Durability Properties of High Performance Concrete Containing High Volumes of Supplementary Cementitious Materials

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ABSTRACT

An experimental study was conducted to evaluate the performance of high performance non-air entrained concrete containing various supplementary cementitious materials. Concrete was prepared for constant value of slump and water-binder ratio. Fresh properties were determined in terms of slump and air content, whereas, hardened properties were investigated in terms of mechanical and durability tests. The maximum carbonation depth observed for concrete exposed for a period of sixteen weeks containing 40% pulverized fuel ash and 7.5% microsilica was about 5 mm. The non-steady state migration and diffusion coefficient of concrete containing different type of supplementary cementitious materials were observed to be appreciably lesser than that of the control concrete. The coefficient was noted to be least one for concrete with 15% microsilica. When 7.5% microsilica was used in 40% pulverized fuel ash and 50% ground granulated blast-furnace slag concrete, the improved resistivity (in terms of lower value) was observed than that exhibited by 15% microsilica concrete. However, both the ternary mixes showed better resistivity values when compared with control concrete. The scaled mass in kg/m^2 for 40% pulverized fuel ash concrete was the maximum among all the mixes. Addition of 7.5% microsilica in concrete did not cause any considerable change in the scaled mass. However, the increased content (15%) of microsilica behaved excellently in reducing the scaled mass. Ternary mixes of 40% pulverized fuel ash and 50% ground granulated blast-furnace slag concrete were found to show reduction in scaled mass.

Keywords: High performance concrete, durability, carbonation, chloride migration, electrical resistivity, salt-scaling

1.0 INTRODUCTION

High performance concretes (HPC) are concretes meeting the special and desired performance that cannot be achieved by using only the traditional materials, normal mixing, placing and curing practices. The desired performance may involve enhancements of characteristics, such as segregation free placement and compaction, faster strength development at early age, improved mechanical properties, volume stability in severe environments (Aitcin, 1998). In most cases HPCs have very low permeation characteristics, due to the dense hydrated cement structure. HPCs are also supposed to exhibit considerable intended resistance to various deterioration mechanisms, such as salt scaling, alkali-silica reaction, freezing and thawing deterioration and abrasion (Khan, 2003).

There are many factors which influence the mix proportion for HPCs. These factors include intended purpose, locally available materials, experience, personal preferences and economic consideration. Therefore, various alternatives can be adopted for

producing mix proportions, which may result in HPCs with the desired properties. It is essential to use low water-binder ratio in HPCs, and such concretes must be transported and placed with relative ease using conventional constructional procedures. Addition of pulverized fuel ash (PFA), ground granulated blast-furnace slag (GGBS), microsilica (MS), and other supplementary cementitious materials (SCMs) are necessary for producing HPCs (alves et al., 2004). These materials can improve mechanical and durability properties of HPCs. In some cases, combinations of two or three types of SCMs have proved to be impressive tool to improve concrete properties (Pandey et al., 2003). For example, the combination of PFA and MS along with cement in a mix results in several synergistic effects related to early-age strength and Sulphate/ chloride resistance of concrete (Kumar, 2000). However, available information regarding the durability properties of HPCs containing high volumes of SCMs are not enough. Therefore, the results reported in this paper are intended to provide an understanding of the effect of high volumes of SCMs on the durability properties of HPCs.

2.0 EXPERIMENTAL OUTLINE

2.1 Materials

Portland cement (PC) complying with BS EN 197-1 (2011) was used in this experimental study. Various other binders were also used like PFA conforming with BS 3892-1 (1997), MS complying with BS EN 13263-1 (2005). Used GGBS was in accordance with BS 6699 (1992). The physical properties and chemical composition of above binders are also reported in Table 1. The Blaine air permeability apparatus is used to determine the fineness of binders in terms of the specific surface area. Poly-carboxylic acid based super-plasticizer was used.

Table 1: Chemical composition and physical properties of binders

Chemical composition (%)	PC	PFA	GGBS	MS
SiO$_2$	20.54	50.7	35.76	92.0
Al$_2$O$_3$	6.06	28.80	13.96	0.7
Fe$_2$O$_3$	2.77	8.8	0.25	1.2
CaO	64.49	2.38	41.21	0.3
MgO	1.72	1.39	8.18	0.2
Na$_2$O	0.14	0.84	-	1.5
K$_2$O	0.61	2.4	-	1.80
SO$_3$	3.03	0.9	-	0.30
Loss on ignition	0.64	3.79	0.64	2.0
Physical properties				
Specific gravity	3.18	2.52	2.91	2.10
Specific surface area (m^2/kg)	322	340	600	2000

2.2 Mixture Proportions

Approach as described in ACI 211-1 (1993) was adopted for the design of HPC mixes. The mix proportions were finalised after attempting a number trials to have a constant value of slump, water-binder ratio (W/B), coarse aggregate content and a fixed total content of binder as shown in Table 2.

The desired slump value was achieved by using different dosages of the superplasticizer. Mass of different ingredients of control mix was in kg to prepare 1 m^3 of concrete. However, mass of ingredients of other mixes was in kg to prepare the volume of concrete slightly above or below 1 m^3 volume depending upon density of SCMs used. Out of eight, seven further mixes, in addition to the control mix, were prepared by using various SCMs contents.

