MAGAZINE OF CONCRETE RESEARCH

Volume 51 Number 1 February 1999

Contents

Guest editorial comment

Technical papers

Magazine of Concrete Research, 1999, **51**, No. 1, Feb., 53–64

Pulverized fuel ash concrete: air entrainment and freeze/thaw durability

R. K. Dhir,* M. J. McCarthy,* M. C. Limbachiya,* H. I. El Sayad* and D. S. Zhang*

University of Dundee

The paper describes a study undertaken to determine the effect of pulverized fuel ash (PFA) and its characteristics on air entrainment, the air void system and the freeze/thaw durability of concrete. The results demonstrate that the admixture demand of PFA concrete was higher than that of Portland cement (PC) concrete and greatly influenced by the type of air-entraining admixture, the level of air required and the characteristics of the PFA used. While PFA fineness had little influence on admixture demand, PFA with high loss on ignition required dosages in excess of two times that of PC. However, PFA was found to have little influence on the rate of air loss with handling and reduced the variability of air content at a given admixture dosage when combined with PC from different sources. Tests to assess the reliability of the ASTM method for examining the air void system confirmed this. The results indicate that improvements in air void parameters were obtained with increasing air content in the concrete. However, similar or slightly enhanced parameters were measured for PFA concrete compared to those of PC concrete. In this case, the characteristics of the PFA had no effect. Following on from this, tests for freeze/thaw durability (ASTM C666: Procedure A) indicated that the critical factors influencing deterioration were the air content and design strength of the concrete. In this respect, no difference was observed between PC and PC/PFA concrete, and all concretes, irrespective of design strength, exhibited very good freeze/thaw resistance above an air content of 3·5%. A nomogram was developed to demonstrate possible routes to material selection/admixture dosages for the practical achievement of durable concrete in freeze/thaw conditions.

Introduction

Deterioration due to repeated freezing and thawing of concrete is a common cause of failure in water-saturated concrete structures under winter exposure conditions, such as outdoor slabs, pavements and bridges.[1] This is often further compounded by the use of de-icing salts, which can lead to corrosion of the embedded reinforcement. Collectively, these processes can leave concrete in need of substantial repairs after very short periods of service. A possible route to minimizing this type of damage lies in the use of air-entraining admixtures (AEAs) in concrete to control frost attack and the use of pulverized fuel ash (PFA) as part of the binder, which is effective in reducing rates of chloride ingress in concrete and thereby reinforcement corrosion.[2–4]

While the use of air entrainment has broadened for concrete in cold climates and become mandatory for pavement-quality concrete,[5] there has been a reluctance to combine this with PFA, since there is uncertainty about their interaction. Recent work[6] has shown that the use of air entrainment and PFA in concrete has little effect on chloride ingress, but concern has been expressed for some time that frost resistance may be compromised.[7–10] Much of this relates to practical difficulties experienced in achieving the desired air contents, at reasonable dosage levels of PFA, and in maintaining these, after mixing, until final placement.[11,12]

Furthermore, little information is available on the influence of PFA on the development of the air void system in hardened concrete or on the evaluation of its performance under the action of freezing/thawing conditions.

---

* Concrete Technology Unit, Department of Civil Engineering, University of Dundee, Dundee DD1 4HN, UK.

(MCR 687) Paper received 23 January 1998; last revised 13 May 1998; accepted 2 July 1998

Given this background, a test programme was devised to establish

(*a*) the influence of PFA and its quality on the AEA requirement and on the air content stability of concrete during production

(*b*) the influence of PFA on the air void system developed in concrete

(*c*) the performance of air-entrained PFA concrete under exposure to freezing/thawing conditions.

Materials and mix proportions

For the main part of the study, a Portland cement PC1 (Grade 42·5 N) to BS 12[13] was used to produce control Portland cement (PC) and PC/PFA concrete mixes. An additional seven PCs (PC2 to PC8) from various sources around the UK were used to consider the influence of cement characteristics on the variability of air entrainment in PC and PC/PFA concrete.

The main PFA tested, PFA1, complied with BS 3892: Part 1.[14] An additional four PFAs (PFA2 to PFA5) from different UK sources were also included to enable the effect of PFA characteristics (fineness, range 3·3–28·6% retained on a 45 µm sieve, and loss on ignition (LOI), range 2·8 to 9·8%) to be studied. These met the requirements of BS 3892: Parts 1 and 2,[15] and most of BS EN450,[16] and meant that the wider range of materials now permitted for use in concrete in the UK were included.

Details of the main physical and chemical properties of these binder materials are given in Tables 1 and 2.

In order to ensure that the study covered the range of air-entraining admixtures available, eight air entrainers (AEA1 to AEA8), all complying with the requirements of BS 5075: Part 2,[17] were used. The details of these are given in Table 3.

As the achievement of frost resistance is recommended in current standards, both through the use of high-strength concrete and through the use of air entrainment, it was decided to consider both design strength and air content as variables in the study. The conventional mix design method[18] was used in the development of the PC concretes, while an optimization method proposed by Munday *et al.*[19] was used for the PFA concretes. The mix proportions for the control PC and PC/PFA concrete mixes (non-air-entrained) are

