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Moisture and ionic transport in concretes containing coarse limestone powder

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ABSTRACT

Concretes containing a coarse limestone powder (median particle size of 72 μm) as a partial cement replacement material are proportioned so as to attain similar 7-day compressive strengths as a 0.40 water-to-cement ratio (w/c) control concrete. The moisture and chloride ion transport behavior of the concretes containing limestone powder with and without small amounts of silica fume are evaluated in this paper. It is shown that a 15% cement replacement with coarse limestone powder at a water-to-powder ratio (w/p) of 0.34 results in concretes of better or comparable compressive strengths, porosities, moisture transport parameters (overall moisture intake, and sorptivity), and rapid chloride permeability (RCP) as that of a 0.37 w/c plain concrete. However, the non-steady state migration coefficients (D_{nssm}) of concretes containing limestone powder are found to be higher than those of plain concretes of even higher w/c. A microstructural parameter ($\phi\beta$ – product of porosity and pore connectivity) is used to relate the pore structure to the moisture and ionic transport. Relationships between $\phi\beta$ and the moisture and ionic transport parameters are provided, which shed light on the combined influence of w/p and a highly reactive cement replacement material such as silica fume on the different transport properties of concretes containing a coarse limestone powder.

1. Introduction

The ever-increasing focus on sustainability of cement-based materials has resulted in a variety of attempts by the research and practicing community on using non-standard cement replacement materials in concrete. While the use of supplementary materials that are either cementitious or pozzolanic has become an accepted practice, the use of inert filler materials to replace a portion of the cement in concrete is still an under-recognized opportunity [1,2]. In high-performance and self-consolidating concretes where there is a requirement for higher powder contents, and when a portion of cement grains remain unhydrated, the use of filler materials such as limestone powder to replace some cement is advantageous both from the economical as well as the long-term material durability standpoints. The current ASTM specification for Portland cement (C 150) allows the use of only up to 5% limestone powder by mass. A recent report [3] that investigated the use of 5% or less limestone powder interground with cement concluded that the fresh and hardened properties of the mortars containing limestone powder are comparable to or better than those of the companion plain mixtures. However, higher cement replacement levels are being discussed and even adopted in many other countries, especially as filler in self-consolidating concretes [4,5].

A number of studies have been reported on the hydration, rheological, mechanical, and durability characteristics of cement pastes, mortars, or concretes containing limestone powder [4,6–10]. Most of these studies have dealt with the use of limestone powder that is as fine as or finer than the Portland cement. In such cases, the dilution effect caused by the incorporation of the inert filler is compensated to some extent by the increased cement hydration, thus producing concretes of comparable properties even at similar w/c as that of the control mixture. In order to effectively use a coarser limestone powder (median particle size 5–6 times as that of Portland cement) as a partial cement replacement material, the water-to-powder ratio (w/p) of the system would need to be reduced. The influence of w/p on dilution, hydration enhancement, and compressive strength of cement pastes containing a coarse partial cement replacement material has been quantified in [11]. It has also been reported that the use of a coarse limestone powder provides a substantial reduction in autogenous deformation [12] and consequently reduced early age cracking. The increased inter-particle spacing in the system facilitated by the incorporation of coarse limestone powder changes the microstructure of the material, thus influencing the transport behavior. Hence the focus of this study is on investigating the influence of a coarse limestone powder on the moisture and ionic transport of concretes proportioned to attain similar early-age (7-day) compressive strengths as a 0.40 w/c conventional concrete. The effects of using small amounts of silica fume on the transport characteristics of concretes containing coarse limestone powder are also explored.

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2. Experimental program

2.1. Materials

Type I/II cement conforming to ASTM C 150, densified silica fume conforming to ASTM C 1240, and a coarse limestone powder obtained from a commercial quarry are used in this study. Table 1 shows the chemical composition and physical characteristics of these materials. Fig. 1a shows a scanning electron micrograph of the limestone powder and Fig. 1b shows the particle size distribution curves of the cement and limestone powder. The median particle size of the cement is approximately 13 µm whereas the coarse limestone powder has a median particle size of about 72 µm.

2.2. Developing mixture proportions for similar 7-day compressive strengths

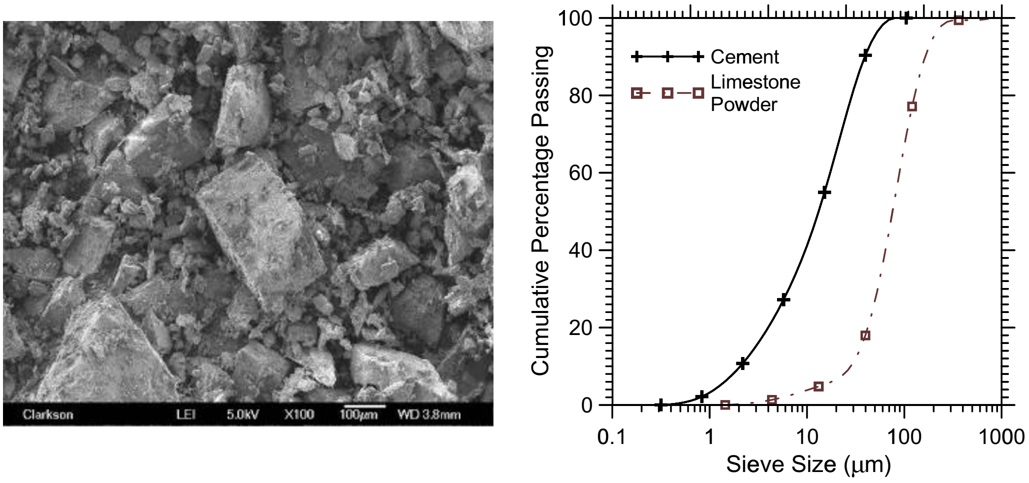
It has been stated that the addition of micro-fillers such as limestone powder can enhance the hydration of cement pastes [7]. The increased hydration could be attributed to limestone powder providing nucleation sites or facilitating the dispersion of the cement particles evenly which allows more cement grains to hydrate [11,13,14]. The compressive strength results of 0.40 water-to-powder (cement + limestone powder) ratio (w/p) pastes where 10% of cement by mass was replaced by the coarse limestone powder are shown in Fig. 2a. The pastes with 10% limestone powder as cement replacement show compressive strengths that are lower by 10% or more as compared to the plain paste, at almost all ages. This can be attributed to either: (i) the ineffectiveness of limestone powder particles in providing nucleation sites due to their low specific surface areas or (ii) the slight improvement in cement hydration, if any, being overshadowed by the significant dilution effect. Fig. 2b shows the microstructure of the paste containing 10% limestone powder after 90 days of hydration.

Table 1
Chemical composition and physical characteristics of cement, limestone powder, and silica fume.