Table 2: Mix Proportions

Mix ID	A/B[1]	FA/CA[2]	Mass of ingredients (kg)						SP[3] (%)
			Water	PC	PFA	GGBS	MS	FA[4]	
CC	3.79	0.60	145	485	-	-	-	689	1.10
PFA40	3.70	0.56	145	291	194	-	-	646	1.75
GGBS50	3.74	0.58	145	243	-	243	-	676	1.75
GGBS70	3.73	0.57	145	146	-	340	-	665	3.00
MS7.5	3.76	0.59	145	449	-	-	36.5	673	1.35
MS15	3.72	0.57	145	412	-	-	73	652	1.75
PFA40+MS7.5	3.68	0.55	145	255	194	-	36	633	2.25
GGBS50+MS7.5	3.76	0.59	145	206	-	243	36	657	2.50

[1] Aggregate- Binder ratio   [2] Fine aggregates- Coarse aggregates ratio

[3] Polycarboxylic acid based superplasticiser by mass of PC   [4] Fine aggregates

2.3 Preparation, Curing and Conditioning of Specimens

The concrete was made by following the procedure as laid in BS 1881: Part 125 (1986). Cubes of size 100 mm and blocks of size 250 x 250 x 110 mm were cast to ascertain the compressive strength and durability characteristics respectively. Both sets of specimens were manufactured by following standard procedures (BS1881: 108, 1983). After a lapse of six hours, samples were protected with a polyethylene sheet. The molds were, then, kept in the lab at temperature of 20°C (±1°C). The specimens were demolded next day (after a lapse of 24hours after casting). Samples were, then, placed for curing in water at 20°C. After 3 days, these sample were sealed by using polyethylene sheets after taking them out of water. Then samples were stored in a room where temperature equal to 20°C (±1°C) and relative humidity equal to 55% (±1%) were maintained. Samples were kept in this environment until these were ready for testing or extracting cores for various durability tests.

2.4 Specimens for Investigating Permeation Properties

Air Permeability and Sorptivity Indices
Tests were carried out on 250×250×110 mm concrete blocks. Three specimens of each mix were tested at the age of 91 days. Before conducting the tests, these blocks were conditioned at 40 ºC for 14 days and then placed at 20 ºC for 1 day to cool down the specimens to the lab temperature.

Specimens for testing chloride ingress resistance and electrical resistivity
For these tests, three numbers of 100mm core specimens were drilled from each of the three

250x250x110mm blocks at an age of 100 days. The cores were then trimmed to achieve a thickness of 50(±2) mm and 60(±2) mm for Chloride migration test as well as chloride diffusion test respectively. Cores, for Chloride migration test, were then placed in an oven at 40(±1) °C for 14 days. One day prior to the chloride migration test, the cores were cooled for 24 hours at 20(±1) °C. Then these were put in a vacuum container for saturating them with solution of calcium hydroxide. The other set of cores was saturated with $Ca(OH)_2$ until the weight stabilized. These cores were used for electrical resistivity test. Chloride diffusion tests were then carried out on the same cores.

Specimens for Testing Carbonation Resistance
Four cores with a diameter of 50mm were drilled from each of the three 250x250x110mm blocks, after Autoclam testing, when they were 100 days of age. Hence, 12 cores were used for this test for each mix. The coat of epoxy emulsion was applied on the curved sides as well as the trowel-finished face. Surface formed by the mold is the only route for carbon dioxide to penetrate during the test. The cores were then conditioned for further 2 weeks to remove moisture from the cores and to enable CO_2 penetration during the exposure in the carbonation chamber. Lastly, the cores were cooled down at a constant temperature for 1 day.

Specimens for Testing Salt-Scaling Resistance
100mm diameter core was cut each from each of the three 250x250x110mm blocks at an age of 100 days to determine the salt-scaling resistance of concrete. Hence, three cores for each mix was tested. Between two and seven days before saturation, the cores were sealed on their curved surface with an epoxy resin. The top and the bottom of the specimens were kept un-coated. The troweled surface was exposed to salt scaling.

2.5   Test Methods

Slump and Air Content
The slump of fresh concrete was measured as per BS EN 12350-2 (2000), whilst the air content was measured as laid down in BS EN 12350-7 (2000).

Thermo-gravimetric analyses
Testing was performed on powder samples obtained by grinding the hardened mortar taken from interior side of one of the concrete specimens crushed for compressive strength testing at the age of 28 and 91 days. Sample equal to 20 mg, in Powdered form from each mix, was heated in an inert nitrogen environment at 10∘C/min up to 1,000∘C, and the TG spectra were obtained to determine the $Ca(OH)_2$ content.

Compressive strength
The compressive strength of the concrete, as per BS EN 12390-3 (2002), was determined at the age of 28 and 91 days for each mix. Three specimens were used for the determination of compressive strength for each mix.

Air Permeability and Sorptivity
Autoclam permeability system (Basheer *et al.*, 1994) was used to measure the air permeability as well as the sorptivity (water absorption) of concrete. Test was used after conditioning the blocks at the age of 91 days. Autoclam permeability system is shown in Fig.1.

The following procedure was carried out to determine the air permeability. The test surface was cleaned free from dust and the base ring was clamped to the concrete. A syringe was attached with its piston retracted (i.e. when the syringe was full of air) to the bleed tube via the lure connecting tube. Autoclam measurement head was secured to the base ring.

