Pergamon

Cement and Concrete Research 32 (2002) 123–131

CEMENT AND CONCRETE RESEARCH

Strength, permeability, and carbonation of high-performance concrete

M.I. Khan[a,]*, C.J. Lynsdale[b]

[a]School of Civil Engineering, University of Nottingham, Nottingham, NG7 2RD, UK
[b]Department of Civil and Structural Engineering, University of Sheffield, Sheffield, S1 3JD, UK

Received 18 May 2001; accepted 30 July 2001

Abstract

This investigation is aimed at developing high-performance concrete and form part of an investigation into the optimization of a blended cementitious system for the development of high-performance concrete. Binary and ternary blended cementitious systems based on ordinary Portland cement (OPC), pulverised fuel ash (PFA) and silica fume (SF) were investigated. PFA up to 40% was used, and to these blends, 0%, 5%, 10% and 15% SF were incorporated as partial cement replacements. Results of compressive strength, tensile strength, oxygen permeability and carbonation of concrete are reported. A water–binder (w/b) ratio of 0.27 was used for the main group of mixes and w/b ratios of 0.40 and 0.50 were used for some selected mixes. Based on the experimentally obtained results, prediction models were developed which enabled the establishment of isoresponse contours showing the interaction between the various parameters investigated. It was found that the incorporation of 8–12% SF as cement replacement yielded the optimum strength and permeability values.

Keywords: Blended cement; Carbonation; High-performance concrete; Permeability; Strength

1. Introduction

The most common cause of deterioration in reinforced concrete is the corrosion of the steel reinforcement. The steel is susceptible to corrosion in the presence of chloride ions or if it becomes depassivated when the alkalinity of the concrete at the location of steel is reduced by carbonation. The transport of aggressive gases and/or liquids into concrete depends on its permeation characteristics. As the permeation of concrete decreases, its durability performance, in terms of physicochemical degradation, increases. Permeation controls the ingress of moisture, ionic and gaseous species into concrete. Chemical degradation, e.g. carbonation, corrosion of steel reinforcement, sulfate attack and alkali–aggregate reaction as a result of reaction between an external agent and the ingredients of concrete, and some physical effects, such as frost attack, can be greatly reduced by reducing the permeation of concrete.

Carbonation is a chemical reaction between carbon dioxide, in the presence of moisture, and calcium hydroxide present in hydrated concrete to form calcium carbonate. Carbonation occurs at the concrete surface including the surfaces of any cracks throughout the life of the concrete. However, as the depth of the carbonated layer of ordinary Portland cement (OPC) concrete increases, the products of carbonation reduce the rate of further carbonation.

The use of blended cements or supplementary cementing materials decreases the permeability, thereby increasing the resistance of concrete to deterioration by aggressive chemicals [1,2]. Therefore, the incorporation of pozzolanic materials such as pulverised fuel ash (PFA) and silica fume (SF) has become an increasingly accepted practice in concrete structures exposed to harsh environments. SF, due to its high pozzolanicity and its extreme fineness, is considered to produce low permeability concrete but, generally, with the drawback of low workability as a result of its high specific surface area. For SF concrete, the incorporation of a superplasticizer is essential for maintaining high workability, but this normally results in an increase in the cost of production. PFA has been widely used in concrete as it helps to reduce cost, conserve energy and resources, reduce environmental impact and enhance the workability.

* Corresponding author. Fax: +44-115-9513898.
E-mail address: iqbal.khan@nottingham.ac.uk (M.I. Khan).

0008-8846/02/$ – see front matter
PII: S0008-8846(01)00641-X

In order to derive the maximum short-term and long-term benefits from the use of these materials for the production of high-performance concrete, ternary blends exploiting the potential synergy between these materials may be necessary. However, information pertaining to these ternary systems is still relatively scarce. The results presented in this paper form part of an investigation into the optimization of a ternary blend based on OPC/PFA/SF for the development of high-performance concrete [3]. The results presented here are on strength, permeability and carbonation of concrete utilising PFA and SF as cement-replacing materials.

2. Experimental programme

2.1. Materials

OPC complying with BS 12:1991, PFA complying with BS 3892: Part 1:1993 and a slurry form SF solids–water ratio of 50/50 (weight–weight) were used throughout the investigation. A sulfonated naphthalene formaldehyde condensate superplasticizer (HRWR) was used. Fine aggregate (Derbyshire quarry sand) and coarse aggregate (uncrushed gravel) of 10 mm nominal size were used. The fine aggregate was of medium grading in accordance with BS 882:1992.

2.2. Mix proportions

PFA at 0%, 20%, 30% and 40% (by weight) was incorporated as partial cement replacement. To these blends, 0%, 5%, 10% and 15% SF replacement levels were incorporated to make various binary and ternary cementitious combinations. A water–binder ratio (w/b) of 0.27 was used for the majority of mixes. Two other w/b ratios were investigated (0.40 and 0.50) for some selected mixes. The slump for all the mixes investigated was maintained at 125 ± 10 mm using the superplasticizer. The water contents of superplasticizer and SF slurry were taken into account when calculating the batch weights for mixing. In order to identify the concrete mixes, PFA is designated as ‘F’ and SF as ‘S.’ The numerical values after F and S represents the percentage of PFA and SF incorporated as cement replacement.

2.3. Sample preparation

Concrete 100 mm cubes were cast for compressive strength and carbonation measurements. Cylinders of 100 mm diameter × 200 mm long and 50 mm diameter × 100 mm were cast for the determination of splitting tensile strength and oxygen permeability, respectively. All the specimens were cast and compacted in accordance with BS 1881. After casting, the samples were covered under damp hessian and polyethylene sheets for 24 h. The samples were demoulded the following day and then immediately kept in a mist room at 20 ± 2 °C and 98 ± 2% RH prior to testing.