Composition (% by mass)/physical characteristics	Cement	Limestone powder	Silica fume
SiO_2	20.2	0.8	85.0
Al_2O_3	4.7	0.17	0.13
Fe_2O_3	3.0	0.1	0.45
CaO	61.9	–	3.0
MgO	2.6	0.5	1.55
Na_2O	0.19	–	0.23
K_2O	0.82	–	0.2
SO_3	3.9	0.05	0.05
$CaCO_3$	–	98.0	–
Loss on ignition (%)	1.9	43.4	2.13
Median particle size (µm)	13	72	<1[a]

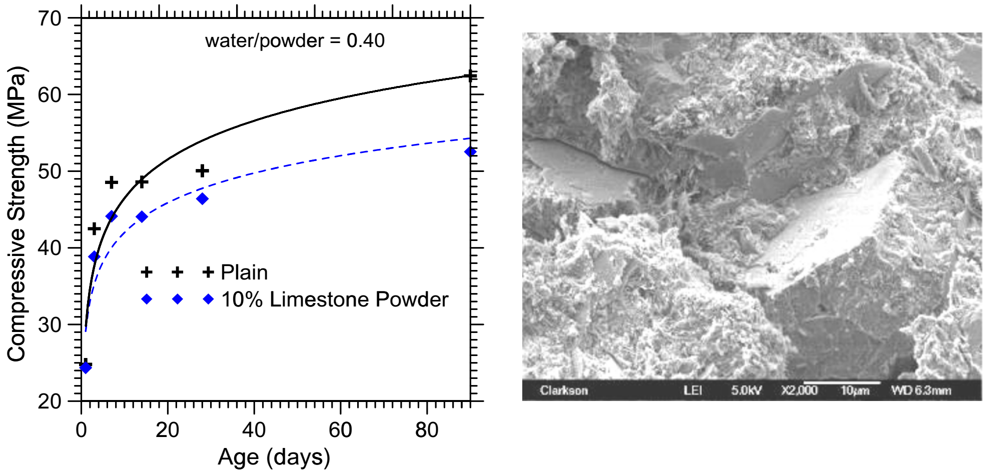
[a] Agglomerates can sometimes be larger than even the cement particles.

The above discussion makes it obvious that a direct comparison of the behavior of plain concretes and those containing coarse limestone powder where a certain amount of cement is directly replaced by the filler without changing any other mixture proportioning parameters will always result in a disadvantage for the concretes containing limestone powder as far as properties are concerned. Strength reduction as a result of such an approach even for mixtures containing a fine limestone filler has been reported [10]. Hence, in this paper, the behavior of concretes incorporating limestone powder are evaluated after proportioning them to provide similar early-age (7 days) compressive strengths as that of a 0.40 water-to-cement ratio (w/c) plain concrete. Several concrete mixtures were proportioned using the chosen limestone powder and silica fume replacement levels at different values of w/p. The w/p of concrete mixtures containing 10% and 15% limestone powder as cement replacement by mass, when reduced to 0.37 and 0.34 respectively, were found to provide similar 7-day compressive strengths as that of the plain concrete with a w/c of 0.40. The effective water-to-cementing materials (cement + silica fume) ratio (w/cm) of these mixtures remained very close to that of the control concrete (between 0.40 and 0.41). Companion plain concrete mixtures with w/c of 0.37 and 0.34 were also prepared for comparison with the lower w/p concretes containing limestone powder. Table 2 shows the final mixture proportions adopted for detailed studies in this paper. For ease of reference, the concrete mixtures are referred to in the tables and graphs using their designations shown in Table 2. The numbers before LS (for limestone powder) and SF (for silica fume) denote the percentage replacement by mass of cement by these materials. As can be seen in Table 2, the dosage of high range water reducer had to be increased in order for the concrete mixtures with lower w/p to obtain similar slump as that of the 0.40 w/c plain concrete, which was 150 mm ± 15 mm.



(a) (b)

Fig. 1. (a) Scanning electron micrograph of the coarse limestone powder. (b) Particle size distribution curves of cement and limestone powder.



(a) (b)

Fig. 2. (a) Compressive strength of cement pastes containing 0% and 10% cement replacement by coarse limestone powder pastes at various ages of hydration. (b) Micrograph of paste containing 10% limestone powder at 90 days of hydration.

Table 2
Mixture proportions for 1 m^3 of concrete.

Mixture	w/c or w/p	Cement (kg)	LS (kg)	SF (kg)	Water (kg)	FA (kg)	CA (kg)	HRWR (%)[a]	AEA (%)[a]	Slump (mm)	7-day f_c' [b] (MPa)
Plain	0.40	416	–	–	167	816	928	0.24	0.017	160	34.2 (1.2)
10LS	0.37	375	41.6	–	154	798	908	0.32	0.017	150	32.8 (0.9)
Plain	0.37	416	–	–	154	831	945	0.32	0.017	145	36.0 (0.7)
15LS	0.34	354	62.4	–	142	797	906	0.45	0.017	145	34.6 (1.1)
Plain	0.34	416	–	–	142	846	962	0.45	0.017	160	52.7 (1.2)
10LS + 5SF	0.37	354	41.6	20.8	154	766	871	0.35	0.017	165	33.4 (0.4)
15LS + 5SF	0.34	333	62.4	20.8	142	764	868	0.45	0.017	160	36.5 (0.5)

CA – coarse aggregate, FA – fine aggregate, LS – limestone powder, SF – silica fume, AEA – air entraining admixture, and HRWR – high range water reducer.

[a] % by mass of powder.

[b] The values in parentheses indicate one standard deviation in MPa as determined for three replicate specimens.

2.3. Determination of porosity using vacuum saturation

The porosities of hardened concretes were determined using a vacuum saturation method detailed in RILEM CPC 11.3 [15]. 50 mm thick discs were cut from 100 mm × 200 mm concrete cylinders, and oven dried at 100 °C for 24 h to remove all of the evaporable water. The masses of the specimens were measured after allowing them to return to room temperature. The specimens were then subjected to vacuum saturation for 3 h, water was then allowed into the vacuum chamber while vacuum was maintained, and the vacuuming continued for an additional 1 h. The specimens were then left undisturbed in water for 12 more hours. The masses of the specimens were then recorded. The difference in the masses, converted into volume, represents the volume of capillary pores. The capillary porosity was calculated by dividing the volume of capillary voids by the volume of the concrete specimen. Two specimens were used for each mixture at each age, and the average values of porosities were used for the analysis.

2.4. Moisture transport test method

The moisture transport tests were carried out in this study in accordance with ASTM C 1585. Three 50 mm × 100 mm concrete discs corresponding to each mixture were placed in a desiccator containing saturated potassium bromide (KBr) solution, and the desiccator kept in an oven at 50 °C for 72 h. The specimens were positioned such that they do not come into direct contact with the KBr solution. After this duration, each specimen was stored in an individually sealed container for 15 days to attain equilibriation of internal humidity. The specimens were then covered with plastic water-proof sheets, completely sealed on their sides and bottom, leaving only the top surface exposed. The exposed surface of the specimen was placed face down on the supporting device (steel rods) inside the pan containing water filled up to 3 ± 1 mm above the top of the supporting device. The mass of the specimens were measured at regular intervals – more frequently for the first 7 h and less frequently afterwards – for 7 days. The initial sorptivity (S_i) was calculated based on mass intake during the first 7 h, and secondary sorptivity (S_s) based on the mass intake in the 24 h to 7 day exposure period. Both S_i and S_s were obtained for all concrete mixtures that were initially cured for 28 or 56 days in saturated curing conditions. Average values of sorptivities for the three specimens corresponding to each mixture at each age are reported.