Fig. 1. Autoclam permeability apparatus

The air permeability test was selected from the control panel. The location for storing the data was selected. When the program prompted for priming, the pressure inside the test area was increased to slightly higher than 500 mBar via the syringe. When the pressure was greater than 500mBar, the air permeability test started automatically. The pressure decay inside the test area was recorded automatically at every minute over the 15-minute test duration (or until the pressure reached 0 bar) by the controller. The natural logarithm of pressure against time is linear and the slope between the 5th and the 15th minute was recorded as the air permeability index (API). If the test duration was less than 15 minutes all available data were used to determine the API.

The following procedure was carried out to determine the water permeability (sorptivity). The test surface was cleaned free from dust and the base ring was clamped to the concrete at the location where the air permeability test was carried out. The Autoclam measurement head was secured to the base ring. The water absorption test was selected from the control panel. The location for storing the data was selected. When the program prompted for filling the

reservoir, the reservoir was filled via syringe. When a request was made on the display to hold the Autoclam vertical, the Autoclam body was held vertically so that the inlet of the reservoir face upwards and then the Autoclam started its internal priming process. When the program prompted to attach the Autoclam to the base ring, the Autoclam body was attached to the base ring and the test was then started. When the pressure in the test area was increased to 20 mBar, the test started automatically. The flow of the water into the concrete was recorded automatically over the 15-minute test duration by the controller. The cumulative volume of water absorbed versus the square root of time elapsed is linear and the slope of this line is taken as the sorptivity index. The portion of the graph between the 5th and 15th minute was used to calculate the sorptivity index.

Bulk Electric Resistivity

Two solid stainless-steel electrodes were fixed around each test core. The wet conductive sponge made of carbon foam was used as contact between the electrodes and the specimen. The upper and lower sponges have a slightly different resistance due to the weight of the specimen. The resistance was measured by using an LCR Data bridge (Potentiostat) followed by calculation of bulk electrical resistivity, ρ_{bulk} ($\Omega.m$).

Chloride Resistance

The non-steady state migration test was carried out as per NT BUILD 492 (1999). The catholyte solution was a solution of 10% NaCl by mass in tap water (100 g NaCl in 900 g water) and the anolyte solution was a solution of 0.3 N NaOH in de-ionized water. The mold-finished surface was exposed to the chloride solution (catholyte). Voltage of 30V was applied between the cathode and the anode and the initial current through the specimen was recorded. Based on this initial current, the recommended test voltage as well as the test duration were selected from a Table proposed in the method. Then the 30V was changed to the recommended test voltage and the new current was measured along with the temperature of the electrolytes. At the end of the test, the current and the temperature of the electrolytes were again measured. After removing the concrete disc specimen from the cell, these were split along the length into two halves and the half section which had a regular broken surface was used for the depth of chloride penetration measurements. This value was used for the calculation of non-steady state migration coefficient. The non-steady state diffusion test was conducted as laid down in NT BUILD 443 (1995). Respective depth of layers was used to plot the chloride profiles. The chloride content within each layer was determined using titration method as defined in NT Build 208 (1984).

2.6   Accelerated Carbonation

After conditioning, the cores were put in a carbonation chamber at an environment of 5($\pm$1) % CO_2

concentration (by volume), 20($\pm$1)^{o}C and 55($\pm$1)% RH for up to 112 days. Carbonation depth (average of three samples) of each mix was measured after an exposure period of 7, 14, 28, 56 and 112 days. After removing from carbonation chamber, the cores which were split longitudinally. Then 1% solution of the phenolphthalein indicator in alcohol was sprayed on the broken concrete surface. This sample was, then left for 24 hours. The formation of pink color was the indication of non-carbonated portion, and Vernier calipers was used for measuring.

2.7   Salt-scaling

Capillary suction of de-icing solution and freeze thaw (CDF) test was used to measure the salt-scaling resistance of concrete (Setzer et al., 1996). The amount of scaling per unit surface area, in the presence of sodium chloride, was calculated against number of freeze and thaw cycles This value is taken as an indication of resistance offered by concrete against the salt-scaling. Seven days before the CDF test began, the specimens were placed in the test containers on a 10mm high spacer and the test liquid (3% by mass of sodium chloride and 97% by mass of de-ionized water) was poured into the container up to a height of 15($\pm$1) mm, without wetting the top of the specimens. The lid was then placed on each of the containers. The level of the test liquid was checked regularly and topped up as the samples might absorb the test liquid by capillary suction. Then the containers were kept in an automatic environmental chamber which was subjected to freeze and thaw cycles as shown in Fig. 2. After every two cycles, loose particles were separated were collected from the specimens. The loose particles were weighed after drying at 100 ^{o}C for 24 h.
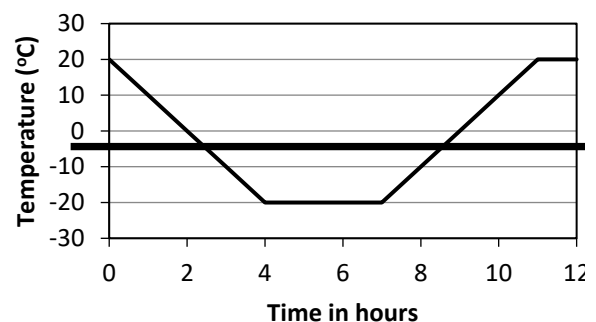

Fig. 2. Freeze-thaw cycle used for salt-scaling test

3.0   RESULT AND DISCUSSIONS

3.1   Slump and Air Content

Values of slump and air content are presented in Table 3. Air – paste ratio for all the mixes has also been included in Table 3.