The specimens (50 mm diameter × 100 mm) for the measurement of oxygen permeability were sliced down the middle, after discarding 10 mm of either end, providing two samples 35–40 mm long per measurement. The samples were then dried in an oven at 105 ± 5 °C for approximately 24 h until constant weight was reached. The samples were then kept in a dessicator for cooling, over the next 24 h, prior to testing for oxygen permeability.

2.4. Testing procedure

Cube compressive strength and splitting tensile strength measurements were carried out in accordance with BS 1881:1983. The oxygen permeability was measured by gas permeameter [4] using the following expression [5]:

$$k = \frac{4.04 P_2 R L \times 10^{-16}}{A(P_1^2 - P_2^2)} \tag{1}$$

where k is oxygen permeability (m^2); R is flow rate (cm^3/s); L is specimen thickness (m); A is specimen cross-sectional area (m^2); P_1 and P_2 are upstream and downstream pressure (bar), respectively (Eq. (1)).

Carbonation measurements were carried out for concrete cubes of 100 mm after 2 years of exposure in a constant temperature room at 20 ± 3 °C and 65 ± 5% RH in normal atmospheric conditions. The carbonation study was limited to concrete prepared with w/b ratio of 0.27. The samples (100 mm cubes) were broken into two halves at the age of 2 years. Phenolphthalein solution (Phenolphthalein 1% in Propan-2-ol) was sprayed on two fresh fracture surfaces. Colourless depth from the edge of the specimen was measured by a microscope (×40 magnification).

3. Results and discussion

Based on the experimentally obtained results, models were developed using the *Minitab* [6]. These models are based on the quadratic response surface model having predictive capabilities and permitted the calculation of the isoresponse curves from the parameters under study over the experimental domain and the optimization of their effects. A response variable $f(x)$ is measured at combinations of values of two-factor variables x_1 (PFA content) and x_2 (SF content) using the following model:

$$f(x) = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 \tag{2}$$

where $f(x)$ is the observation of the responsive variable; x_1 and x_2 are the experimental factor variables for $f(x)$; β_0, β_1, $\beta_2, \ldots \beta_{12}$ are the coefficients of the model (Eq. (2)).

3.1. Compressive strength

Models for compressive strength of concrete prepared with w/b ratio 0.27 at various ages are as follows. Terms, which were statistically insignificant, have been excluded from Eqs. (3)–(6).

$$f_{cu7} = 72.2 + 1.5x_2 - 0.01x_1^2 - 0.05x_2^2 - 0.03x_1x_2;$$
$$(R^2 = 0.90) \quad (3)$$

$$f_{cu28} = 85.1 + 3.2x_2 - 0.01x_1^2 - 0.13x_2^2 - 0.04x_1x_2;$$
$$(R^2 = 0.85) \quad (4)$$

$$f_{cu90} = 99.4 + 0.2x_1 + x_2 - 0.01x_1^2 - 0.02x_1x_2;$$
$$(R^2 = 0.93) \quad (5)$$

$$f_{cu180} = 106.9 + 0.23x_1 + 0.55x_2 - 0.01x_1^2 - 0.01x_1x_2;$$
$$(R^2 = 0.94) \quad (6)$$

where f_{cu7}, f_{cu28}, f_{cu90} and f_{cu180} are compressive strength (MPa) at 7, 28, 90 and 180 days, respectively; x_1 is the amount of PFA as partial cement replacement (% by weight); x_2 is the amount of SF as partial cement replacement (% by weight); R^2 is the coefficient of determination and measures the variation in the response, which is attributed to the model rather than to the random error. These equations were plotted as isoresponse contours for prediction purposes as shown in Fig. 1.

It can be seen that compressive strength decreased with an increase in PFA content for all ages investigated (Fig. 1). At 7 days, SF affected the strength of PFA mixes and this seems to be related to the PFA content. An increase of strength is registered for PFA levels lower than 10% when SF is incorporated. However, the results suggest that at higher PFA levels (>30%), the incorporation of SF results in a reduction in strength. At 28 days, up to 10% SF increased the strength for all levels of PFA replacements, whilst SF above 10% did not result in any advantage in improving the strength. At 90 and 180 days, only a modest improvement in strength has resulted from SF incorporation and this was evident for low levels of PFA (<10%) only. The isoresponse curves for mixes with higher than 20% PFA are almost vertical lines, indicating that the presence of SF no longer has an influence on the strength.

The influence of w/b ratio on compressive strength of concrete at various ages is shown in Fig. 2. From Fig. 2, it can be seen that the strength of concrete decreased with increasing w/b ratio for all ages, as to be expected. As curing age increases, the reduction in strength with increasing PFA content becomes less apparent, especially for PFA contents <30%. As SF is incorporated at 10%, the overall level of strength is increased. The results also show that