2.5. Chloride transport test methods

Rapid chloride permeability (RCP) and non-steady state migration (NSSM) tests were used to evaluate the chloride penetration resistance of concretes containing coarse limestone powder. Two 50 mm thick discs corresponding to all the different concretes were used for the RCP and NSSM tests and the average values are reported. The RCP test was performed in accordance with ASTM C 1202. This test provides an indication of the resistance of the concretes to chloride ion penetration under an externally applied potential of 60 V. The test records the total charge passed through the specimen during the 6 h testing duration. The RCP values depend on both the microstructure of the concrete as well as the conductivity of the pore solution. The RCP test was performed after 28 and 56 days of curing in saturated conditions. The catholyte used was a 3% NaCl solution and the anolyte was a 0.3 N NaOH solution.

The NSSM test was performed in accordance with NT Build 492 [16]. 50 mm thick specimens were saturated with a 2% calcium hydroxide solution, and enclosed in the test cell containing 2 N NaCl in the catholyte chamber and 0.3 N NaOH in the anolyte chamber. The voltage to be applied was chosen based on the initial value of the current when a 30 V potential was applied between the electrodes. The applied electrical potential forces the chloride ions in the cell to migrate into the specimen. After the specified test duration (which was 24 h for all the concrete mixtures used in this study), the specimen was axially split and a 0.1 N silver nitrate solution sprayed on the split surfaces to determine the chloride penetration depth. Five to seven measurements of penetration depth were made on each split surface. The NSSM coefficients, (D_{nssm}) were calculated using the average values of the penetration depths (x_d) and Eqs. (1) and (2).

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

where

$$E = \frac{U-2}{L} \quad \text{and} \quad \alpha = 2\sqrt{\frac{RT}{zFE}} * erf^{-1}\left(1 - \frac{2C_d}{C_0}\right) \tag{2}$$

In the above equations, 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's constant (9.648×10^4 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 at which white silver chloride precipitates, and C_0 is the chloride concentration in the catholyte solution ($C_0 \approx 2$ N).

3. Results and discussion

3.1. Compressive strengths and porosities of concretes containing coarse limestone powder

As described earlier, concretes containing limestone powder as partial cement replacement were proportioned to obtain similar 7-day compressive strengths as the control concrete proportioned using a w/c of 0.40. Table 3 shows the compressive strengths of all concretes used in this study at 28 and 56 days of curing, along with the standard deviation for three replicate specimens. The lower w/c plain concretes show higher compressive strengths at all ages. When 15% of the cement is replaced by limestone powder in a 0.34 w/p mixture, the compressive strengths at 28 and 56 days are very similar to those of plain concrete made with a w/c of 0.37. It can also be noticed from this table that 15% replacement of cement by limestone powder at a w/p of 0.34 results in better 28-day and 56-day compressive strengths than mixtures with 10% limestone powder content and a w/p of 0.37. This points to the effectiveness of fillers such as coarse limestone powder in lower w/p (or w/c) concrete mixtures. Even though the water reducing admixture requirement for the concrete with 15% limestone powder content at a w/p of 0.34 is higher than that required for a 0.37 w/c plain or limestone powder concrete to produce similar workability, the cost savings that could be realized from a 15% cement reduction will be significant. When 5% of silica fume by mass also replaces cement in concrete mixtures in addition to the limestone powder, it is observed that the strength improvement is marginal at 10% limestone powder content (w/p of 0.37). At a 15% limestone powder content (w/p of 0.34), the strength enhancement becomes prominent, again indicating the influence of w/p reduction when coarse fillers are used.

Table 3
Compressive strengths and porosities of concretes after 28 and 56 days of curing.

Mixture	w/p (w/c)	28 days		56 days	
		f'_c [a] (MPa)	ϕ [a] (%)	f'_c [a] (MPa)	ϕ [a] (%)
Plain	0.4	45.7 (0.6)	15.7 (0.3)	46.8 (2.3)	12.3 (0.2)
10LS	0.37	39.7 (0.2)	14.4 (0.2)	41.9 (0.6)	13.9 (0.5)
Plain	0.37	46.8 (0.6)	13.6 (0.4)	47.8 (0.8)	11.8 (0.9)
15LS	0.34	44.3 (1.7)	13.6 (0.2)	46.1 (1.5)	12.0 (0.4)
Plain	0.34	58.9 (1.2)	10.7 (0.4)	60.9 (3.8)	9.7 (0.4)
10LS + 5SF	0.37	41.1 (1.2)	16.0 (0.6)	42.7 (0.8)	13.5 (0.4)
15LS + 5SF	0.34	48.5 (1.0)	11.4 (1.0)	53.7 (0.3)	10.9(0.8)

[a] The values in parentheses indicate one standard deviation from the average value (units of MPa for f'_c).

The porosities of all the concretes as determined using the vacuum saturation method are also listed in Table 3. It can be seen that the mixtures containing limestone powder have higher porosities than the plain concrete of the same w/p but generally lower porosities than the control mixture (0.40 w/c) of similar 7-day compressive strength. The mixtures that contain both limestone powder and silica fume have higher porosities than that of the plain concretes of the same w/p, but their porosities are lower than those of mixtures containing only limestone powder as the cement replacement material. Even though these mixtures also have higher effective w/c, the pore filling and the pozzolanic effects of silica fume result in slightly lower porosities.

The compressive strength (f'_c)–capillary porosity (ϕ) relationship for all the concrete mixtures used in this study at all ages is shown in Fig. 3. It can be seen that porosity is inversely proportional to compressive strength regardless of w/p or cementing materials content. The compressive strength of all the mixtures can be adequately expressed as a function of porosity using a single equation.

3.2. Moisture transport parameters

Moisture transport tests can provide an indication of the pore structure of concretes. Moisture transport tests, in accordance with ASTM C 1585 were conducted after 28 and 56 days of curing for all the concrete mixtures.

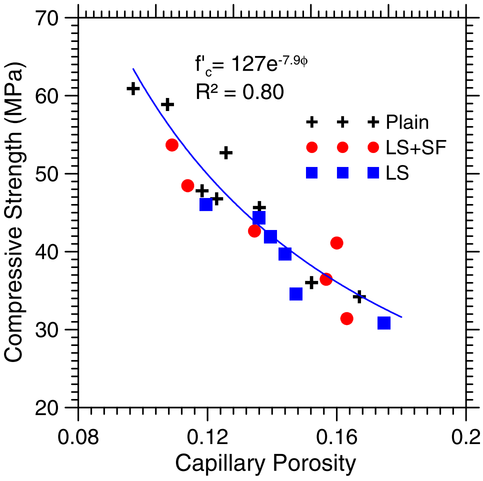


Fig. 3. Relationship between compressive strengths (f'_c) and porosities (ϕ) of concretes evaluated in this study.