Table 3: Slump, air content and air- paste ratio

Mix#	Slump (mm)	Air content (%)	Air-paste ratio
CC	65	3.5	0.23
PFA40	85	2.5	0.26
GGBS50	80	2.75	0.18
GGBS70	70	2.5	0.16
MS7.5	60	3	0.20
MS15	75	2.5	0.16
PFA40+MS7.5	80	2.5	0.16
GGBS50+MS7.5	85	2.75	0.18

3.2 Thermo-Gravimetric Analysis

Thermal analysis data was made for the samples at the age of 28 and 91 days. The $Ca(OH)_2$ contents obtained from this analysis are reported in Fig. 3. A considerable decrease in $Ca(OH)_2$ content was observed for binary blends of GGBS and both ternary blends compared with that of CC at both ages. It is also clear from Fig. 3 that amount of $Ca(OH)_2$ was the highest for CC, and decreased for MS7.5, MS15 and PFA40, respectively. Addition of 7.5% MS to binary blended mixes of PFA (at replacement level of 40%) and GGBBS (at replacement level of 50%) caused marginally lower quantities of $Ca(OH)_2$. This could be due to depletion of OPC particles due to its substitution with the SCMs. Another reason associated with lower quantities of $Ca(OH)_2$ might be because of pozzolanic reactivity of the SCMs which transformed free $Ca(OH)_2$ into additional calcium silicate hydration products. A better pozzolanic reactivity was observed in case of both ternary mixes than their binary counterparts, indicating better impact of MS7.5 to the hydration of PFA and GGBS mixes. PFA mixes (binary as well as ternary) were found to have continued hydration from 28 days to 91 days, whereas, no further hydration was seen for its GGBS counterparts beyond the age of 28 days.
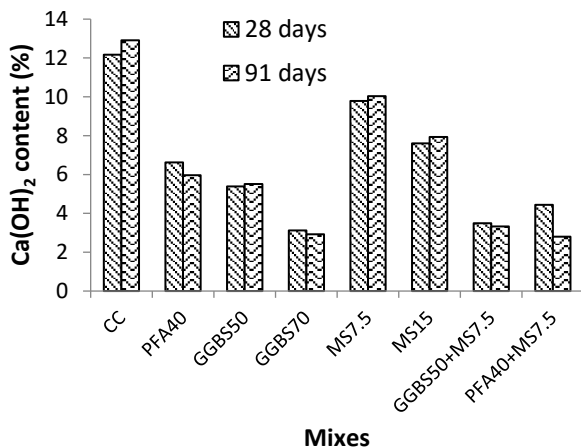
Fig 3. $Ca(OH)_2$ contents for various mixes

3.3 Compressive Strength

Figure 4 shows the compressive strength results along with error bars. Replacement cement with 15% MS showed highest values of compressive strength at both the ages (28 as well as 91 days) followed by mix with 7.5% MS. Comparatively slower enhancement in strength was observed for mixes with MS (MS15 as well as MS7.5) beyond 28 days. This could be due to relatively slower rate of pozzolanic reaction of MS after 28 days as presented in Fig. 3.
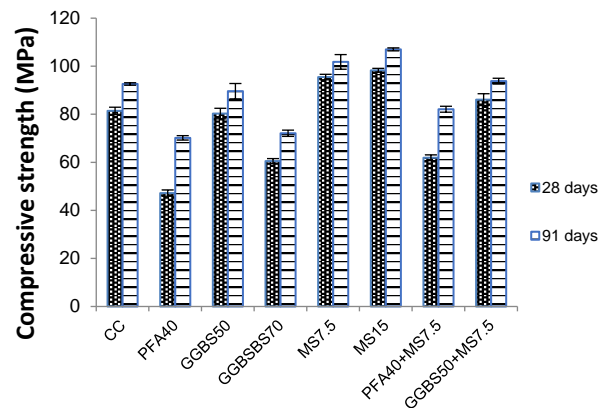
Fig. 4. Compressive strength of various mixes

Similar trend was noted for 50% GGBS mix as that of CC at both 28 and 91 days. The addition of MS (7.5%) to the 50% GGBS mix resulted in an enhancement in strength at both the ages. GGBS content at 70%, decreased the compressive strength at both the ages. Addition of GGBS and PFA to MS7.5 mix caused an adverse effect on compressive strength. The presence of PFA (PFA40+MS7.5) reduced the compressive strength relative to the MS7.5 mix more than the presence of GGBS (GGBS50+MS7.5). Rate of gain of strength for binary and ternary mixes of PFA is more as compared with its GGBS counterparts after 28 days. TG data in Fig. 3 also reflects the compressive strength development results at later ages in case of PFA mixes. Chemical and physical effects, within the mix due to inclusion of MS, increased the compressive strength of concrete mixes. Main chemical effect is because of the chemical reactions with $Ca(OH)_2$ produced from OPC hydration. As a result, secondary calcium-silicate-hydrates (C–S–H) are formed (see Fig. 3). The physical effect (filler effect) is due to better packing ability of the solid MS materials (ACI Committee 234, 1995).

The comparatively smaller particle size of MS as compared to that of GGBS), is responsible of higher rate of hydration of MS than that of GGBS. This increased rate of hydration led towards strength development at an early stage in case of MS as compared to GGBS. The compressive strength of binary and ternary mixes of PFA can also be seen in Fig, 4. Concrete mix with 40% PFA showed lesser strength development than that of the control mix at

both the ages. Slower pozzolanic reaction of the PFA might be the reason for reduction in the strength of PFA mixes. The addition of MS enhanced the compressive strength at both the ages. Figure 3 indicates that the enhancement is also because of the observed pozzolanic reaction in PFA40+MS7.5.

