analysis (TGA) was carried out on powdered samples obtained from regions closer to the cathodic face of these paste specimens. The endothermic peak corresponding to Friedel's salt occurs at temperatures in the range of 300–360 °C [19,28]. The mass losses corresponding to Friedel's salt were determined from TGA as 1.57%, 1.10% and 2.0%, respectively for the plain, glass powder, and fly ash modified pastes subjected to NSSM tests. The higher amount of Friedel's salt in the fly ash modified mixture confirms the reason for higher increase in resistance observed in Fig. 5b for this mixture compared to the glass powder modified concretes. The XRD spectra of these pastes after they were subjected to NSSM test are shown in Fig. 5. The peak corresponding to the Friedel's salt is observed at a 2θ angle of 12°. The area under Friedel's salt peak (in arbitrary units) was determined as 6.12 for the fly ash modified paste while the corresponding values were 3.98 and 3.23 for pastes from plain and glass powder modified pastes. The area under the Friedel's salt peak is found to be the highest for the fly ash modified mixture, which is in line with the quantitative thermal analysis results. Since the glass powder has a lower alumina content than the cement it replaces, it is understandable that the Friedel's salt content is lower for glass powder modified concrete as compared to that of the plain mixture. The increased amounts of chloride binding in fly ash modified concretes compared to the plain and glass powder modified concretes give rise to the observations from rapid chloride test results detailed in Sections 3.1 and 3.2.

3.4. Equivalent electrical circuit model parameters and their relationship to microstructure

Different equivalent circuit models that relate to the material microstructure have been used to fit experimentally determined EIS spectra of cement pastes and concretes in several studies [29–31]. These equivalent circuits are typically a combination of resistances, capacitances, and constant phase elements that are arranged in a certain manner so as to represent the behavior of the real material. The use of equivalent circuit electrical models and the microstructural parameters derived from the model to quantify chloride binding is detailed in this section. The equivalent circuit model used in this study is shown in Fig. 6a, which is similar to a model reported previously in [24,26] for cement pastes and concretes. In the circuit model shown in Fig. 6a, R_e corresponds to the resistance of electrolyte between the measuring electrode and the specimen, R_c is the resistance attributed to the connected or percolating pores (that connect both faces of the specimen), and R_{uc} is the resistance of the unconnected pores in the sample. C_s and C_p are the capacitances associated with solid fraction of the specimen (aggregates and paste) and the pore walls, respectively. C_i and R_i are the capacitance and resistance related to the electrolyte-concrete interface. The circuit model was fit to the Nyquist plots using ZView™ software. Fig. 6b shows the experimental spectra and its fit for the plain and modified concretes cured for 90 days. Only the bulk arc in the Nyquist plot is fitted using this model. Though physical interpretations can be provided for each of the model parameters, the remainder of this paper focuses on the parameter R_c, the resistance of the connected pores, extracted from the circuit model. This parameter assumes significance in the representation of the transport behavior in porous materials like concrete since it is the connected pores that dominate the transport. Thus the aim is to relate the values of R_c which essentially is a microstructural parameter, to the chloride transport parameters (RCP and D_{nssm} values).

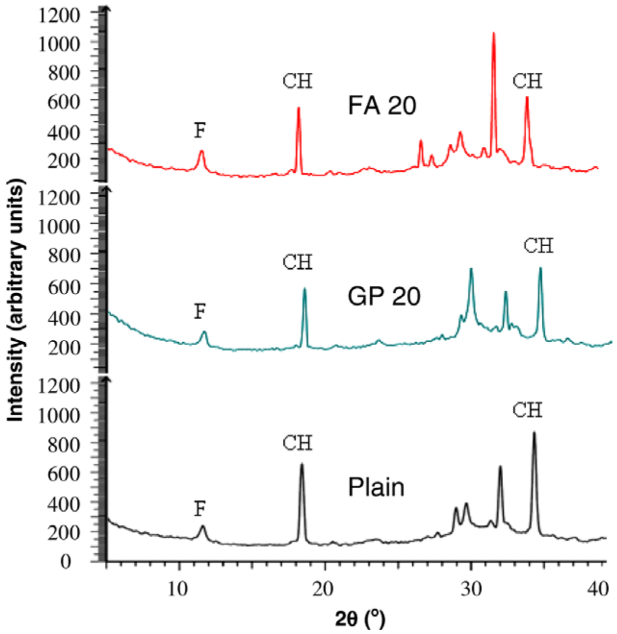

Fig. 5. XRD spectra of the paste fraction of the specimens subjected to NSSM tests.