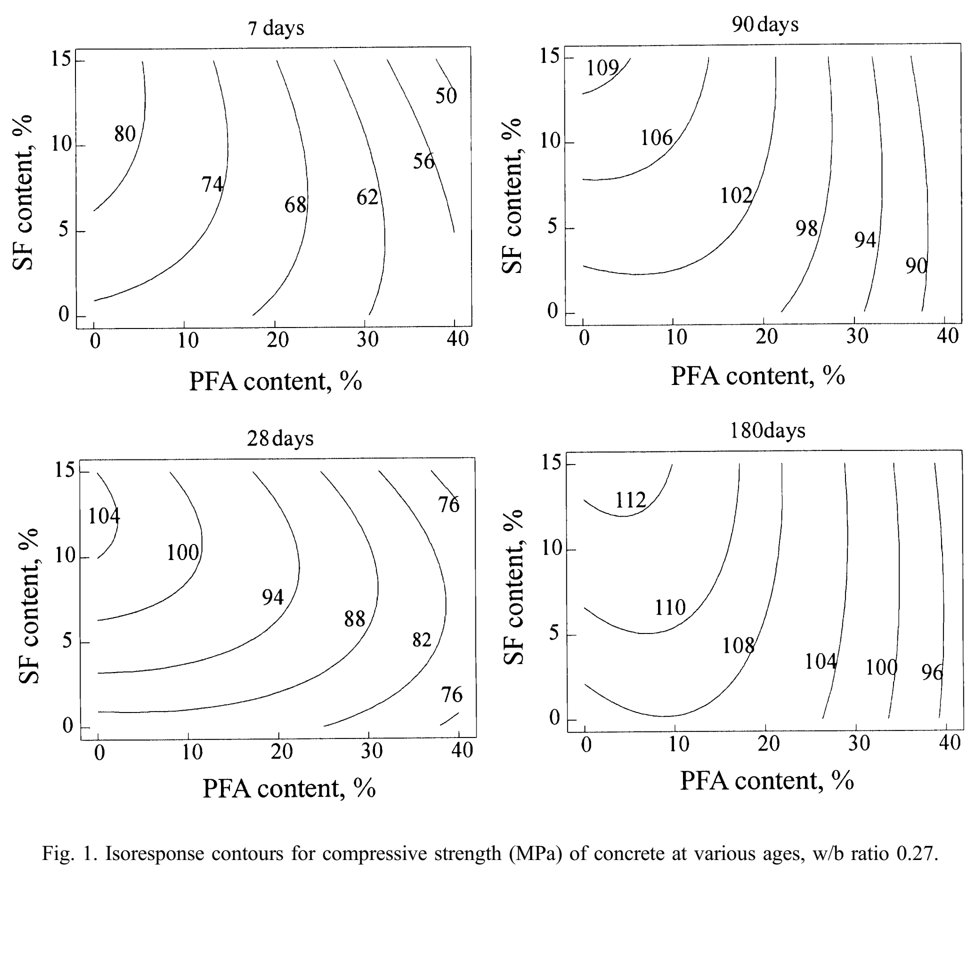

Fig. 1. Isoresponse contours for compressive strength (MPa) of concrete at various ages, w/b ratio 0.27.

for > 20% PFA content, the influence of the w/b ratio becomes more apparent when SF is not incorporated.

The results indicate that early-age loss of strength of concrete as a result of incorporating PFA was compensated by the inclusion of SF to an extent depending on the quantity of PFA and SF. Similar type of influence was found in paste systems published elsewhere [7]. The gain in strength as a result of SF inclusion is attributed to its high reactivity [8].

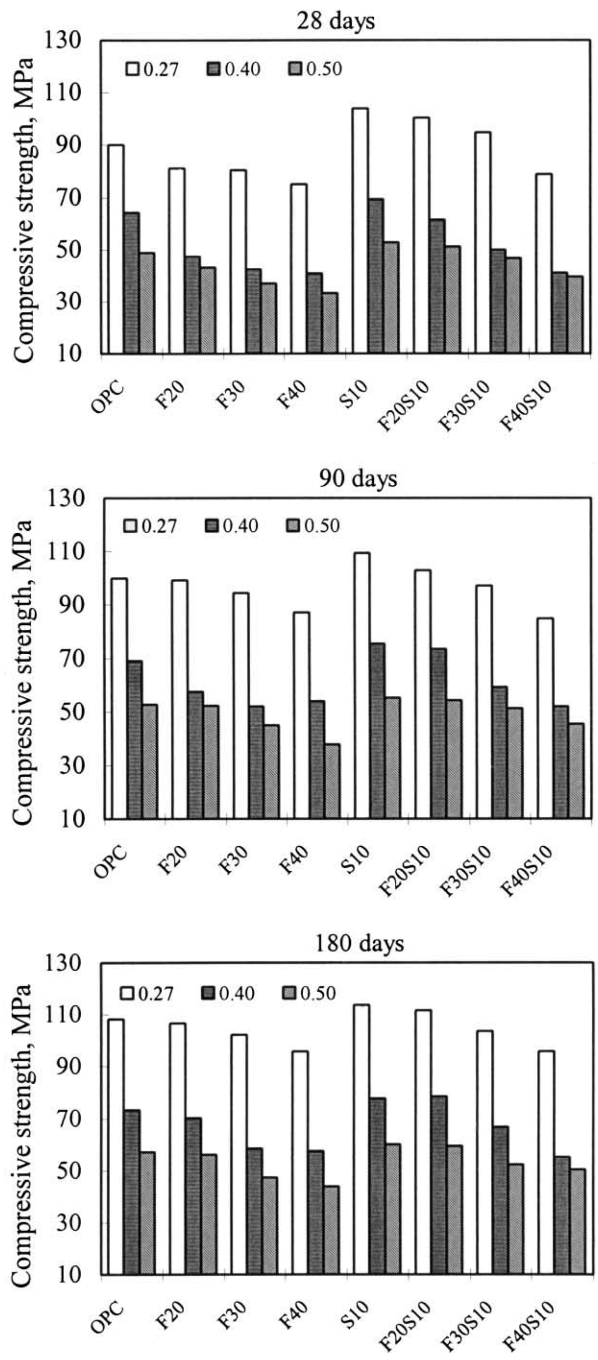

Fig. 2. Influence of w/b ratio on compressive strength of concrete at various ages.

3.2. Tensile strength

Models for tensile strength of concrete f_t (MPa) prepared with w/b ratio 0.27 at 7, 28, 90 and 180 days are as follows:

$$f_{t7} = 4.4 + 0.2x_2 - 0.001x_1^2 - 0.01x_2^2 - 0.002x_1x_2;$$

$$(R^2 = 0.85) \quad (7)$$

$$f_{t28} = 6.2 + 0.1x_2 - 0.001x_1^2 - 0.005x_2^2; \; (R^2 = 0.60) \quad (8)$$

$$f_{t90} = 6.7 + 0.004x_2^2 - 0.001x_1x_2; \; (R^2 = 0.55) \quad (9)$$

$$f_{t180} = 8.0 - 0.001x_1^2 + 0.0003x_1x_2; \; (R^2 = 0.95) \quad (10)$$

Statistically insignificant terms have been excluded from Eqs. (7)–(10). These equations were plotted as isoresponse contours for prediction purposes as shown in Fig. 3.