Table 2. Properties of PFAs used in the study

Property	Pulverized fuel ashes				
	PFA1	PFA2	PFA3	PFA4	PFA5
Oxide composition: %					
CaO	1·5	4·5	2·9	3·5	2·4
SiO_2	48·1	49·1	44·9	43·4	43·3
Al_2O_3	26·4	28·4	26·4	24·1	26·4
Fe_2O_3	11·7	8·4	10·1	10·1	10·5
SO_3	0·8	0·7	0·8	0·8	0·5
MgO	1·9	1·7	2·5	3·1	3·0
Na_2O	1·2	0·7	4·0	1·7	0·5
K_2O	3·0	1·9	1·9	1·6	2·8
LOI	3·6	2·8	4·4	9·8	9·3
Mineral composition: %					
Glass	80·2	81·2	82·2	77·2	78·2
Mullite	8·0	10·1	7·6	7·6	5·7
Quartz	1·8	1·5	2·1	2·1	1·7
Magnetite	4·7	4·1	1·4	1·2	2·3
Haematite	1·6	1·5	2·3	2·1	2·8
Physical properties					
Fineness: % retained on 45 µm	7·0	3·3	11·6	19·5	28·6

Table 1. Properties of PCs used in the study

Property	Portland cements							
	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8
Oxide composition: %								
CaO	65·3	62·4	67·2	65·2	64·2	66·0	65·9	65·1
SiO_2	20·6	21·9	22·3	20·7	22·4	23·1	23·2	21·5
Al_2O_3	4·2	4·9	3·9	4·9	4·6	3·6	3·6	4·6
Fe_2O_3	3·2	3·5	1·5	3·0	2·6	1·5	2·3	2·8
SO_3	2·2	2·6	1·9	2·8	1·9	3·3	2·2	2·4
MgO	3·4	3·4	1·9	1·8	2·5	1·7	1·8	2·0
Na_2O	0·2	0·3	0·2	0·5	0·4	0·2	0·2	0·4
K_2O	0·5	0·8	0·6	1·2	0·7	1·0	0·3	0·7
LOI	1·9	1·5	0·7	1·1	0·7	1·2	1·1	1·1
Bogue compound composition: %								
C_3S	70·2	42·3	70·1	63·2	50·9	57·2	58·0	65·0
C_2S	6·5	31·1	11·2	11·8	26·2	23·3	23·0	12·9
C_3A	5·6	7·0	8·0	7·9	7·7	7·1	5·7	7·3
C_4AF	9·8	10·5	4·4	9·2	8·0	4·6	7·1	8·6
Physical properties								
Specific surface: m^2/kg	455	388	369	355	369	355	348	370

Table 3. Generic types of air-entraining agents used in the study

Air-entraining agent	Description/technical information from manufacturer
AEA1	Synergistic blend of synthetic and naturally occurring surfactants. Supplied as a brown solution. Specific gravity = 1·020 at 20°C
AEA2	Protein-based liquid foaming agent based on blend of naturally occurring surfactants. Supplied as a dark brown solution. Specific gravity = 1·120 at 20°C
AEA3	Vinsol-based resin. Supplied as a brown solution. Specific gravity = 1·050 at 20°C
AEA4	Blend of sodium salt of vinsol resin and sodium alkyl sulphonate. Supplied as a brown solution. Specific gravity = 1·020 at 20°C
AEA5	Aqueous solution of neutralized vinsol resin. Supplied as a dark brown liquid. Specific gravity = 1·036 at 25°C
AEA6	Epoxy sulphate. Supplied as a brown solution. Specific gravity = 1·010 at 20°C
AEA7	Modified fatty acid based on talloil fatty acid. Supplied as amber-coloured liquid. Specific gravity = 1·014 at 20°C
AEA8	Sodium salt of a blend of short-chain fatty acids. Supplied as a pale, straw-coloured liquid. Specific gravity = 1·010 at 20°C

given in Table 4. All mixes were proportioned to have a slump of 30–60 mm.

For the air-entrained concrete mixes, a range of air contents was considered, from 2·5 to 5·5%. For these mixes, the cement, PFA (when used) and coarse-aggregate contents were kept the same as the control. The fine-aggregate content was reduced by 20 kg/m^3 for every 1·0% of air entrained and the water content was reduced to give a water/binder ratio approximately 0·05 below that of the control. Trial mixing was then carried out to establish the required admixture dosages for each air content (the variation permitted for acceptance on air contents was ±0·5%) and the water contents required to achieve workability and strength corresponding to the control concretes. The proportions of the binder, water and sand for the PC1 and PC1/PFA1 concretes for the range of air contents used are given in Fig. 1. The same basic mix proportions were used for concrete mixes prepared with the other PFAs (PFA2 to PFA5).

Air entrainment of PFA concrete

Dosage requirements

An initial series of tests was carried out to examine the dosage requirements of PC/PFA concrete mixes, over a range of variables likely to be encountered in practice, including air-entraining agent type, air content, concrete design strength and both Portland cement and PFA material variability. Tests for air content of the fresh concrete were carried out using the method described in BS 1881: Part 106,[20] within 15 minutes of mixing, following slump (5 min) and wet-density (5 min) tests.

Air-entraining admixture type. Preliminary tests were carried out with a range of air-entraining admixtures in PC and PC/PFA concretes. This enabled the range of admixture performances in the fresh concrete to be examined and identification/selection of suitable admixtures for the subsequent parts of the study to be made.

The relationship obtained between the dosage requirement and air content for PC1 and PC1/PFA1 concrete mixes (30 N/mm^2) for the various air-entraining agents is given in Fig. 2. As may be expected, for all mixes there was an increase in AEA dosage requirement with air content. It is also clear that the PC concrete had the least admixture demand of the two concretes for a given air content. In addition to being higher, the PFA concrete admixture demand was greatly influenced by the admixture type. Indeed, the results indicate that at 5·5% air content, the variation of the dosages between PC1 and PC1/PFA1 concrete ranged from 2·0 to 6·5 times for the eight admixtures tested,