Fig. 7a shows the values of the resistance of connected pores (R_c) at all ages for all the specimens before the RCP test. As can be observed from this figure, R_c increases with time for both plain and modified concretes as expected. The reduction in overall porosity as well as the pore sizes because of cement hydration and/or pozzolanic reaction is responsible for this behavior. Between 28 and 56 days of hydration, the mixture with a 20% replacement of cement by glass powder shows a much larger increase in R_c compared to the plain or the fly ash modified mixture. This could be attributed to the faster pozzolanic reaction in the glass powder modified concretes, as was explained in an earlier section. The mixture with 20% cement replacement by fly ash shows a large increase in R_c between 56 and 90 days, which can be attributed to the pozzolanic reaction of fly ash. Thus it can be seen that R_c captures the changes in material microstructure because of hydration quite adequately. After 90 days of curing, the R_c values of the modified mixtures with similar cement replacement levels are identical.

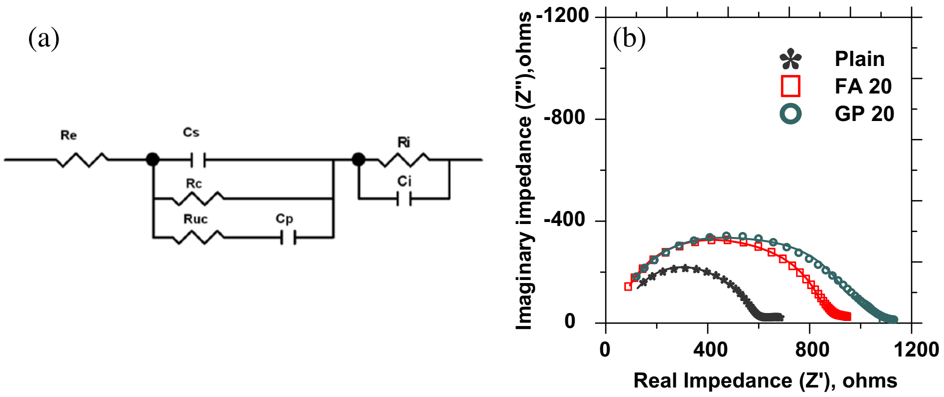

Fig. 6. (a) Equivalent electrical circuit used to model the RCP and NSSM test, and (b) experimental data and circuit model fit for the bulk arc.

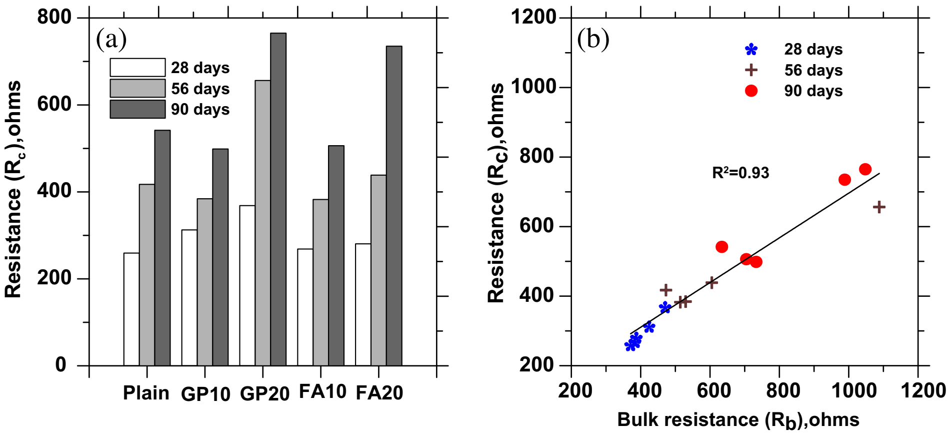

Fig. 7. (a) Resistance of connected pores for RCP specimens for plain and modified concretes, and (b) relationship between the bulk resistance (R_b) and resistance of connected pores (R_c).