The incorporation of PFA decreased the tensile strength at all ages (Fig. 3). Up to 10% SF increased the tensile strength for all PFA replacement levels, whilst incorporation of more than 10% SF did not show any advantage. An increase in SF content increased the tensile strength at 90 days, whilst at 180 days, SF inclusion did not exhibit significant influence on tensile strength.

The influence of w/b ratio on tensile strength of concrete at various ages is shown in Fig. 4. As expected, the tensile strength of concrete decreased with an increase in w/b ratio. There is a gradual decrease in tensile strength with an increase in w/b ratio. For a given w/b ratio, at 28 days, tensile strength is significantly reduced as the PFA content is increased. However, as age increased, the reduction in tensile strength with increasing PFA content became less significant. The incorporation of 10% SF increased the overall tensile strength of concrete especially up to 90 days. It can be seen that at >20% PFA content, the influence of w/b ratio was more significant when SF was not present.

3.3. Oxygen permeability

Models for oxygen permeability of concrete (w/b ratio 0.27) at various ages are as follows:

$$k_{28} = 0.37 - 0.001x_1 - 0.047x_2 + 0.002x_2^2;$$

$$(R^2 = 0.93) \quad (11)$$

$$k_{90} = 0.25 - 0.38x_2 + 0.002x_2^2 + 0.0001x_1x_2;$$

$$(R^2 = 0.93) \quad (12)$$

$$k_{180} = 0.24 - 0.003x_1 - 0.03x_2 + 0.001x_2^2 + 0.0001x_1x_2;$$

$$(R^2 = 0.93) \quad (13)$$

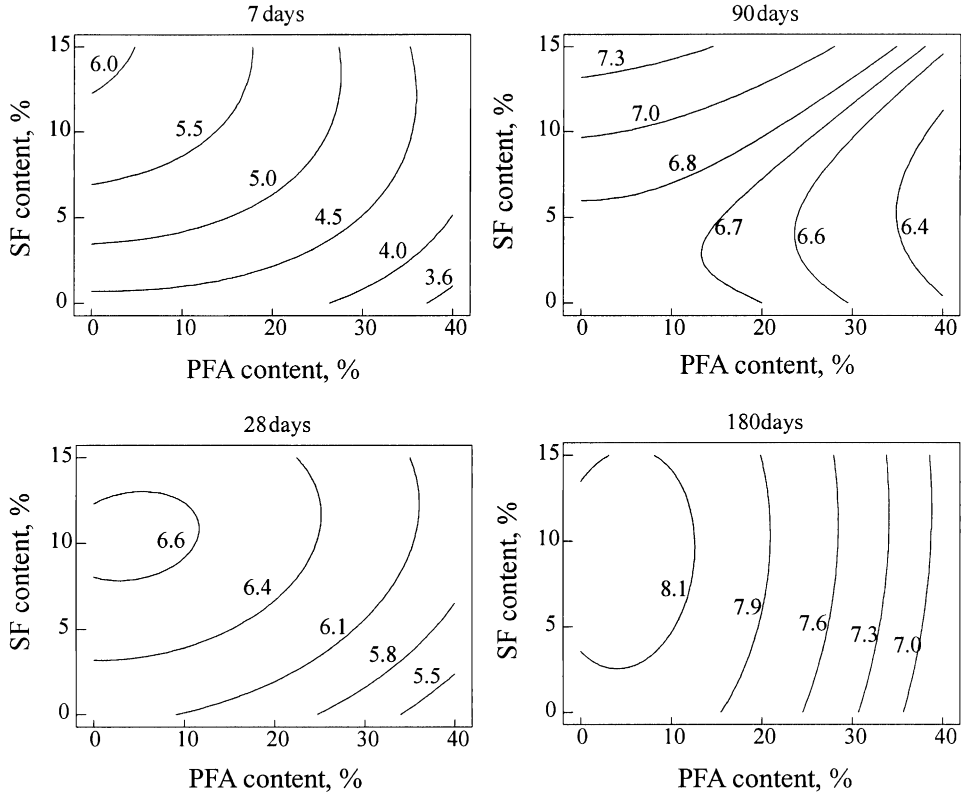

Fig. 3. Isoresponse contours for tensile strength (MPa) of concrete at various ages, w/b ratio 0.27.

where k_{28}, k_{90} and k_{180} are oxygen permeability ($\times 10^{-16}$, m^2) at 28, 90 and 180 days, respectively. Terms, which were statistically insignificant, have been omitted from Eqs. (11)–(13).

Fig. 5 shows the change in oxygen permeability of concrete at 28, 90 and 180 days caused by the interaction of PFA and SF contents. It is evident from the results that the incorporation of PFA had a very limited influence on permeability at ages up to 90 days, but at 180 days, slight reductions in oxygen permeability, associated with the level of replacements, were recorded for SF levels up to 5%. The inclusion of SF however, resulted in more significant reductions in permeability for mixes with and without PFA at all ages investigated. The reduction in the permeability was greater when SF was incorporated at up to 10% replacement level; however, above that level, the reduction was marginal or reversed. The incorporation of 8–12% SF gave the optimum performance, resulting in the lowest permeability values for all levels of PFA. The reduction in permeability as a result of SF incorporation is attributed to its pore refinement [2] which also confirmed by authors published elsewhere [9].