The addition of MS in binary mixes of PFA and GGBS caused increase in compressive strength. MS improved the interfacial transition zone (ITZ) in by decreasing the porosity concrete. Improvement in the bond between hydrated cement matrix and the aggregate is another factor responsible for enhancement in strength of ternary mixes. Strength results of ternary mixes of PFA and GGBS is reflection of results observed from Fig. 2. Conversion of $Ca(OH)_2$ for ternary mixes of PFA (From 28 days to 91 days) and GGBS (Up to 28 days) from TG data of Fig. 3 confirmed the strength results obtained. Finer particle size of MS contributes to the grain refinement of the ternary mixes containing PFA and GGBS.

## 3.4   Permeation Properties

Air permeability and sorptivity
The air permeability and sorptivity values of the mixes at 91 days are shown in Fig. 5. To have an idea on the variation of the results and to see whether differences between mixtures are significant or not, error bars indicating the standard deviations are included. From the Fig. 5(a), the behaviour of different mixes in terms of resistance to air permeability can be seen.

Improvement in microstructure due to addition of MS is vital as discussed in section 3.2. The air permeability of mixes, after the addition of MS, was supposed to be improved but it was not observed. This apparently un-proven deviation needs to be investigated further. It could be due to the lack of sensitivity of the apparatus used for measuring air permeability for denser concrete. Figure 5(b) presents the values of sorptivity at 91 days. The sorptivity results for binary mixes of MS and GGBS were comparable to that observed for CC mix. Adverse effect was noted when GGBS content was increased beyond 50%. MS addition in the GGBS mix caused remarkable decrease in sorptivity. These results do not match with those experienced in case of air permeability. Air permeability and sorptivity are related to two independent physical characteristics of the pore structure of concrete. The replacement of OPC with PFA at replacement level of 40% increased the sorptivity. MS showed improvement in sorptivity when added to the binary mix of PFA. These favorable results can be due to chemical and physical effects associated with MS.

3.5   Bulk electrical resistivity

The electrical resistivity is an important concrete property that allows the evaluation of the access facility of aggressive agents before the corrosion

process starts. It also estimates the velocity of the same process after it begun. The results of electrical resistivity for various mixes are shown in Fig. 6. From this figure, the resistivity of binary mixes containing PFA and GGBS was found to be higher than that of the control concrete. The best results were obtained for binary mix of MS at replacement level of 15%. When 7.5% MS was used in binary mix of PFA and GGBS (at replacement level of 50%) concrete, the resistivity was still less than that of the 15% MS concrete. MS7.5 concrete showed the performance in between those of ternary mixes with PFA and GGBS. It shows that 7.5% MS improved the resistivity in combination with GGBS rather than its addition to PFA or 100% OPC mixes.
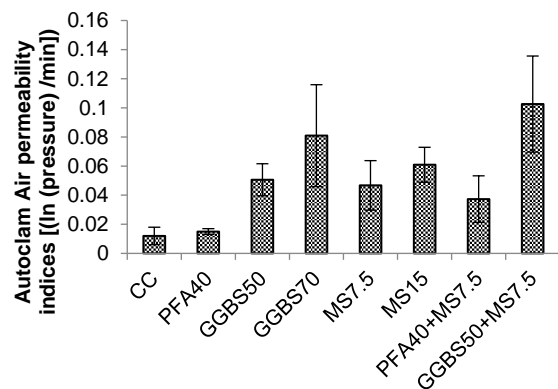

a) Autoclam air permeability indices
[(ln (pressure)/min)]
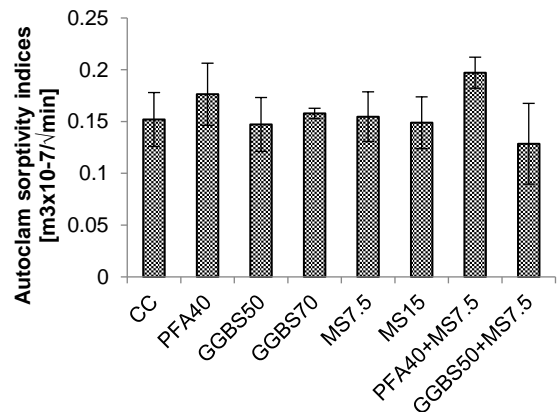
b) Autoclam sorptivity indices [$m^3 \times 10^{-7}/\sqrt{min}$]

Fig. 5. Air permeability and sorptivity indices of various mixes at the age of 91 days

The denser microstructure in the mixes with SCMs leads to generally discontinuity in the pores of concrete. In addition, the pores may also become blocked because of the products achieved after hydration of the binders. Therefore, greater value of resistivity was observed in case of these mixes. It can also be observed that the trends of electrical resistivity in the specimens are like that of the resistance to chloride migration (see later on Fig. 7).
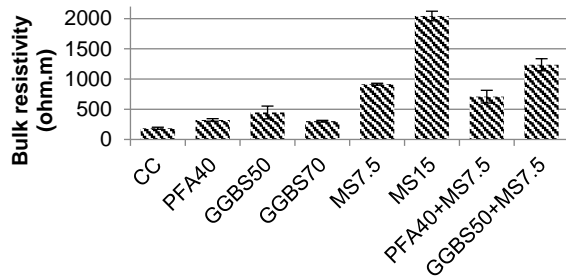
Fig. 6. Bulk resistivity of concrete mixes

Flow of electrical current is mainly due to the flow of ions through the pore spaces of concrete, hence, resistivity leads towards porosity and diffusivity of concrete (Gu *et al.*, 1995) The high electrical resistivity of concrete would lead greater resistivity of HPC which leads towards lower rate of corrosion after the expiry of passivity. This is due to the pore refinement due to chloride binding.