3.2.1. Overall water intake

Fig. 4a and b shows the mass of water taken in per exposed unit area of the specimen as a function of the square root of time for plain concretes and the concretes containing limestone powder respectively after 28 days of curing. The total amount of water absorbed by the plain concretes during the testing duration decreases when the w/c is lowered, as expected, which is shown in Fig. 4a. From Fig. 4b, it can be noticed that the concretes containing 10% limestone powder absorb the highest amount of water during the testing duration. The use of silica fume as an additional cement replacement material reduces the overall water intake slightly. The concrete mixture with 15% limestone powder replacement (made with w/p of 0.34) shows lower amounts of water absorbed as compared to plain concrete with a w/c of 0.40. When the concrete containing 15% limestone powder is augmented with 5% silica fume as a further cement replacement, the overall water intake is found to be similar to plain concrete with a w/c of 0.37. Thus it can be seen that the overall water intake behavior of concretes containing limestone powder can be made to approach that of companion plain concrete mixtures by modifying the w/p and/or using a certain amount of pozzolanic materials that are known to improve the material microstructure. For instance, if 15% of cement could be replaced by a coarse inert limestone powder, reducing the w/p to 0.34 in order to produce comparable properties as that of a 0.37 w/c plain concrete is definitely an attractive option as far as sustainability, economy, and long-term durability of concretes are concerned.

3.2.2. Initial and secondary sorptivity

In addition to the overall water intake, another parameter of importance in water transport characterization of concretes is the sorptivity or the rate of water absorption. ASTM C 1585 defines the initial sorptivity (S_i) as the slope of the curves shown in Fig. 4 up to 6 h, and the secondary sorptivity (S_s) as the slope of the curves from 1 day up to 7 days.

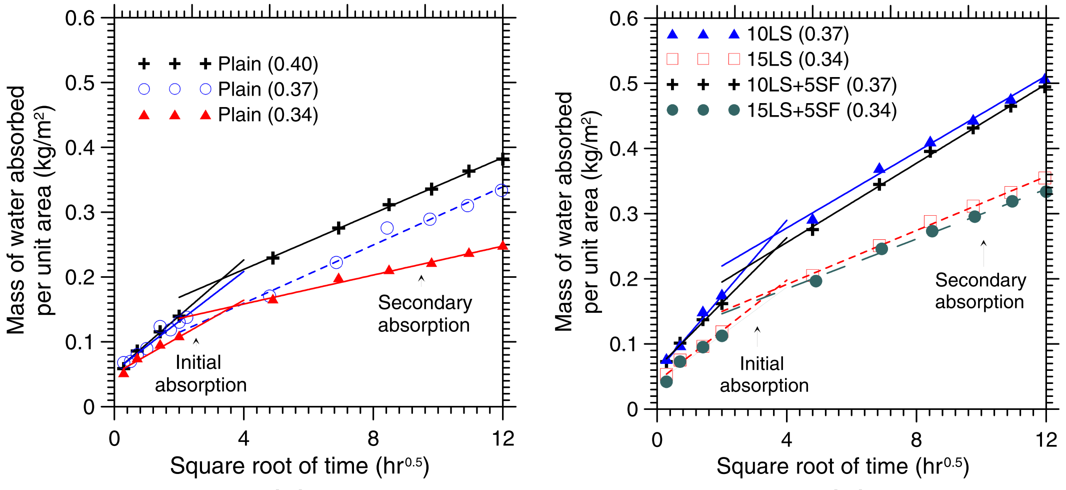
Fig. 5a and b shows the initial sorptivity of the plain and limestone powder concretes respectively, when the test was carried out after 28 and 56 days of curing. The decrease in initial sorptivities (S_i) with reducing w/c and increasing curing duration for the plain concretes is obvious from Fig. 5a. The concrete containing 10% limestone powder (w/p of 0.37) shows similar S_i values as that of plain concrete with w/c of 0.40. Similarly, the concrete containing 15% limestone powder (w/p of 0.34) shows similar S_i values as that of plain concrete with a w/c of 0.37, especially at early ages (28 days). When 5% silica fume is used as an additional cement replacement material, the initial sorptivities are slightly lower than the mixtures with the same limestone powder dosage and w/p. However, these values are higher than those of plain concrete mixtures of similar w/p.

Fig. 5c and d presents the secondary sorptivities (S_s) of the plain and limestone powder concretes of different w/p values. The improvement in material microstructure that facilitates the lower rate of water intake at later times also for lower w/c concretes is evident from Fig. 5c. The S_s values of concretes containing 10% limestone powder (w/p of 0.37) are roughly similar to that of plain concrete of w/c of 0.40, and those of concretes containing 15% limestone powder (w/p of 0.34) similar to those of plain concrete of w/c of 0.37. This is similar to the observations on initial sorptivity. The use of silica fume is seen to reduce the S_s values also as compared to mixtures at the same w/p where limestone powder is the only cement replacement material.

3.2.3. Sorptivity–porosity-compressive strength relationships

The transport of water through concrete is highly dependent on the pore structure features of the material. Since porosity is the most commonly used pore structure feature of concretes, it is common to express the moisture intake parameters such as sorptivity as a function of porosity [17,18]. Fig. 6a shows the relationship between the initial and the secondary sorptivities and porosities of all the concrete mixtures at all ages. As can be seen in this figure, both S_i and S_s are found to increase with increasing porosity. S_i is better correlated to porosity than S_s (R^2 of 0.83 for S_i as compared to 0.77 for S_s) because the initial sorptivity is highly dependent on the pore volume closer to the exposed surface of the concrete. Secondary sorptivity, in contrast, is a function of moisture transport through the bulk of the specimen, and depends also on the pore sizes and pore connectivity, resulting in a weaker correlation to the porosity. In a later section of this paper, relationships of a combined pore structure feature (that includes porosity and pore connectivity) to the sorptivities are explored. It is known that the use of silica fume results in a much more pronounced reduction in pore sizes and connectivity than a reduction in the porosity [19,20], and thus the concretes containing limestone powder and silica fume are likely to show lower S_s values at similar porosities than those of concretes without silica fume.

The relationship between compressive strengths and sorptivities of all the concretes at ages of 28 and 56 days is shown in Fig. 6b. Even though a linear fit has been previously proposed for



(a) **(b)**

Fig. 4. Total amount of water absorbed as a function of time for: (a) plain concretes and (b) concretes containing limestone powder, after 28 days of curing.