Table 4. Mix proportions of control PC1 and PC/PFA1 concrete mixes

Mix	Concrete grade	Concrete mix proportions: kg/m^3						w/b ratio
		Free water	Binder		Aggregate			
			PC	PFA	Sand	10 mm	20 mm	
Control concrete PC1	C20	180	225	—	810	380	765	0·80
	C30	180	275	—	785	380	750	0·65
	C40	180	315	—	755	370	750	0·57
	C50	180	375	—	690	375	750	0·48
PC1/PFA1	C20	155	160	85	780	395	790	0·63
	C30	155	210	100	665	410	825	0·50
	C40	155	245	110	575	425	855	0·44
	C50	155	300	120	485	435	875	0·37

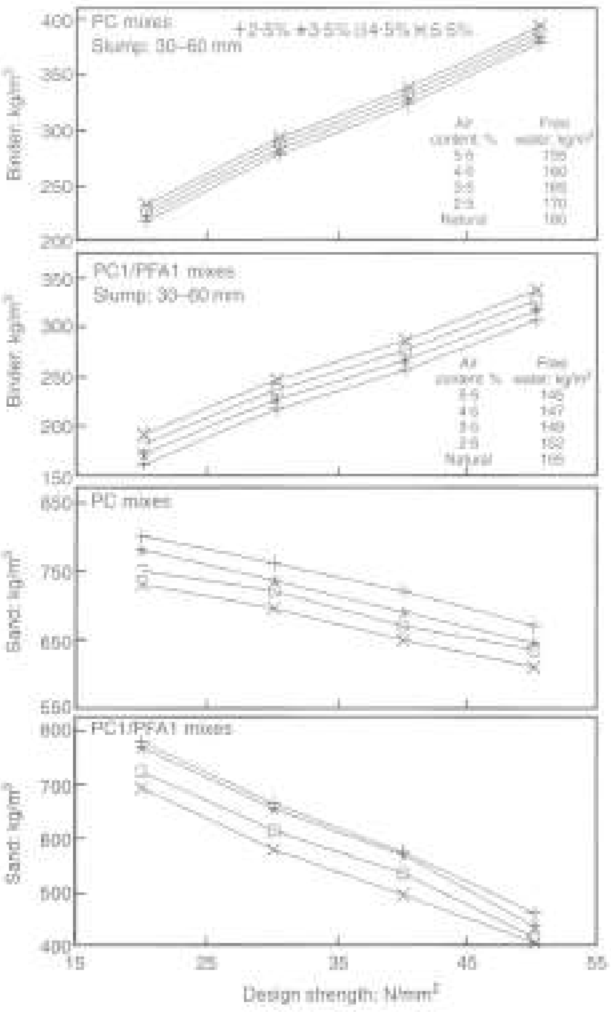


Fig. 1. Mix proportions of PC1 and PC1/PFA1 concretes

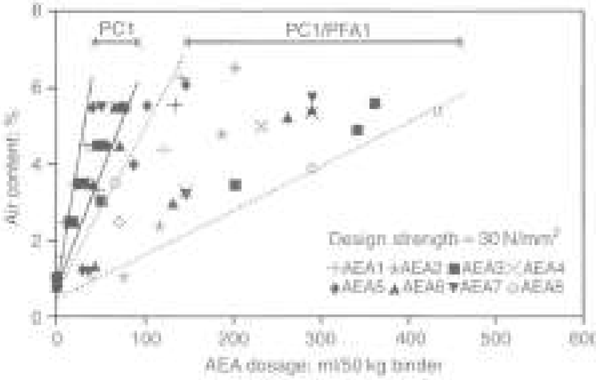


Fig. 2. Air content and dosage of air-entraining agents in PC1 and PC1/PFA1 concretes

with the blend of synergistic synthetic and naturally occurring surfactant (AEA1) requiring the least admixture, while the sodium salt of a blend of fatty acids (AEA8) the greatest.

These data, therefore, suggest that the presence of PFA has an effect on the dosage of air-entraining admixture required to produce a given air content. Clearly, the chemical characteristics of the admixture and its interaction with the materials in the mix are critical, and the results suggest that with careful admixture selection, the effects of PFA can be controlled and minimized.

Concrete design strength. In order to examine the effect of concrete design strength on admixture dosage, the binders used above with AEA8 were considered over the design strength range 20–50 N/mm². This admixture was selected because of its apparent extreme effect when combined with PFA. The results obtained are given in Fig. 3 and indicate that, for both PC and PFA concretes, there was a spread in the results at a given air content, but no clearly identifiable trend was apparent. In addition, the results also suggest that the relationships between AEA dosage and binder content for both PC and PC/PFA mixes remain approximately constant for up to 4·5% air content. Therefore, the admixture dosage demand simply follows increasing specific surface area of the mix with increasing design strength. However, for air contents in excess of this level, the AEA dosage requirement in PFA concrete was found to increase significantly, suggesting that there may be a limiting air content beyond which it becomes difficult to increase air contents in PFA concrete. This disproportionate increase in the quantity of admixture in relation to the air content suggests inactivity of part of the admixture beyond a certain level of addition.

PC source. Concretes containing PCs (PC1 to PC8) in combination with PFA1 at a design strength of 30 N/mm², with AEA1 and AEA8 at an air content of 5·5% were tested to examine the effect of the PC source. For both concrete types, the dosage used was that required to obtain a 5·5% air content in PC1 or PC1/PFA1 concrete. The results from these tests are given in Fig. 4 and indicate that for AEA1 and the PC concretes, variations in air content of between 3·8 and 7·0% with a coefficient of variation of 20% were