The oxygen permeability increased with an increase in w/b for all ages (Fig. 6). The results also show permeability reduced with curing age. In the 0% SF mixes, the influence of PFA replacement was only noticed at 90 days and above, with permeability reducing with increased PFA content. The incorporation of 10% SF decreased the overall range of permeability values for all ages investigated. The slight reductions in permeability as a result of PFA incorporation seen earlier, at 90 and 180 days, were not in evidence here. However, for the low w/b ratios (i.e. up to 0.30) 10% SF mixes, the contours for 90 and 180 days suggest an optimum level of PFA, in the range of 15–20%, for which oxygen permeability reduced to its lowest level.

3.4. Carbonation

The carbonation depth of concrete containing PFA and SF as partial cement replacements with w/b ratio of 0.27 at the age of 2 years is shown in Fig. 7. It can be seen that the carbonation depth increases with an increase in the PFA content. The influence of PFA and SF on carbonation depth of concrete is demonstrated in Fig. 8. From Fig. 8, it is evident that SF incorporation of its own demonstrated less significant increase of carbonation as compared to PFA concrete, whilst the carbonation linearly increases with an increase in PFA content. For every increase of 10% PFA content, there is approximately 0.3 mm increase in carbonation depth. The maximum carbonation depth observed for concrete (containing 40% PFA) was about 2 mm, which is far less than the cover of reinforcing steel bars to cause corrosion.

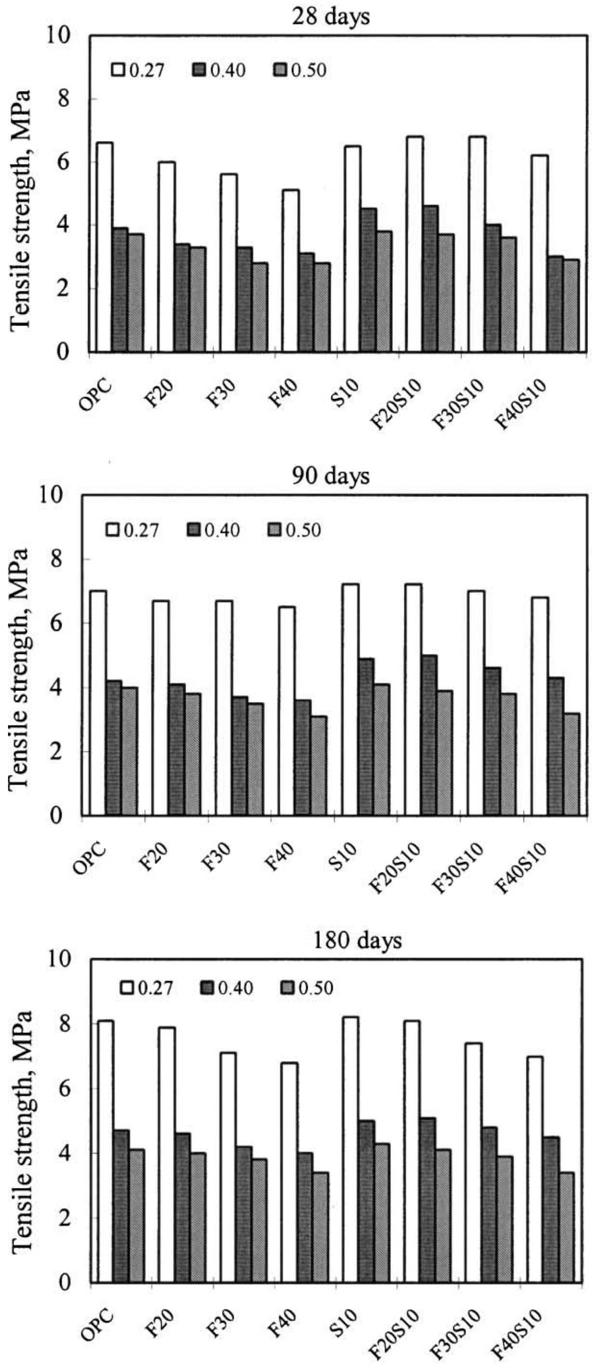

Fig. 4. Influence of w/b ratio on tensile strength of concrete at various ages.

The results clearly demonstrated that there is an increase in carbonation with an increase in PFA content, whilst SF inclusion of its own did not exhibit significant influence on the carbonation; this is in good agreement with earlier findings [10,11]. Byfors [10] investigated the carbonation of PFA and SF blended cement concrete (compared on equal w/b ratio) and found that the incorporation of 10–20% SF has no effect on carbonation as compared to OPC control, whilst 15–40% PFA exhibited higher rate of carbonation.

3.5. Relationship between compressive and tensile strengths

The compressive strength of concrete is commonly considered in structural design, but for some purposes, the tensile strength is of interest for example in the design of highway and airfield slabs, shear strength and resistance to cracking [12]. A relationship between tensile strength and compressive strength exists, but there is no direct propor-