Fig. 7b shows the relationship between bulk resistance (R_b) and the resistance of connected pores (R_c) of specimens before they were subjected to any of the chloride transport tests. A linear relationship can be observed between the R_b and R_c values at all ages of curing for all the specimens. It can also be seen that the R_b values are always higher than R_c because of the contribution of the electrolyte, unconnected pores, and the solid phase to the bulk resistance.

Fig. 8a shows the relationship between the RCP values and the R_c values obtained from the circuit model for the EIS spectra before the transport tests for all the specimens. It can be seen that there is a linear trend of decreasing RCP values with increase in R_c values. The values for all the specimens at all ages fall along a single linear fit line, similar to the relationship between RCP values and initial conductivity. However, a different picture emerges from Fig. 8b that relates the D_{nssm} values to the R_c values obtained from the

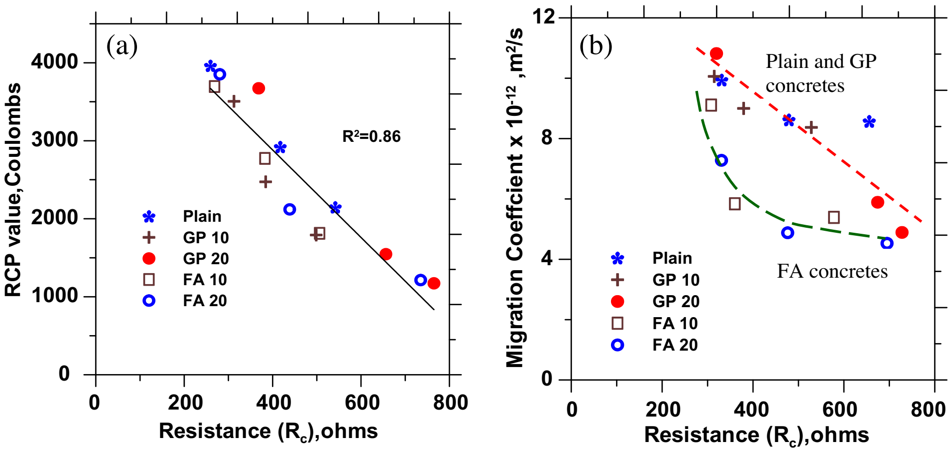

Fig. 8. (a) Relation between RCP charge and R_c, (b) D_{nssm} and R_c from electrical circuits using EIS data.

EIS spectra before the NSSM test. The D_{nssm} values are always lower for the fly ash modified concretes for similar initial resistances (before the NSSM test) of the connected pores. The increased chloride binding in fly ash modified concretes causes this reduction in the measured migration coefficients. This is similar to Fig. 3b, where two separate relationships were observed for fly ash and glass powder modified concretes when D_{nssm} and initial conductivity were related. The reasons for this observation were also elaborated in Section 3.2.

Fig. 9 shows the resistances of connected pores before and after NSSM tests for plain concrete, and the concretes containing 20% glass powder or fly ash as cement replacement, cured for 90 days. It can be seen that the R_c value before the test is the highest for the glass powder modified concrete, similar to the R_b values shown in Fig. 4b. The R_c value increases for the plain and fly ash modified concretes after the test, due to the formation of Friedel's salt. Friedel's salt formation is found to be more prominent in the case of fly ash modified concretes from the R_c values, as was shown earlier using XRD and TGA results. For the 20% glass powder modified concrete, the R_c value after the test is slightly lower than the value before the test, i.e. a more conductive connected pore network is inferred. In addition to the lowering of resistance caused by the penetrating Cl^- ions, which should happen in all the specimens, the reason for this behavior is the following. It has been reported that the chloride binding capacity increases with increasing Cl^--to-OH^- ratio in the pore solution [18]. The CH contents in 90 days cured glass powder and fly ash modified concretes are very similar, but for the glass powder modified concretes, the potential presence of a small amount of NaOH in the pore solution contributed by the alkali content of the glass powder increases the OH^- ion concentration, thus reducing the Cl^--to-OH^- ratio. Also, a higher value of R_c (or R_b) before the test results in the penetration of fewer Cl^- ions (because of a more refined microstructure), which also contributes to the reduction in the Cl^--to-OH^- ratio. This results in reduced chloride ion binding during the NSSM test for glass powder modified concretes. It can also be seen from Fig. 9 that the R_c value of the glass powder modified concrete is higher than that of the fly ash modified concrete after the test, even with higher chloride binding for the fly ash modified concrete.