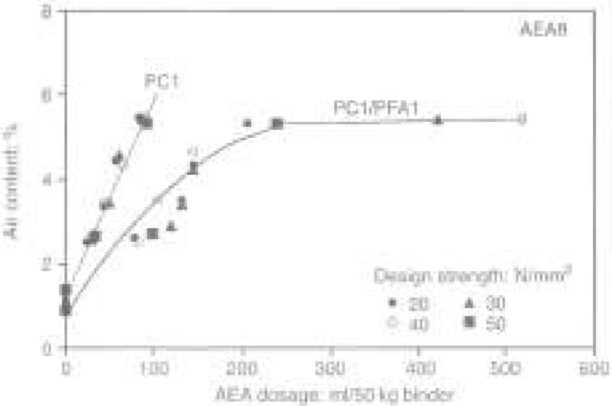


Fig. 3. Effect of design strength on level of air-entraining agent dosage

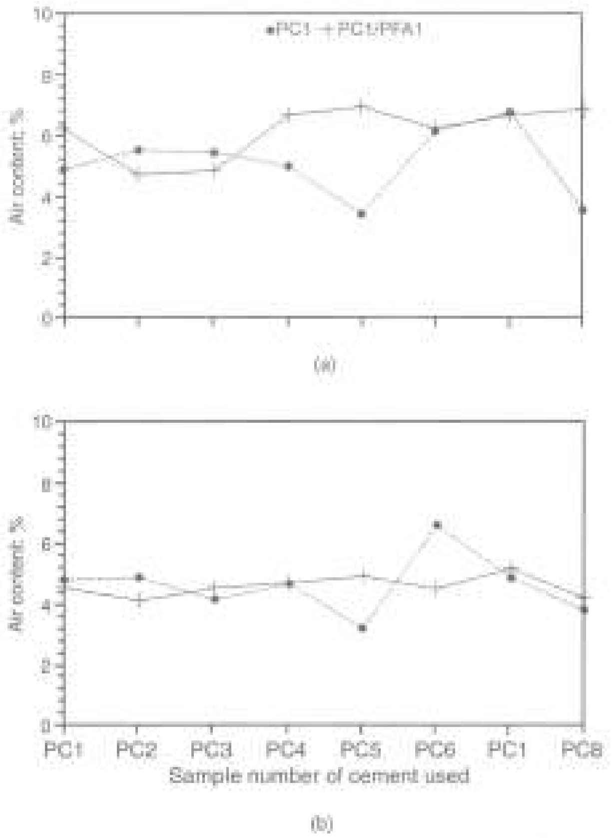


Fig. 4. Variability of air entrainment caused by PC from different sources (design strength = 30 N/mm²): (a) AEA1; (b) AEA8

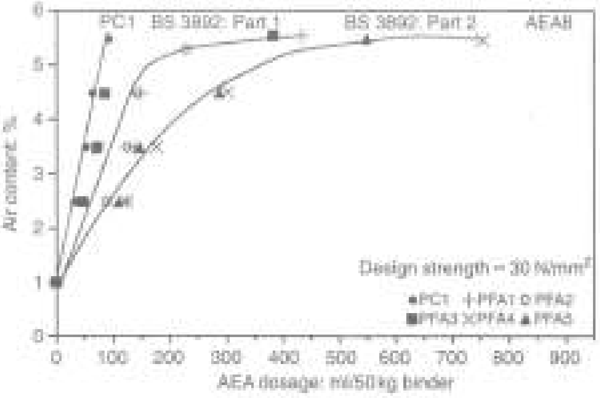


Fig. 5. Air-entraining agent dosage levels for PC1 and PFA concretes

obtained. On the other hand, for the PFA concrete there was a reduction in air-content variability which ranged from 4·8 to 7·0%, with a coefficient of variation of 14%. For AEA8, the corresponding values for PC concrete were 3·6–7·0% with a coefficient of variation of 19%, and for PFA concrete, 4·1–5·2% with a coefficient of variation of 7·0%. Thus, it would appear that PFA in concrete can help to reduce the variability of air content caused by Portland cements from different sources. Such effects seem likely to be due to the increased admixture dosage (concentration) present in PFA concrete to achieve the required air content and, therefore, a wider distribution of admixture in the mix compared to that in the PC concrete.

PFA characteristics. Tests considering the effect of PFA fineness and loss on ignition were carried out using PC1 and concrete of 30 N/mm² design strength with AEA8 over a range of air contents. The results are given in Fig. 5 and again indicate that there was an increase in admixture demand with air content. A sudden increase in admixture demand was also observed for PFA concretes with air contents greater than 4·5%. In addition, it is clear that, at a given air content, there was little effect of PFA fineness on admixture demand over the BS 3892: Part 1 range. This suggests that any influence of PFA fineness on the specific surface area of the concrete mix is relatively minor in relation to admixture dosage requirements. However, higher demands were observed for PFAs with increasing LOI and the differences between the PC and PFA concretes increased with air content. These effects would appear to reflect the known influence of carbon particles present in PFA and their significant adsorption capacity for AEAs,[21] thereby increasing demand until this consumption process ceases on saturation; entrainment of air can occur normally thereafter.

Air-content stability

In order to assess the effect of PFA on the maintenance of air content in concrete with time, tests were also carried out up to 60 min, following alternate mixing and standing for 5 min periods to simulate transportation and handling conditions in practice. In this case PC1 and PC1/PFA1 concretes of design strength 30 N/mm² and air content of 5·5% with admixtures AEA1 and AEA8 were tested. The differences in air contents between the two test times indicate that losses in air content of up to 1·2% were obtained (Fig. 6). However, there was no difference in air loss between PC and PFA concretes and no identifiable effect of PFA characteristics or AEA admixture type on this pro-

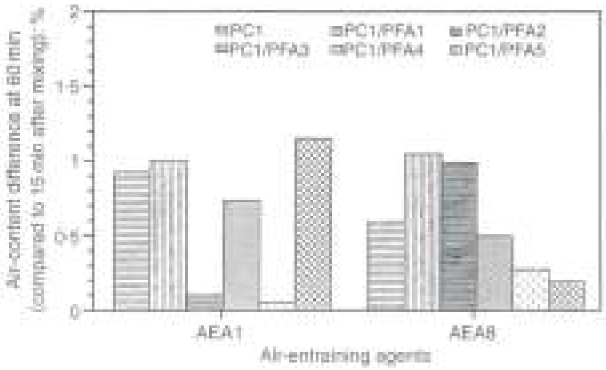


Fig. 6. Variability of air-content measurements in fresh concrete

cess. Thus, it would appear that the constituent materials have a negligible effect on maintaining the stability of the entrained air.