3.6   Chloride Resistance

The results of non-steady state chloride migration and chloride diffusion tests are presented in Fig. 7. Figure 7 depicts that non-steady state migration as well as diffusion coefficient of concrete, containing different type of SCMs, were significantly lower than the control concrete. The coefficient of migration was minimum for concrete with high content of MS. However, least diffusion coefficient was observed for ternary mix of GGBS at replacement level of 50%. Addition of MS, at both the replacement levels, was found to decrease the chloride migration coefficient and chloride diffusion coefficient (De) by more than three times compared to the control mix. GGBS also showed the same trend in resisting chloride ingress as decrease of three folds was observed in case of binary mix with 50% GGBS. Another interesting thing that can be observed in this figure is that compared to the PFA, GGBS was relatively more effective in reducing the chloride coefficients. This could be due to the secondary chemical reaction of GGBS that contributes to make the microstructure denser. 50% GGBS seems to be optimum as beyond this content there was no improvement in the resistance to chloride migration, however, a marginal improvement is noted in the resistance to chloride diffusion as content of GGBS is increased from 50% to 70%. The concrete containing 7.5% MS performed the best after 15% MS concrete in resisting chloride migration.

The concrete containing 7.5% MS in combination with 40% PFA and 50% GGBS also performed better (in terms of resistance to chloride migration) than that of the control and 40% PFA concrete. Determination of chloride transport coefficients has a considerable amount of variability. In addition to the pore structure, penetration of chloride depends on all the factors used for its determination.
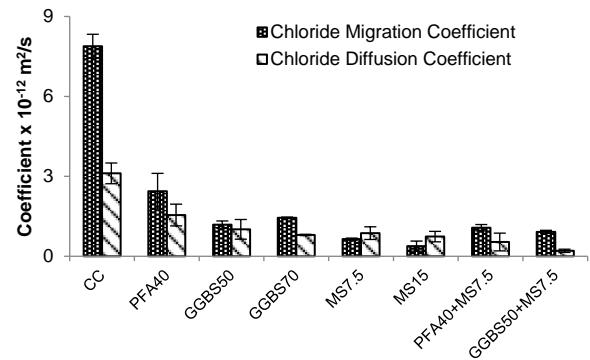
**Fig. 7.** Chloride transport coefficients for various mixes

Mix containing 40% PFA also showed decrease in De. Further decrease in De was noticed by the addition of MS by 7.5%. Addition of MS to binary mixes showed better performance in terms of resisting chloride diffusion as compared with binary systems. However, MS at a replacement level of 7.5% did not perform well as compared to its performance in ternary mixes with PFA and GGBS in resisting chloride diffusion. Bulk resistivity of concrete was found to be inversely proportional to the diffusivity.

A general qualitative agreement is observed between chloride diffusion and chloride migration (see Fig. 8). Diffusion and migration coefficients are directly proportional to each other. This suggests that overall, it is probably the improvement in microstructure that causes the increase of both coefficients. The correlation coefficient $R2$ was 0.9, indicating a good relationship between the coefficients. However, data points for intermediate diffusion and migration coefficients are missing, the validity of the high R^2 value remains a bit doubtful. Therefore, more intermediate data points are needed to find further confirmation for the now observed correlation.
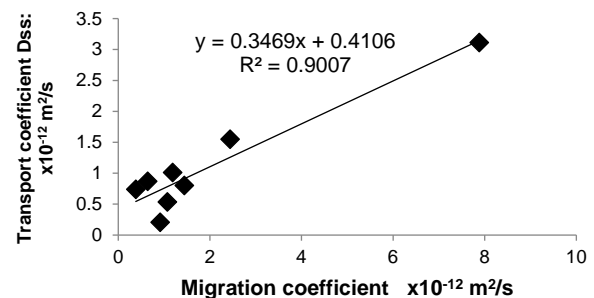
Fig. 8. Relationship between transport coefficients

Figure 9 shows the relationship between sorptivity indices and coefficients of chloride migration. The relationship shows that there is no significance difference in the values of sorptivity as compared to the difference observed in case of Chloride migration coefficients. The improved microstructure helped in increasing resistance to water absorption in almost all the mixes.
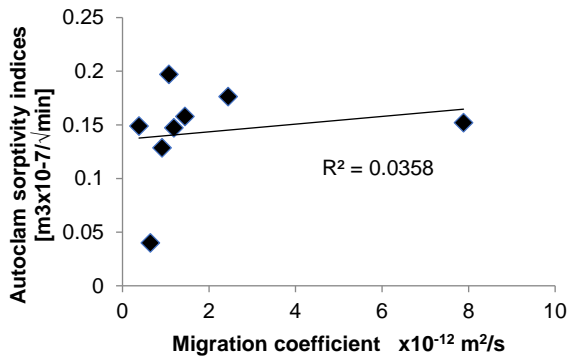
Fig. 9. Sorptivity indices and chloride migration coefficients relationship

The difference in sorptivity values were observed to be marginal. However, resistance to chloride migration was different for different mixes. This could be due to a difference in chloride concentration and, thus, generation of different species flux in the direction of concentration gradients. Further study is needed in this regard.