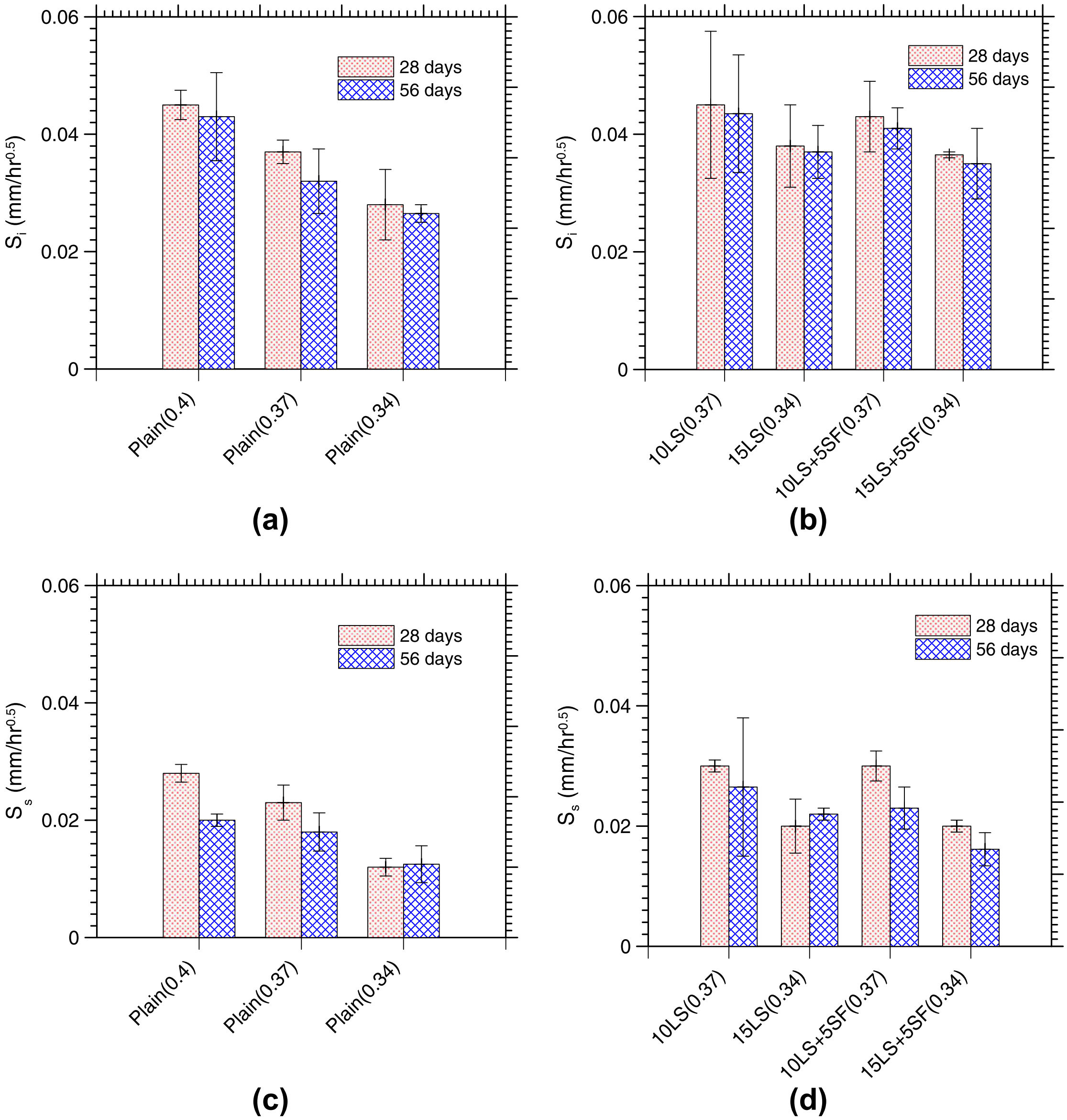


Fig. 5. Initial sorptivities of: (a) plain concrete and (b) concretes containing limestone powder after 28 and 56 days of curing. Final sorptivities of: (c) plain concrete and (d) concretes containing limestone powder after 28 and 56 days of curing.

the relationship between sorptivity and compressive strength [21], an exponential fit is chosen here. In addition to better correlation, an exponential fit is more appropriate than a linear fit because this eliminates the extrapolation to zero sorptivity at a very high compressive strength, which is unrealistic. A stronger relationship between the compressive strength and the initial sorptivity (S_i) is observed, because S_i is better related to porosity, and it is well known that compressive strength is related to porosity.

3.3. Chloride transport in concretes containing coarse limestone powder

3.3.1. Rapid chloride permeability (RCP)

RCP test is one of the most commonly used chloride transport tests, even though several of its drawbacks have been pointed out [22,23]. It is basically a conductivity (or resistivity) test; however, in practice, it is used to prequalify concrete mixtures or to ascertain the effectiveness of cement replacement materials in reducing the chloride ion ingress into concretes.

Fig. 7a and b shows the RCP values of plain concretes and the concretes containing limestone powder after 28 and 56 days of curing. The results shown in Fig. 7a are self explanatory: the RCP values decrease with a reduction in w/c for the plain concretes. Decreasing the w/c from 0.40 to 0.34 results in a reduction of about 35% in the 28-day RCP values. From Fig. 7b, it can be observed that the concrete with a 10% limestone powder content (w/p of 0.37) shows a similar 28-day RCP value as that of the 0.40 w/c plain concrete mixture, and the concrete with a 15% limestone powder content (w/p of 0.34) shows a similar RCP value as that of the 0.37 w/c plain concrete. This is similar to their water transport behavior as explained in a previous section. One very significant observation from this figure is the reduction in RCP values of concretes containing limestone powder when 5% of silica fume is used as an additional cement replacement material. For the concretes with 10% and 15% limestone powder as cement replacement, along with 5% silica fume, the RCP values are about 30–40% lower than the companion mixture of the same w/p that does not contain silica fume. Also, these values are lower than those of plain mixtures

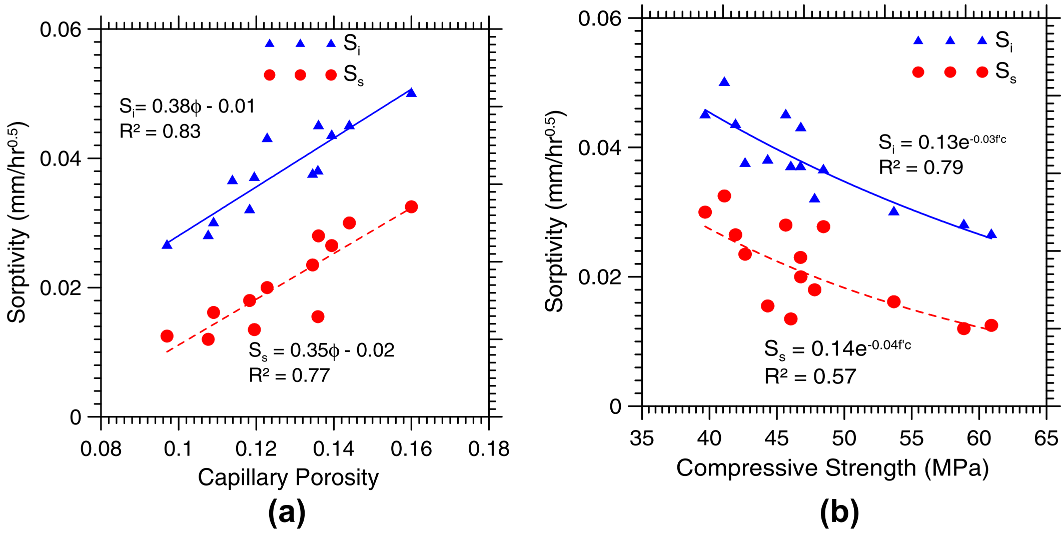


Fig. 6. Relationships between sorptivity and: (a) porosity and (b) compressive strength.