Air void system parameters

The importance of the air void system in protecting concrete against frost attack has been recognized for many years.[22–25] It is also widely acknowledged that to achieve good frost resistance requires a reasonable air content and distribution at close spacing to protect the paste. Air entrainment is normally evaluated in hardened concrete using the microscopic method described in ASTM C457.[26] This technique involves (horizontal) traversing of a prepared concrete surface (cut and ground with silicon carbide) and noting the number of stops, the frequency of voids between stops, and voids and paste at stops. This allows determination of the various air void parameters and paste content in a single analysis and hence characterization of the air void system. Details of their calculation from the measurements taken and definitions are summarized in Table 5. Of these, the spacing factor has found the widest use in providing an indication of frost resistance. Indeed, it has been applied practically as a specification parameter[22] for frost-resistant concrete.

Reliability of the microscopy test method

Prior to testing material effects, it was decided to examine the technique for variability, to enable differences obtained in subsequent tests to be interpreted. This examination considered the variability associated with (i) the operator, by testing the same sample a number of times, and (ii) the materials, by testing a number of samples prepared from a single concrete mix and single samples from a number of concrete mixes. For both of these, eight or nine tests were performed, using PC1 and PC1/PFA1 concretes of 30 N/mm^2 design strength and an air content of 5·5% obtained using AEA8.

The results obtained are given in Table 6. These indicate that for operator variability and the different air void parameters, the coefficients of variation were between 5 and 11%, with only minor differences between PC and PC/PFA concrete. As may be expected, there were slight increases in the variability of the parameters when concrete from within (6·4 and 11·9%) and between (5·1 and 14·9%) batches were considered. However, these figures compare favourably with those of published data referred to within ASTM C457[26] and in the literature[27–29] and confirm that reliable data were being obtained.

In order to examine the test methodology further, air-content measurements for the hardened concrete were compared with those of the corresponding fresh concrete. These tests used PC1 and PC1/PFA1 concretes (with AEA8) across the range of design strengths and air contents used in the study. In addition, concrete of design strength 30 N/mm^2, containing PFA of different characteristics and a range of air contents, was also included. The results obtained are given in Fig. 7 and indicate that there was a good relationship between the measurements of air content in the fresh and hardened states (coefficients of correlation = 0·96), thereby providing further confirmation of the reliability of the tests.

Material influences

The same concretes used to consider the effects of PFA on the air content of fresh concrete were used to examine the influence of PFA on the air void system.

Table 5. Definition of air void parameters from microscopic analysis[32]

Air void parameters	Definition	Calculation	Units
Air content (A)	The proportional volume of air voids in the concrete expressed as a volume percentage of the hardened concrete	$\frac{\text{traverse length through air}}{\text{total length of traverse}} \times 100$	%
Paste content (p)	The proportional volume of cement paste in the concrete expressed as a volume percentage of the hardened concrete	$\frac{\text{traverse length through paste}}{\text{total length of traverse}} \times 100$	%
Number of voids/mm (n)	The number of air voids intercepted by a line of microscopical traverse per length of traverse	$\frac{\text{total number of air voids intersected}}{\text{total length of traverse}}$	—
Chord intercept (l)	The average length of the chord across the cross-sections of the air voids intercepted by a line of microscopical traverse	$\frac{\text{traverse length through air}}{\text{total number of air voids intersected}}$	mm
Specific surface (α)	The surface area of the air voids in the hardened concrete per unit volume of air	$\frac{4}{l}$	mm^{-1}
Spacing factor (L)	An index related to the maximum distance of any point in the paste to the periphery of an air void	When $p/A < 4·33$ mm, $\frac{p}{400n}$	mm
		When $p/A > 4·33$ mm, $\frac{3}{\alpha}\left[1·4\left(1+\frac{p}{A}\right)^{1/3}-1\right]$	mm

Table 6. Variability of air void parameter tests, using AEA8

	Air content: %		Paste content: %		Specific surface: mm^{-1}		Spacing factor: mm	
	PC1	PC1/PFA1	PC1	PC1/PFA1	PC1	PC1/PFA1	PC1	PC1/PFA1
Single operator								
Mean	5·39	5·94	20·38	27·01	16·58	19·36	0·23	0·22
Standard deviation	0·31	0·51	0·93	0·80	1·80	1·99	0·02	0·02
CV: %	5·72	8·63	4·58	2·95	10·87	10·28	7·95	7·34
Within mix								
Mean	4·63	3·78	21·81	24·30	22·52	20·27	0·20	0·26
Standard deviation	0·42	0·33	2·04	2·33	2·67	1·39	0·02	0·02
CV: %	8·99	8·84	9·38	9·58	11·85	6·88	9·93	6·39
Between mixes								
Mean	5·04	5·34	21·50	22·90	18·80	20·07	0·21	0·24
Standard deviation	0·26	0·45	1·56	1·90	2·80	1·54	0·03	0·02
CV: %	5·08	8·49	7·27	8·31	14·90	7·66	12·74	6·33

CV, coefficient of variation.