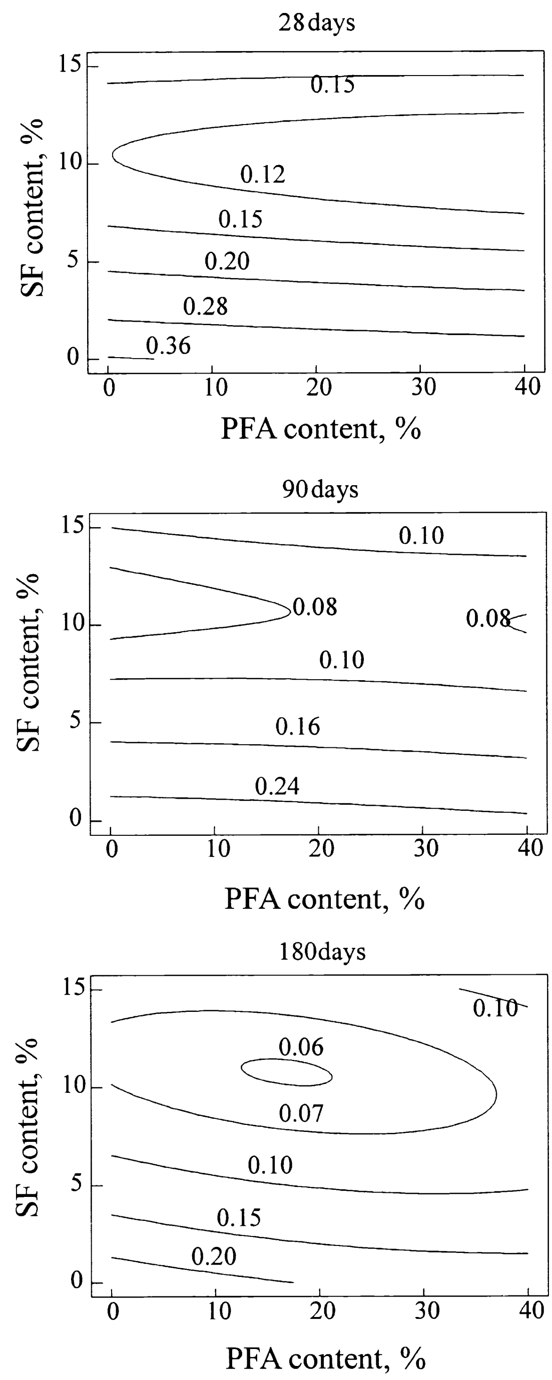

Fig. 5. Isoresponse contours for oxygen permeability ($\times 10^{-16}$, m^2) of concrete at various ages, w/b of 0.27.

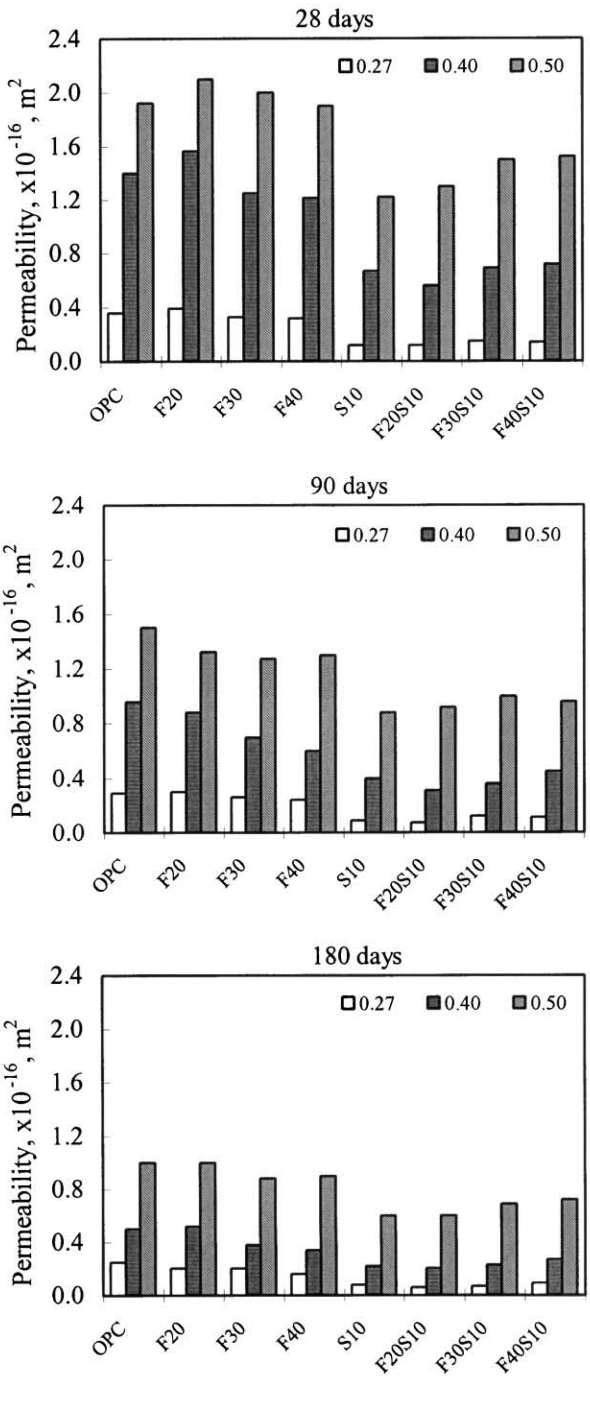

Fig. 6. Influence of w/b ratio on oxygen permeability of concrete at various ages.

tionality and the ratio of the two strengths depends on the general level of strength of the concrete. In the past, a number of empirical relationships between compressive strength and tensile strength have been suggested. Many of them are presented in the following form:

$$f_t = k f_{cu}^{a} \tag{14}$$

where k and a are coefficients and the values of a have been suggested between 0.5 and 0.75. British Code of Practice

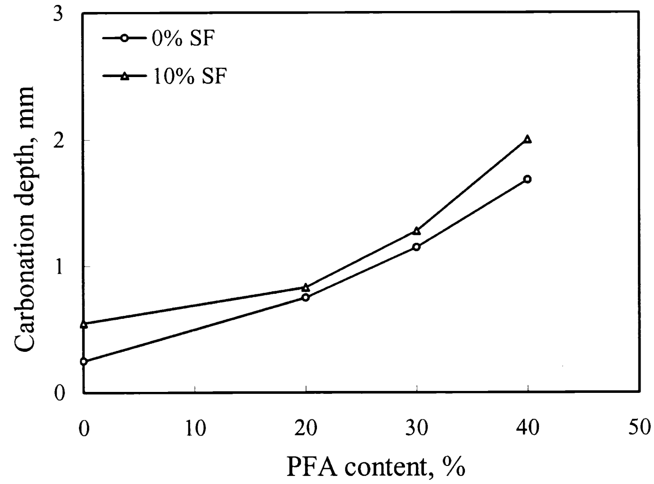

Fig. 7. Carbonation depth of concrete at the age of 2 years, w/b ratio of 0.27.