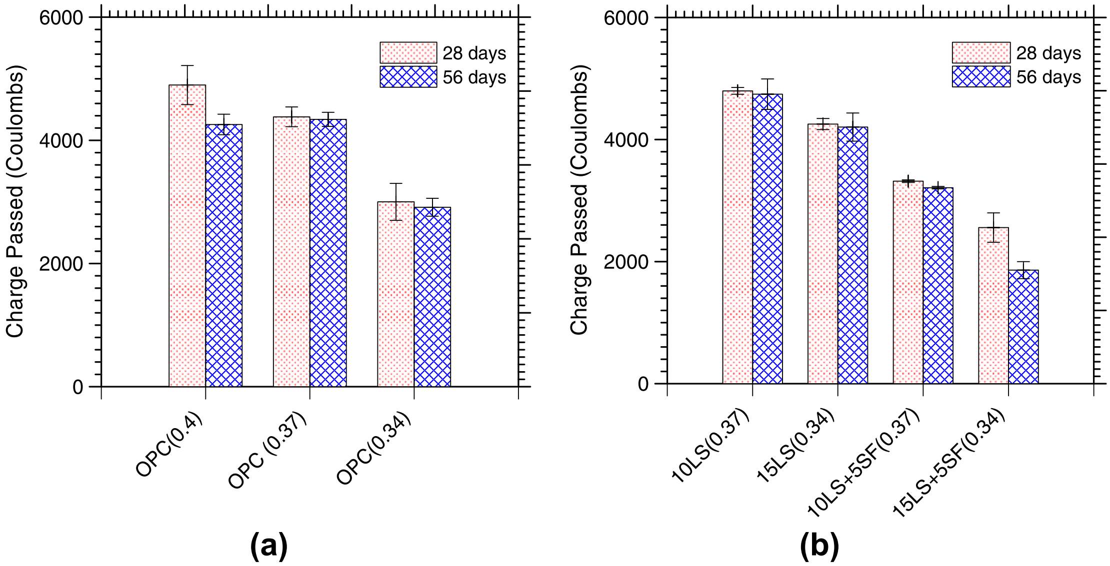


Fig. 7. RCP values for: (a) plain concretes and (b) concretes containing limestone powder after 28 and 56 days of curing.

of the same w/p. It is well known that silica fume facilitates densification of the material microstructure and reduces the pore sizes and connectivity. Also, since the RCP values basically provide an indication of the material conductivity, the pore solution conductivity also is influential along with the pore structure features. The incorporation of silica fume as a cement replacement material reduces the pore solution conductivity because of the reduction in concentration of the highly conductive Na^+ and K^+ ions. In concretes containing limestone powder, where a certain amount of cement is replaced by limestone powder which is also devoid of highly conductive ionic species, the pore solution conductivity is reduced further. Hence the RCP values cannot provide an accurate indication of the pore structure of these mixtures. Therefore, to obtain an indication of the pore structure features of the mixtures containing limestone powder, the following procedure is adopted in this study.

3.3.2. A pore structure parameter from electrical property measurements

The resistances of the specimens at the start of the RCP test were determined from the initial currents recorded (at 1 min) and the applied voltage (60 V). These resistances were converted into conductivities (σ) using the specimen length (50 mm) and the area of cross section (7854 mm^2). The pore solution conductivities of all the mixtures were obtained from the equivalent ionic conductivity of the highly conductive species in the pore solution (OH^-, Na^+, K^+), the ionic concentrations, and the species valences [24]. The ionic concentration was obtained from the cement and the replacement materials content, w/c (or w/p), and the degrees of hydration. The degrees of hydration of companion cement pastes of the same w/c (or w/p), and containing the same amount of replacement material as the concretes, were obtained at different ages [25]. The conductivities of concretes can be expressed as a function of the pore solution conductivity (σ_{pore}), porosity (ϕ), and pore connectivity factor (β) as:

$$\sigma = \sigma_{pore}\,\phi\beta \tag{3}$$

The product of porosity (ϕ) and pore connectivity factor (β) can be obtained from this equation and can be used as a characteristic microstructural feature of the concretes.

Fig. 8 shows the $\phi\beta$ values of the plain concretes and those containing limestone powders at both ages of curing. It can be seen that the $\phi\beta$ values decrease with increasing curing duration and decreasing w/c for the plain concretes. At 56 days of curing, the $\phi\beta$ value of the 0.34 w/c plain concrete is only about half of that of the 0.40 w/c concrete. The concretes containing limestone powder are found to show higher $\phi\beta$ values than the corresponding plain concretes of the same w/c. This is because of the influence of the coarser limestone powder particles in increasing the inter-particle spacing between the cement grains as well as the effective w/c in the system, both of which result in the cement hydration products being less connected. The incorporation of silica fume reduces the $\phi\beta$ values considerably when compared to the limestone powder modified concretes without silica fume because of the pore filling and pozzolanic effects of silica fume. The combined pore structure feature ($\phi\beta$) of the concretes containing limestone powder and silica fume are very similar to those of the corresponding plain concretes of the same w/c. However, this does not mean that the ϕ and β values of the plain concretes and the concretes containing limestone powder and silica fume are similar, which partly explains the observed differences in both moisture and chloride transport characteristics. Table 3 shows that the porosities of concretes containing limestone powder and silica fume are slightly higher than the plain concretes of the same w/p. Previous studies have shown that the addition of up to 9% by mass of silica fume as a cement replacement material results in a significant reduction in the pore sizes and connectivities of the cement pastes or concretes [19,26]. If their $\phi\beta$ values have to be similar, then the pore connectivities (β) of the concretes containing limestone powder and silica fume should be lower than those of plain concretes. It is also obvious from the porosities shown in Table 3 and the $\phi\beta$ values in Fig. 8 that the pore connectivities of concretes containing limestone powder alone as a cement replacement material are higher than those of plain concretes of the same or even higher w/p.

The relationships between $\phi\beta$ and RCP values for all the concrete mixtures at all ages are shown in Fig. 9. Two separate relationships, one for the mixtures without silica fume and another for the mixtures containing both limestone powder and silica fume, can be observed. The concretes containing limestone powder and silica fume exhibit lower RCP values for a given value of $\phi\beta$ because of the reduced pore solution conductivity resulting from the incorporation of silica fume and limestone powder. Though the incorporation of limestone powder alone in the concrete mixtures also reduces its pore solution conductivity, the RCP values of these mixtures are still higher than plain concrete of the same w/p (Fig. 7a and b). This is because of the higher $\phi\beta$ values of the concretes containing limestone powder alone as can be observed in Fig. 8.

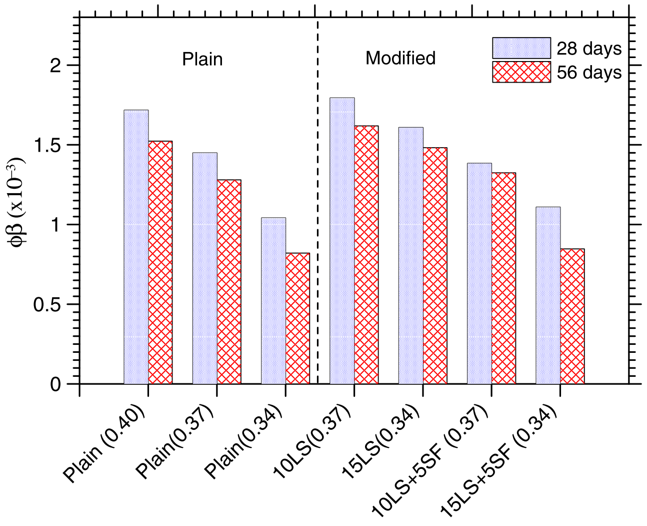


Fig. 8. Pore structure feature ($\phi\beta$) of concrete mixtures evaluated in this study.