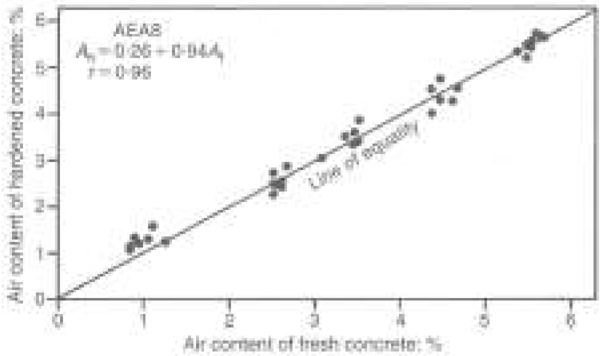


Fig. 7. Relationship between air contents of fresh and hardened concrete mixes

Concrete design strength. The results obtained for the air void parameters for concretes over the range of design strengths are given in Fig. 8. These indicate that, with increasing air content, there was an increase in the number of voids per millimetre and in the specific surface, and a reduction in the spacing factor. These changed very little with concrete design strength, although there was a slight improvement in PC1/PFA1 concrete compared to PC concrete. Thus, it would appear that the air content included in the mix is the main controlling factor of the air void system, and material effects are of lesser importance. The beneficial effect of PFA may be due to the increased admixture dosage level required to achieve the air content, as the air void parameters are thought to be direct functions of the AEA dosage used.[30] This also holds for the strength series, since the admixture demand was also found to vary little with binder content. The fact that there is little difference at the 5·5% air content, where significant dosage differences were observed, may simply reflect the inactivity of a portion of the AEA as suggested above.

PFA characteristics. The spacing-factor results obtained for the effect of the PFA characteristics are given in Fig. 9. These show that the PFA fineness (range retained on 45 μm sieve = 3·3–28·6%) and LOI (range 2·8–9·8%) for a given air content had little or no influence on the spacing factor. Hence, it would appear that PFA variability has no significant effect on hardened-concrete and air void parameters. These results again

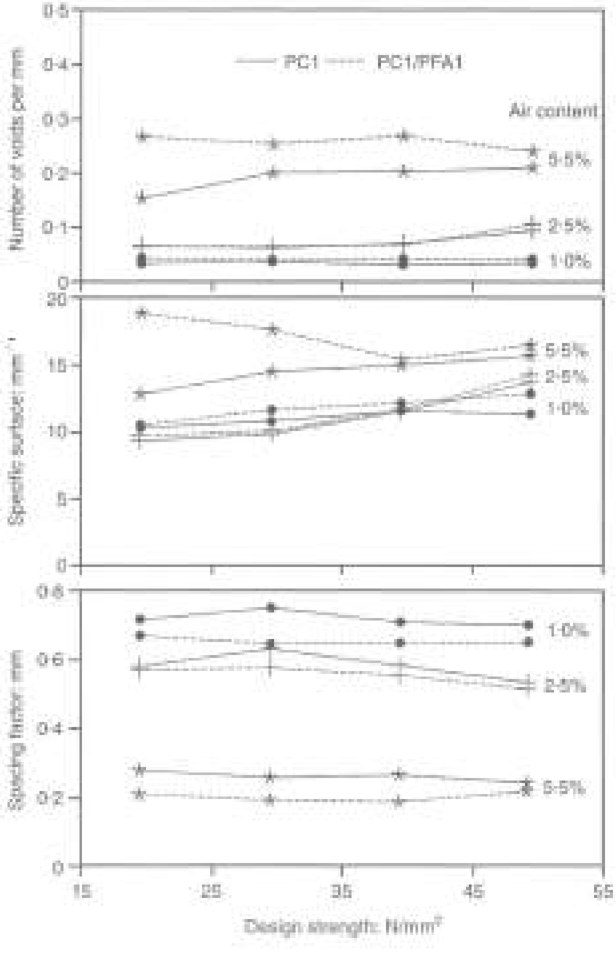


Fig. 8. Air void parameters of PC1 and PC1/PFA1 normal and air-entrained concretes

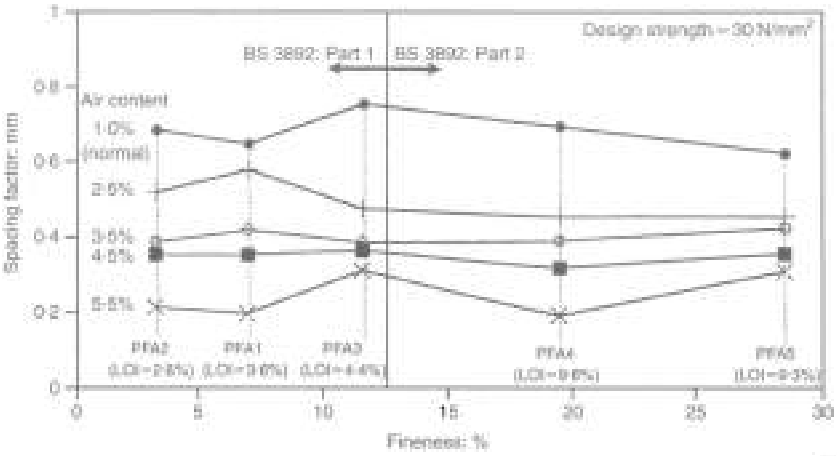


Fig. 9. Effect of PFA fineness on spacing factor

suggest the inactivity of a certain portion of the AEA, but that, providing the air content is achieved by a suitable admixture dosage, the performance thereafter should be unaffected by the characteristics of the PFA.

Freeze/thaw resistance

The main process of damage in a freeze/thaw environment includes (i) internal deterioration due to freezing/thawing cycles and (ii) surface scaling due to the presence of de-icing salts. The precise mechanisms associated with these remain unclear[31] and there is still disagreement about which is the most prevalent in practice. While there are a number of techniques available to assess concrete performance in relation to these, it was decided to use the well-established ASTM C666: Procedure A (freezing/thawing in water),[32] since the aim of the study was to compare the frost resistance of air-entrained concrete mixes.