BS 8007:1987 also suggests similar form of relationship and the values for k and a as 0.12 and 0.70, respectively. In this investigation, the relationship between the compressive strength and the tensile strength was developed as shown in Fig. 9 and the equation is presented as follows:

$$f_t = 0.14 f_{cu}^{0.85}; \quad (R^2 = 0.95) \tag{15}$$

It is worth noting here that the above relationship (Eq. (15)) is similar to that of Eq. (14), irrespective of presence of PFA and/or SF. It can be observed that the concrete mixes containing PFA and/or SF behave in a similar manner to that of OPC plain concrete.

3.6. Relationship between strength and permeability

In practice, the quality of concrete and its fitness for purpose is often judged by its compressive strength. Therefore, the relationship between compressive strength and durability-related properties is of particular interest. The

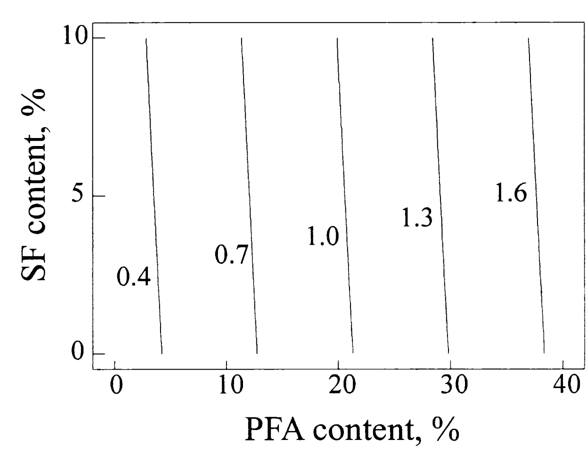

Fig. 8. Influence of PFA and SF on carbonation depth of concrete at the age of 2 years, w/b ratio of 0.27.

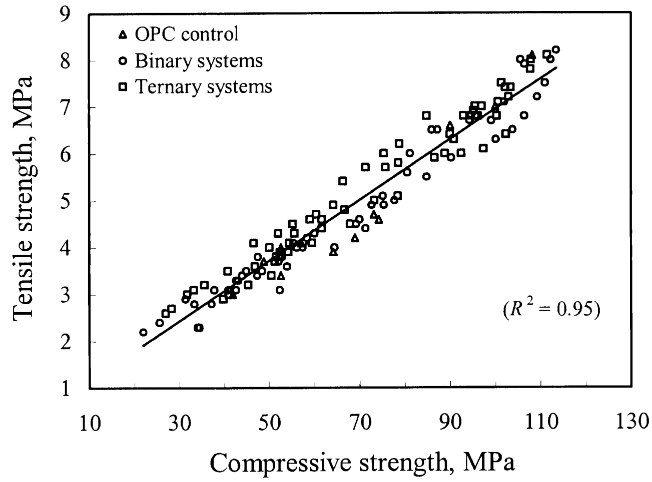

Fig. 9. Relationship between compressive strength and tensile strength of concrete for various cementitious systems and w/b ratios.

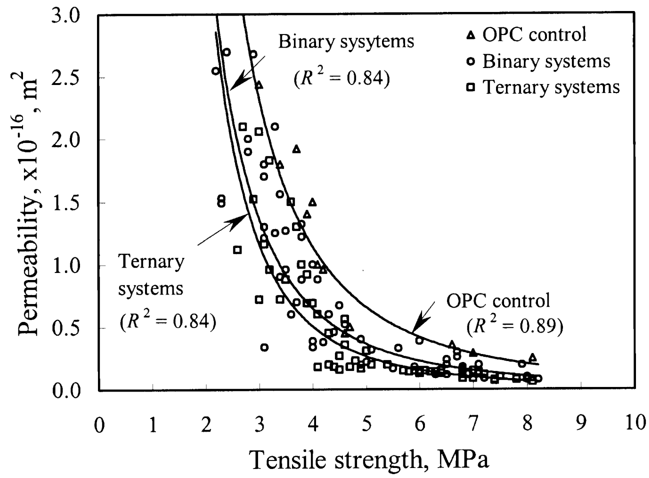

Fig. 11. Relationship between tensile strength and oxygen permeability of concrete for various cementitious systems and w/b ratios.

relationships between compressive strength and oxygen permeability are shown in Fig. 10. It can be seen from Fig. 10 that the pattern of influence of OPC control, binary systems and ternary systems is similar irrespective of presence of PFA and/or SF, as the strength increases and the permeability reduces as expected. This indicates that concrete containing PFA and/or SF behaves in a similar manner to that of OPC plain concrete but the relationship is sensitive to the blended cementitious systems. The ternary systems offer the least permeability values for given strength values in comparison with the binary systems and OPC control. It is interesting to note that the variations between the different cementitious systems become smaller and less significant as strength values increase (or permeability values decrease). Similar relationship was obtained when comparing tensile strength with permeability (Fig. 11).