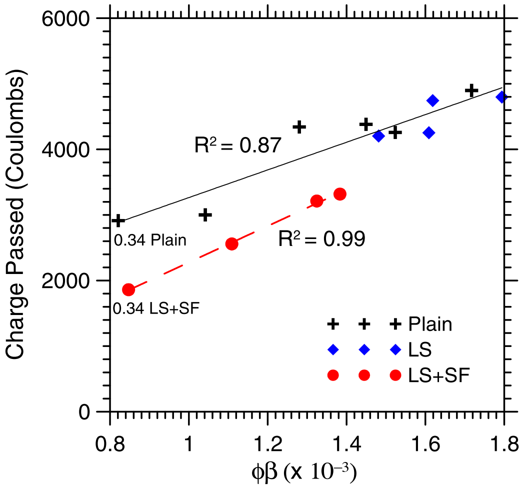


Fig. 9. Relationship between RCP values and the pore structure feature ($\phi\beta$) of all the concrete mixtures at both curing durations.

3.3.3. Non-steady state migration coefficients (D_{nssm})

The non-steady state migration (NSSM) test overcomes some of the drawbacks of RCP test, and also provides a coefficient (D_{nssm}) that could be more realistically related to the transport of chloride ions through concrete. Fig. 10a and b shows the NSSM coefficients (D_{nssm}) of all the concrete mixtures after 28 and 56 days of curing. The trends in Fig. 10a are very similar to those discussed earlier for RCP and moisture transport tests. A lower D_{nssm} value indicates better resistance against chloride ion migration under the influence of an applied electric field. The trends in D_{nssm} values of the plain concretes shown in Fig. 10a are similar to those of the RCP values, for the same reasons. From Fig. 10b, it can be seen that the D_{nssm} values of concretes containing limestone powder are higher than those of plain concretes of the same or even higher w/p, which can be explained based on the following two aspects. First, the $\phi\beta$ values are higher for the concretes containing limestone powder as shown in Fig. 8, which facilitates increased transport of chloride ions under the action of an electric field. Second, replacement of cement that contains aluminate phases by a replacement material devoid of aluminates could result in a reduced amount of chloride binding leading to higher D_{nssm} values. It has been shown that the NSSM test results are influenced by chloride binding [27], especially when the concentration of catholyte chloride solution is high (such as the 2 N NaCl solution used in this case).

The concretes containing limestone powder and silica fume show lower D_{nssm} values than those mixtures containing only limestone powder as a cement replacement material, as observed in Fig. 10b. This can once again be attributed to the lower $\phi\beta$ values of these mixtures. Even though the $\phi\beta$ values of mixtures that contain both limestone powder and silica fume are similar to those of

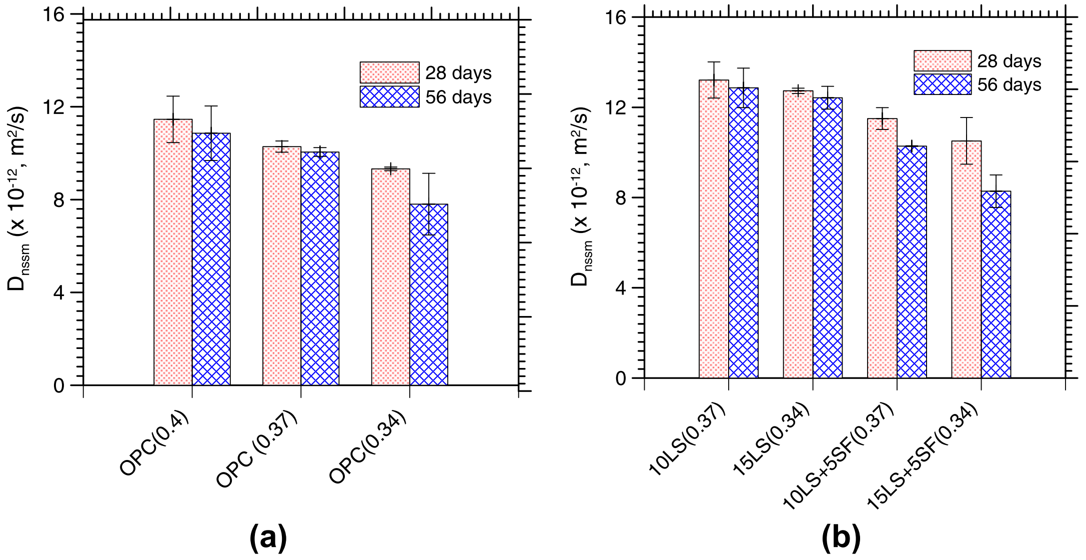


Fig. 10. D_{nssm} values for: (a) plain concretes and (b) concretes containing limestone powder, after 28 and 56 days of curing.

plain concretes of the same w/p as shown in Fig. 8, the D_{nssm} values of these concretes are slightly higher than those of plain concretes of the same w/p. This could also be attributed to the effect of reduced chloride binding in the modified concretes (even lower binding than the concretes with limestone powder alone as the cement replacement material since silica fume also do not contain aluminates).

The relationship between $\phi\beta$ and D_{nssm} values for all the mixtures are shown in Fig. 11. Two trends are immediately discernible – one for the plain concretes and another for the concretes containing limestone powder. The concretes containing limestone powder show the highest $\phi\beta$ and the highest D_{nssm} values, attributable to a combination of their high $\phi\beta$ values and reduced chloride binding due to the presence of cement replacement materials that does not contain aluminate phases. The influence of silica fume in reducing the D_{nssm} values of the concretes containing limestone powder through microstructure densification is evident from this figure. Also noticeable from this figure is the fact that at lower values of $\phi\beta$, the D_{nssm} values of the plain concretes and those containing limestone powder become quite similar. This shows that by designing the concretes containing limestone powder for lower $\phi\beta$ values (through a combination of lower w/p and the incorporation of silica fume), comparable D_{nssm} values as those of the control concrete can be achieved.

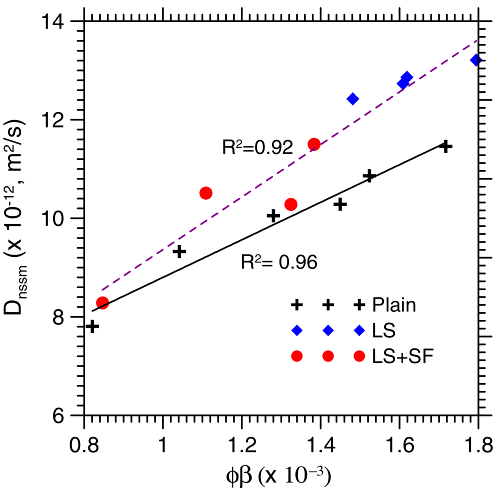


Fig. 11. Relationship between D_{nssm} and the pore structure feature ($\phi\beta$) of all the concrete mixtures at both curing durations.