Deterioration was monitored on 75 × 75 × 300 mm specimens by measuring the dynamic modulus, determined using a resonant-frequency tester in accordance with BS 1881: Part 209.[33] The tests were continued to 300 cycles, or until the achievement of the predefined ASTM failure criterion (60% reduction in dynamic modulus). A durability factor was then calculated in accordance with the standard. Again, the mixes considered above for the air void parameters were tested to evaluate their freeze/thaw durability performance.

Concrete design strength

The durability factors obtained from this test series are shown in Fig. 10(a) with respect to design strength and air content. The results indicate that across the range of design strengths and air contents, both PC and PC/PFA concrete mixes exhibited similar freeze/thaw resistance. In addition, at a given air content, there was an increase in durability factor with design strength and, at a given design strength, the durability factor increased with air content. However, in both cases, a point was reached where an increase in either parameter had little further influence on performance. The 40 and 50 N/mm² concrete mixes with at least 2·5% air content had durability factors in excess of 90%, indicating little or no deterioration and therefore little need for higher air contents. The 20 and 30 N/mm² concretes had durability factors of around 30% at the 2·5% air content, for both the PC1 and PC1/PFA1 mixes, but the freeze/thaw durability performance improved significantly (in excess of 90%) when the air content was increased to 3·5%.

A comparison between durability and spacing factor for the concretes is shown in Fig. 10(b). This indicates that a relationship between these parameters exists with similar behaviour for both PC1 and PC1/PFA1 concrete. It is also clear that for PC concrete, in general, up to a spacing factor of approximately 0·5–0·6, good freeze/thaw durability was obtained (durability factors in excess of 90%), but beyond this, values indicative of average to poor performance were noted. However, for PC/PFA concrete, the corresponding range was 0·4–0·55. In agreement with previous work,[34,35] and as might be expected, for both concrete types an increasing maximum spacing factor for good frost resistance was obtained with increasing strength. This is likely to reflect an enhanced ability to resist the build-up of the pressure associated with freezing, due to the higher tensile strength of such concrete.

PFA characteristics

The results obtained for the effect of the PFA characteristics are shown in Fig. 11. These indicate that there was essentially no difference at a given air content between PFA concrete performances under freeze/thaw conditions (Fig. 11(a)). Indeed, for all concretes at the 30 N/mm² design strength with 3·5% air content, good durability performance (durability factor in excess of 90%) was obtained. It should be noted, however, that the dosage of air-entraining admixture required to achieve a specific air content was greater for concrete using PFA4 (LOI = 9·8%) than for the other PFA concretes.