3.7. Relationship between strength and carbonation

Strength of concrete is believed to relate the rate of carbonation because carbonation is fundamentally controlled by diffusivity of hardened cement paste [12]. In the past, a relationship between 28-day compressive strength and carbonation depth of concrete containing PFA and SF as cement replacement had been established [10]. In this investigation, the 28-day compressive strength was related to the carbonation depth as shown in Fig. 12. In Fig. 12, the results reported by Byfors [10] have also been included. Fig. 12 indicates that the effects of PFA and SF increase the depth of carbonation in high-performance concrete. It can be seen that there is a good agreement between the results obtained in two independent investigations. It is worth noting here that this relationship repre-

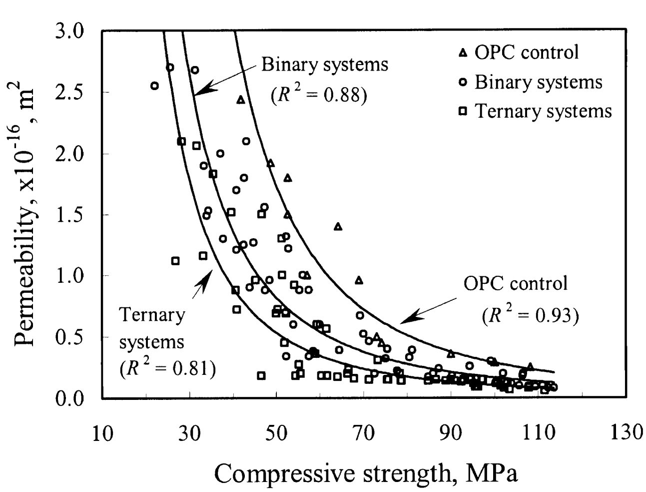

Fig. 10. Relationship between compressive strength and oxygen permeability of concrete for various cementitious systems and w/b ratios.

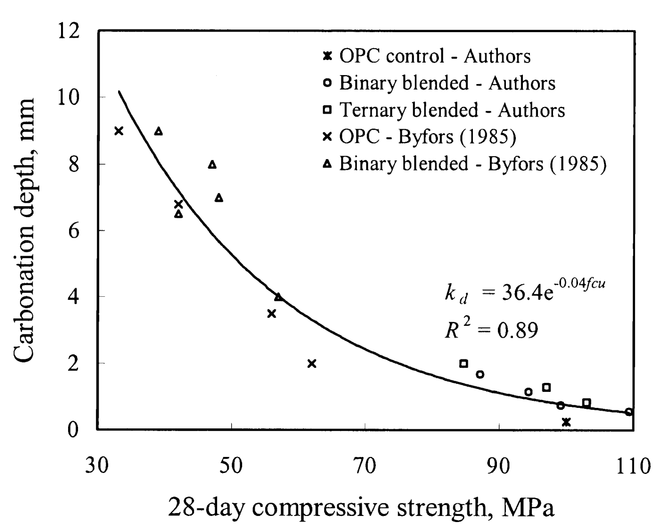

Fig. 12. Relationship between 28-day compressive strength and 2-year carbonation depth of concrete, highlighting for various cementitious systems.

sents wide range of strength approximately between 30 and 110 MPa.

4. Conclusions

The incorporation of SF content increased the early-age strength for all mixes, compensating for the early-age strength loss as a result of PFA inclusion. It is worth noting that all the mixes were adjusted to equal workability by varying the amount of superplasticizer in each mix.

Concrete mixes containing 30% PFA and above with or without SF were not able to achieve the strength of OPC control. However, these systems are viable given the level of performance achieved when economical and environmental benefits are concerned.

SF inclusion, by up to 10% replacement level, significantly reduced oxygen permeability for all levels of PFA replacements. The incorporation of 8–12% SF yielded the optimum strength and permeability values.

The incorporation of PFA resulted in a slight reduction in the oxygen permeability values, in comparison with that observed with SF, especially at later ages. With 10% SF, an optimum level of PFA replacement, in the range of 15–20%, was found to yield the lowest oxygen permeability values measured.

SF inclusion slightly increased the depth of carbonation as compared to the OPC control. The depth of carbonation significantly and linearly increased with an increase in PFA content. For every increase of 10% PFA content, the carbonation depth increased approximately by 0.3 mm. However, the maximum carbonation depth observed was about 2 mm, which is far less than the cover of reinforced steel bars to cause corrosion.

References

[1] V.M. Malhotra, P.K. Mehta, Pozzolanic and Cementitious Materials — Advances in Concrete Technology, vol. I, Gordon and Breach, Netherlands, 1996, p. 189.
[2] FIP Report, Condensed silica fume in concrete, FIP state-of-art report, FIP Commission of Concrete, Thomas Telford House, 1988, UK.
[3] M.I. Khan, Development of high performance concrete incorporating ternary blended cementitious systems. PhD thesis, University of Sheffield, UK.
[4] J.G. Cabrera, C.J. Lynsdale, A new gas permeameter for measuring the permeability of mortar and concrete, Mag. Concr. Res. 40 (1988) 177–182.
[5] H. Grube, C.D. Lawrence, Permeability of concrete to oxygen, Durability of Concrete Structures Under Normal Outdoor Exposure, RILEM, Germany, 1984, pp. 68–79.
[6] B. Ryan, Minitab Handbook, Belmont, CA, USA, 1994.
[7] M.I. Khan, C.J. Lynsdale, P. Waldron, Porosity and strength of PFA/SF/OPC ternary blended paste, Cem. Concr. Res. 30 (2000) 1225–1229.
[8] D.M. Roy, Fly ash and silica fume chemistry and hydration, in: V.M. Malhotra (Ed.), Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SP 114, ACI, Detroit, 1989, pp. 117–138.
[9] M.I. Khan, C.J. Lynsdale, B.S. Choo, Pore structure of high strength cement mortar containing fly ash and microsilica, in: V.M. Malhotra (Ed.), Sustainable Development and Concrete Technology, ACI, Detroit, 2001 (In press).
[10] K. Byfors, Carbonation of concrete with silica fume and fly ash, J. Nord. Concr. Res. 4 (1985) 26–35.
[11] M. Maage, Carbonation in concrete made of blended cements, in: G.J. McCarthy, M. Maage, F.P. Glasser, D.M. Roy (Eds.), Symposium of Materials Research Society, vol. 65, Boston, USA, 1986, pp. 193–197.
[12] A.M. Neville, Properties of Concrete, fourth ed., Longman, UK, 1995.