3.4. Transport, microstructure, and test methods

A comparison of Figs. 9 and 11 provides information about the influence of pore structure (combination of porosity and pore connectivity) on chloride ion transport of concretes containing limestone powder as determined by two different methods. The trends in both these figures are different. For a given value of $\phi\beta$, the RCP values are higher for the plain concretes as compared to the concretes containing limestone powder and silica fume, whereas the D_{nssm} values are lower. The lower RCP values of concretes containing limestone powder and silica fume can be attributed to the reduced pore solution conductivity (because both the 0.34 w/c plain concrete and 0.34 w/p limestone + silica fume concrete have very similar $\phi\beta$). The higher D_{nssm} values of the concretes containing limestone powder could be a result of the reduced amounts of chloride binding in these mixtures as explained earlier. However, the mixture containing limestone powder with a low $\phi\beta$ value (facilitated by the lower w/p and incorporation of silica fume) demonstrates a similar D_{nssm} as that of a plain concrete of the same w/c, indicating the beneficial effects of low w/p and small amounts of a highly reactive pozzolanic material in concretes containing coarse limestone powder.

In order to understand the influence of $\phi\beta$ on moisture transport in concretes containing coarse limestone powder, the relationships between $\phi\beta$ and sorptivities (S_i and S_s) are plotted in Fig. 12a and b. Sorptivity can be considered to be strongly related to the connected pore structure in the system, which can be adequately expressed using the pore structure feature $\phi\beta$. The $\phi\beta$-sorptivity relationships of concretes without silica fume can be represented using a single linear fit as seen from these figures. The $\phi\beta$ values in the higher range represent the higher w/c plain concretes and the concretes incorporating limestone powder of all w/p. The $\phi\beta$ values of mixtures containing both limestone powder and silica fume are very similar to those of plain concretes of same w/p (as seen in Fig. 8), but both S_i and S_s are higher than that of the plain concrete at a given $\phi\beta$ value. This is because the porosities of these concretes are still higher than those of plain concrete of the same

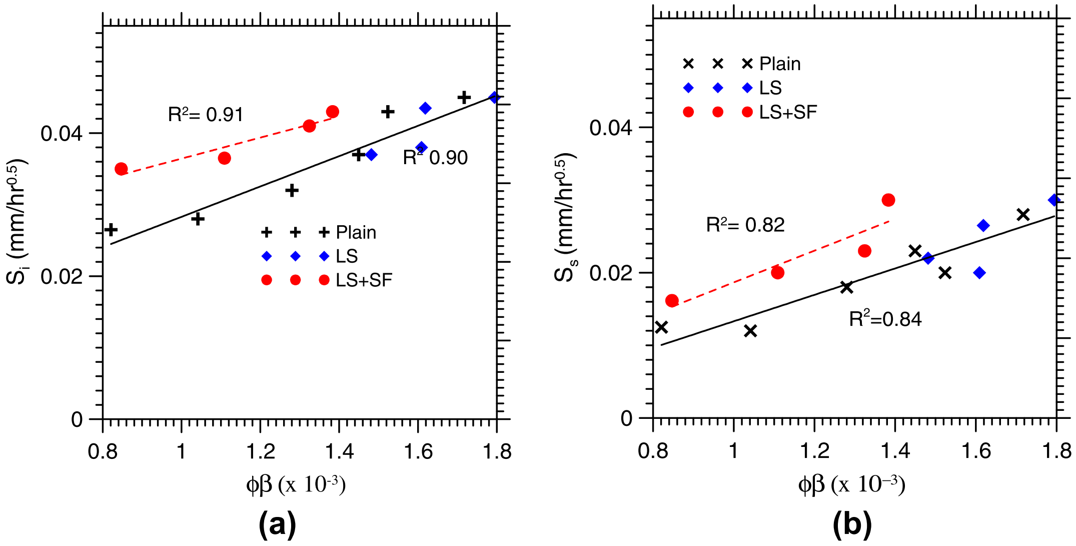


Fig. 12. Relationship between $\phi\beta$ and: (a) initial sorptivity (S_i) and (b) secondary sorptivity (S_s).

w/c (w/p). Hence to obtain similar transport performance characteristics (S_i, S_s, or D_{nssm}) for concretes with limestone powder and silica fume as that of plain concrete of a certain w/c, the w/p of the concrete mixtures containing limestone powder should be reduced. This is seen in Figs. 11 and 12a and b, where, to obtain the same S_i, S_s or D_{nssm}, the concretes with limestone powder need to have lower $\phi\beta$ values, which can be accomplished by a combination of a reduction in w/p and incorporation of silica fume. On the contrary, to obtain similar RCP values as that of plain concrete, the concretes containing limestone powder and silica fume can afford to have a higher $\phi\beta$ value, but this is an artifact likely contributed by the lower pore solution conductivity because of incorporation of silica fume. Thus, it is clearly shown here that the test methods for moisture and ionic transport for concretes containing inert fillers and/or pozzolanic materials need to be used carefully, especially if the intent is to obtain an understanding of the influence of the microstructure on transport behavior.

4. Conclusions

The influence of a coarse limestone powder as a partial cement replacement material (10% and 15% by mass) with or without a small amount of silica fume, on the moisture and chloride ion transport behavior of concretes was studied in detail. The following conclusions pertain to this study:

(i) The overall water intake characteristics of concretes with coarse limestone powder were comparable to those of companion plain concrete mixtures when the w/p was reduced for the mixtures with limestone powder. The incorporation of silica fume provided a slight reduction in overall moisture intake of concretes containing limestone powder. The initial and secondary sorptivities of the concretes containing limestone powder also followed trends similar to that of overall moisture intake.

(ii) The RCP values of the concretes also showed a similar trend as that of the moisture transport parameters – the behavior of concrete with15% limestone powder at a 0.34 w/p being similar to that of a 0.37 w/c plain concrete. However, the incorporation of silica fume reduced the RCP values, rendering them similar to plain concretes of the same w/c. Microstructure densification as well as the reduction in pore solution conductivity resulted in this observation. The concrete mixtures with limestone powder showed higher D_{nssm} values as compared to plain concrete mixtures of similar w/p. The incorporation of silica fume reduced the D_{nssm} values of these mixtures, indicating pore structure refinement, but the D_{nssm} values remained higher than those of plain concrete mixtures of similar w/p. Reduced chloride binding (due to the reduction in aluminate phases) in concretes containing limestone powder and silica fume could have resulted in higher D_{nssm} values for these mixtures.

(iii) In order to relate moisture and ionic transport to the pore structure, a microstructural parameter ($\phi\beta$), the product of porosity and pore connectivity factor, was used. The $\phi\beta$ values of the concretes containing limestone powder alone were found to be higher than those of the plain concretes of the same w/p. The incorporation of 5% silica fume as an additional cement replacement material resulted in their $\phi\beta$ values being similar to those of plain concretes of the same w/p.

(iv) In order to obtain similar transport parameters (S_i, S_s, or D_{nssm}) as that of plain concrete of a certain w/c, $\phi\beta$ values of the concretes containing coarse limestone powder should be lower, which could be accomplished by using a lower w/p and/or incorporation of a small amount of a highly active pozzolan such as silica fume. For a specified RCP value, it was observed that the concretes containing limestone powder and silica fume could afford to have a higher $\phi\beta$, but this is a result of the influence of RCP values on the pore solution conductivity. The need to use transport test methods carefully when relating transport to microstructure is emphasized.

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