3.7 Carbonation

The carbonation depth of concrete containing different type of high volumes of SCMs for exposure period of one to sixteen weeks is shown in Fig. 10. This figure shows that the carbonation depth for most of the exposure periods was maximum for concrete containing 40% PFA. At early ages, the incorporation of 15% MS was found to have no effect on the carbonation depth as compared to the control concrete. However, from 28 days onwards the carbonation depth of 15% MS concrete was found to be less than that of the control concrete. Also 7.5% MS has carbonation like that of control concrete at early ages. This is in good agreement with the findings of other researchers Byfors, 1985). The carbonation depth of concrete with 50% GGBS was lower than the 40% PFA concrete for all the exposure periods. The content of $Ca(OH)_2$ and carbon dioxide penetration rate are the two key factors controlling the carbonation rate of concrete. GGBS is generally much more active than the PFA. Moreover, from Table 1, the GGBS used in this study had better fineness, which indicates that the HPC with GGBS might have a denser concrete matrix. Therefore, HPC with GGBS having lower $Ca(OH)_2$ content and denser matrix showed a better carbonation resistance than HPC with PFA. However, 70% GGBS showed an increase in the carbonation depth. This could be because the replacement level was too high; hence, leaving behind very low content of OPC responsible for producing $Ca(OH)_2$. This low quantity of $Ca(OH)_2$ was not enough to cause considerable pozzolanic reaction to occur. MS15 exhibited the best performance showing resistance against carbonation followed by MS7.5. The performance of MS7.5 was almost the same as that of ternary mix of PFA. The maximum carbonation depth observed for this

concrete mix (containing 40% PFA and 7.5% MS) was about 5 mm after an exposure period of sixteen weeks. Therefore, it can be said that if this combination is used, there is less risk of corrosion due to carbonation.
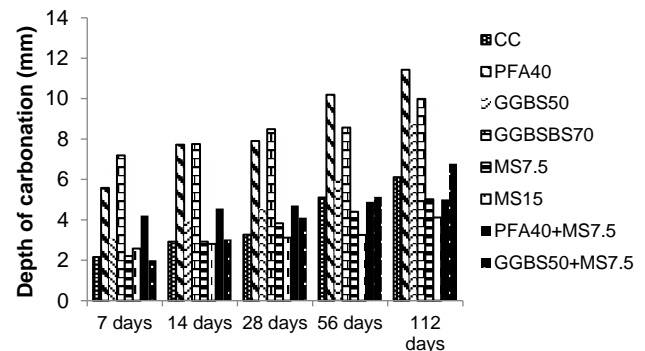
Fig. 10. Carbonation depth

MS significantly reduced the rate of carbonation in ternary blend with PFA as compared to that with GGBS. MS at a replacement level of 15% content in binary mix showed positive effect in lowering carbonation depth. However, rather than its binary mix, lower content of MS (7.5%) showed the better performance in ternary mix with PFA in reducing the carbonation rate.

Figure 11 represents the rate of carbonation of various mixes. PFA and GGBS addition caused an increase in rate of carbonation. This rate of carbonation is more significant for PFA mix. Inclusion of MS behaved differently in GGBS and PFA concretes.
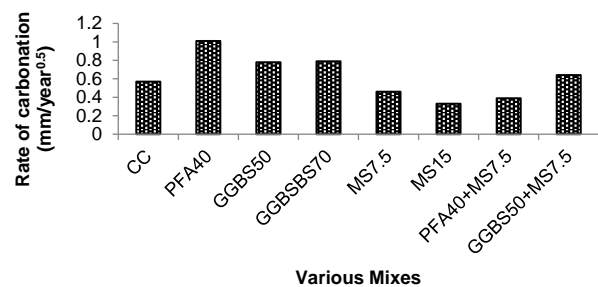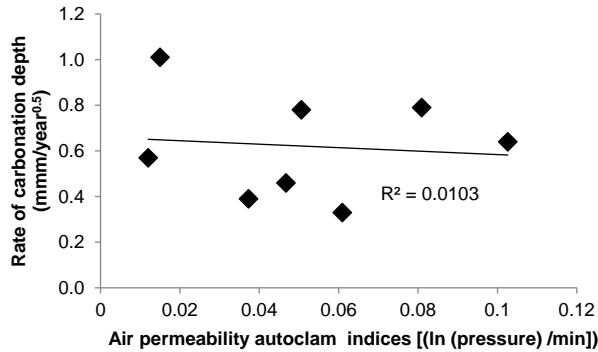

Fig. 11. Rate of carbonation for various mixes

One possible explanation for the higher carbonation rates exhibited by PFA and GGBS concretes may be the less availability of $Ca(OH)_2$ for secondary pozzolanic reaction. The reduced $Ca(OH)_2$ content in PFA/GGBS concrete, due to the dilution of OPC and consumption by pozzolanic reaction, means that a reduced quantity of CO_2 is required to carbonate a given depth of concrete. The filling effect along with pozzolanic reaction of ternary mix of GGBS might cause pore refinement leading towards reduction in rate of carbonation. Reactivity of MS is greater than FA and GGBS which caused increased depletion rate of $Ca(OH)_2$.