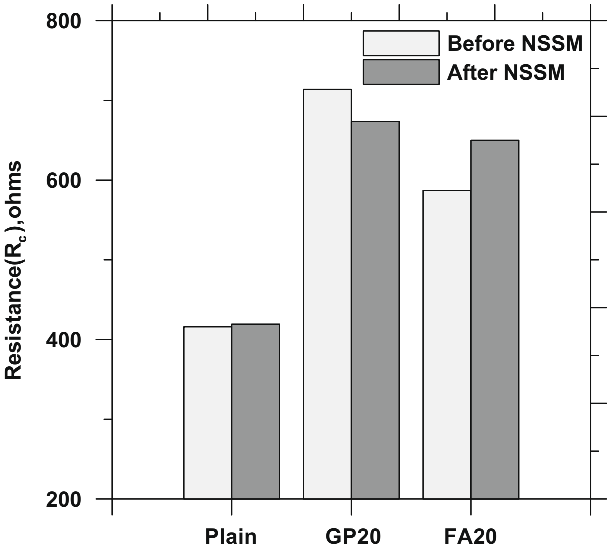

Fig. 9. Resistance of the connected pores before and after the NSSM test for 90 days cured specimens.

4. Conclusions

The chloride transport parameters of Class F fly ash or glass powder modified concretes were evaluated in this study using commonly adopted rapid test methods. The influence of testing conditions such as the concentration of the catholyte chloride solution, testing duration, and the pre-conditioning regime, as well as the chemical composition of the cementing materials on the measured transport parameters were evaluated and the following conclusions were made.

- Both glass powder and fly ash modified concretes showed lower RCP values as compared to the plain concrete, especially at later ages, indicating the influence of these materials in microstructure refinement. Even with a pore solution having a slightly higher conductivity because of the presence of a higher alkali content in glass powder, the glass powder modified concretes demonstrated similar or lower RCP values as compared to fly ash modified concretes of the same replacement level. A very good linear relationship was obtained between the RCP values and the initial conductivity of concretes determined from impedance spectroscopy.
- The fly ash modified concretes exhibited lower non-steady-state migration coefficients as compared to the plain and glass powder modified concretes. When D_{nssm} and initial conductivity (conductivity before the transport test started) were related, the fly ash modified concretes showed lower D_{nssm} values than the plain and glass powder modified mixtures for the same initial conductivity. The fly ash modified concretes also showed higher values of bulk resistance (from electrical impedance spectra) after the NSSM test than the values before the test. All of this could be attributed to the formation of higher amounts of chloride binding products in fly ash modified concretes (because of the higher alumina content) that resulted in lower pore sizes and increased tortuosity. The longer test duration and higher chloride ion concentration in the catholyte as compared to the RCP test was found to facilitate the formation of more chloride binding products under the conditions of the NSSM test. Thermal analysis tests and XRD spectra confirmed the presence of increased amount of chloride binding products in fly ash modified concretes under these testing conditions. The fly ash modified concretes showed much lower conductivity values under the conditions of the steady state conductivity (SSC) test also, again attributable to the increased formation of chloride binding products during pre-conditioning with a very high concentration NaCl solution.
- The resistance of connected pores (R_c) obtained from equivalent electrical circuit modeling was used to compare the transport behavior of plain and modified concretes. While the R_c–RCP relationship was found to be unaffected by the presence of cement replacement materials, the incorporation of fly ash was found to significantly change the R_c–D_{nssm} relationships. The influence of chloride binding on D_{nssm} was quantified using the R_c values determined before and after the migration tests. For the fly ash modified concrete, the R_c value after the test was higher than that before the test, indicating the formation of increased amounts of chloride binding products that alter the sizes of the pores and the connectivity of the pore structure.

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