Relationship between air permeability indices and rate of carbonation for various mixes are shown in the Fig. 12. No general conclusion could be made. In fact, values of air permeability index do not seem to be logical. These values were opposite to what might be expected as discussed in section 3.4.

Fig. 12. Air permeability indices and carbonation depth relationship

The relationship between rate of carbonation and the compressive strength at the age of 91 days for various concretes is shown in Fig. 13. These test results have the trend which is much similar as reported from other investigations (Fattuhi, 1986). Rate of carbonation is inversely proportional to the compressive strength of concrete containing SCMs. Both carbonation and compressive strength are significantly controlled by the pore structure of concrete and therefore, there exists a relationship between both the properties. The value of R2 is different from other studies due to the complex microstructure developed in HPC concretes.
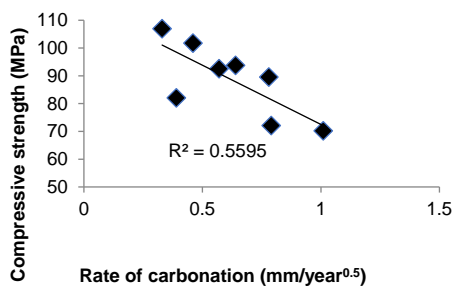

Fig. 13. Compressive strength and rate of carbonation relationship

3.8 Salt-scaling

The scaled mass of various mixtures measured in kg/m^2 after 400 cycles is presented in Fig. 14. Out of all the mixes, maximum scaled mass noted for 40% PFA concrete. Laboratory test data (Setzer *et al.*, 1996) achieved in accordance with ASTM C 672 have proved that air-entrained concretes having high volumes of PFA exhibited poor performance when

exposed to freezing and thawing cycles in the presence of de-icing salts. In contrast, there are several reports narrating good performance of concretes with PFA when exposed to de-icing salts in the field (Byfor, 1985). So far, there is no clear explanation for this contradictory report between laboratory observation and field experience.

From Fig. 14, it can be observed that both the binary mixes of concrete containing GGBS, scaled mass was almost the same as that noted for the control concrete. However, the use of 15% MS was found to reduce the scaled mass. Like carbonation resistance, chloride migration resistance and bulk electrical resistivity tests, 7.5% MS behaved the same in improving 50% GGBS concrete as compared to its behaviour in binary mix of PFA. It can also be observed that concrete containing 40% PFA + 7.5% MS and 50% GGBS + 7.5% MS reduced the scaled mass. The findings agree with that of the other researchers (Valenza and Scherer, 2007), which show that SCMs usually do not increase the scaling potential if most of the factors (e.g., low W/B, proper finishing and curing practices) are satisfied. Considerable resistance against salt scaling of these mixes with SCMs might also be due to their relatively higher strengths. This finding agrees with previously reported comments by Valenza and Scherer (2007) while reviewing various experimental studies.
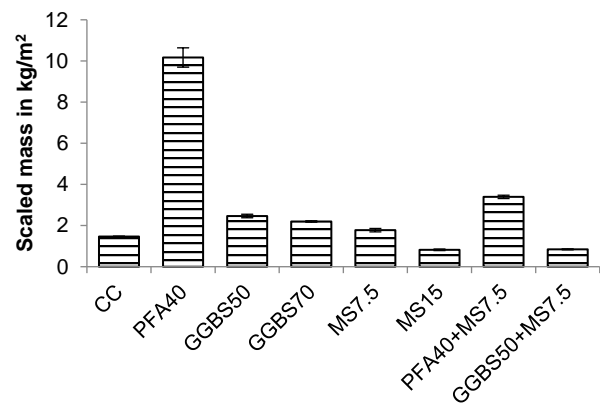
Fig. 14. Scaled mass of concrete after 400 cycles

4.0 CONCLUSIONS

Based on the investigation, the following conclusions can be drawn:
(i) The carbonation depth was maximum for concrete containing 40% PFA. Although at early ages, the incorporation of 15% MS was found to have no effect on carbonation depth, from 28 days onwards the carbonation depth of 15% MS concrete was found to be less than that of the control concrete. Similarly, 7.5% addition of MS showed good results with 40% PFA as compared with 50% GGBS at the age of 91 days. Like Mix MS7.5, PFA40+MS7.5 showed almost the same

performance in resisting carbonation after the age of 28 days.

(ii) The non-steady state migration coefficient and diffusion coefficient of concrete containing different type of SCMs were significantly lower than the control concrete. The coefficient was minimum for concrete containing 15% MS. Ternary mixes of PFA/GGBS with 7.5%MS performed better as compared to binary blend of MS at replacement level of 7.5% in showing resistance against chloride diffusion.

(iii) The resistivity of concrete containing 40% PFA and GGBS (both 50% and 70%) was higher than that of the control concrete. Binary mix of MS at replacement level of 15% showed the best performance. Addition of 7.5% MS in binary mixes with 40% PFA and 50% GGBS caused reduction in the resistivity, even less than that of the 15% MS concrete. However, in both cases, this was greater than the control concrete.

(iv) Out of all the mixes, the maximum scaled mass was noted for 40% PFA concrete. Inclusion of 7.5% MS did not improve the control concrete in resisting salt scaling. However, 15% MS reduced the scaled mass. The role of 7.5% MS in 40% PFA and 50% GGBS concrete was found positive in reducing the scaled mass.

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