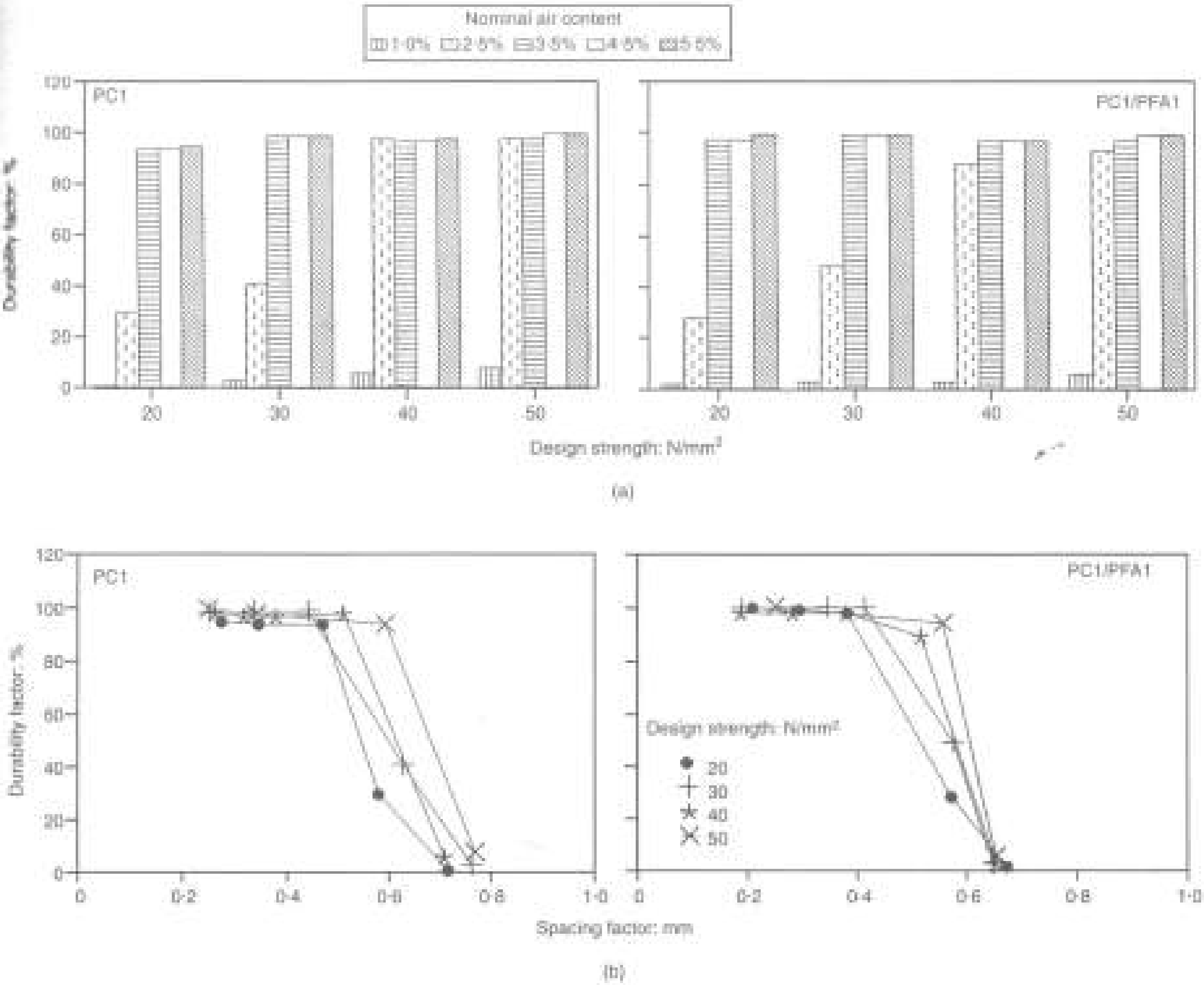


Fig. 10. Effect of (a) air content and (b) spacing factor on durability factors of PC1 and PC1/PFA1 concretes

A comparison of the durability and spacing factor for these concretes is shown in Fig. 11(b). Once again, the results from these concretes indicate that excellent freeze/thaw durability was obtained in concretes of spacing factor up to 0·4 mm and that the performance declined at spacing factors above this.

The spacing factors required for good freeze/thaw durability are slightly higher than those that have been reported in the literature for specifying durable concrete for frost conditions (0·2 mm)[7,34] but they are in line with values given in other studies.[35–37] It would appear that the differences in spacing-factor values corresponding to serious damage between the studies and the specification relate to different rates of freezing during testing.[36] In general, faster freezing rates give serious damage at lower spacing factors. In addition, the results of both sets of tests suggest that slightly reduced spacing factors are required in PC/PFA concrete to ensure enhanced freeze/thaw durability. This may relate to the enhanced permeation properties of PC/PFA concrete compared to those of PC concrete, and therefore a greater degree of difficulty in water movement and hence pressure relief during periods of freezing in the former.[38] However, given the limited data and the variability associated with the test method, this warrants further testing for confirmation.

Practical implications

The results of this investigation are of direct relevance to engineers specifying concrete for low-temperature/winter conditions. In fresh concrete the inclusion of PFA in the concrete is likely to increase the admixture demand for a given air content compared to PC concrete, and this depends on the level of air required, the type of air-entraining admixture and the characteristics of the PFA. However, for a PFA to BS 3892: Part 1 and a suitable admixture, increases in the AEA dosage of up to a factor of only 2 will generally be necessary, and substantial increases will only be required at air contents in excess of 4·5% and in PFAs of high LOI.

The results indicate that beyond the influences of PFA on the dosage requirements, the material has a negligible effect on the characteristics of fresh air-entrained concrete, the air void system or the subse-

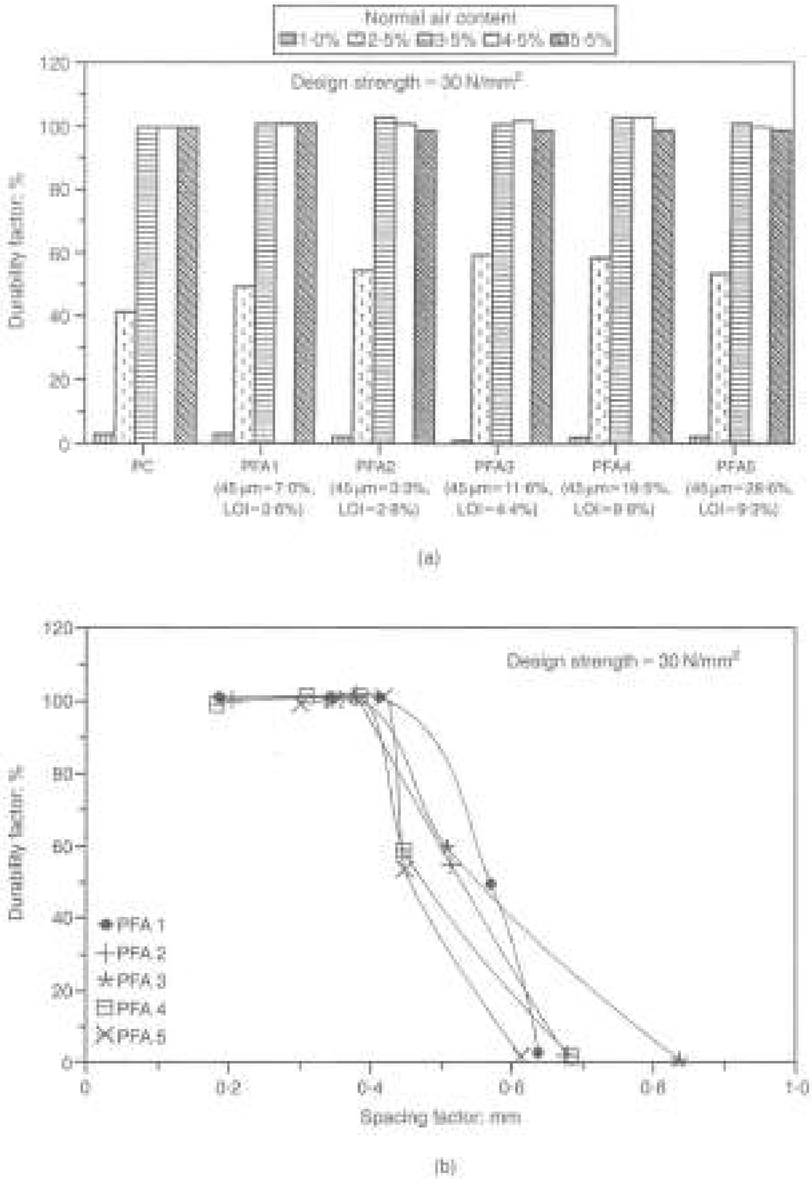


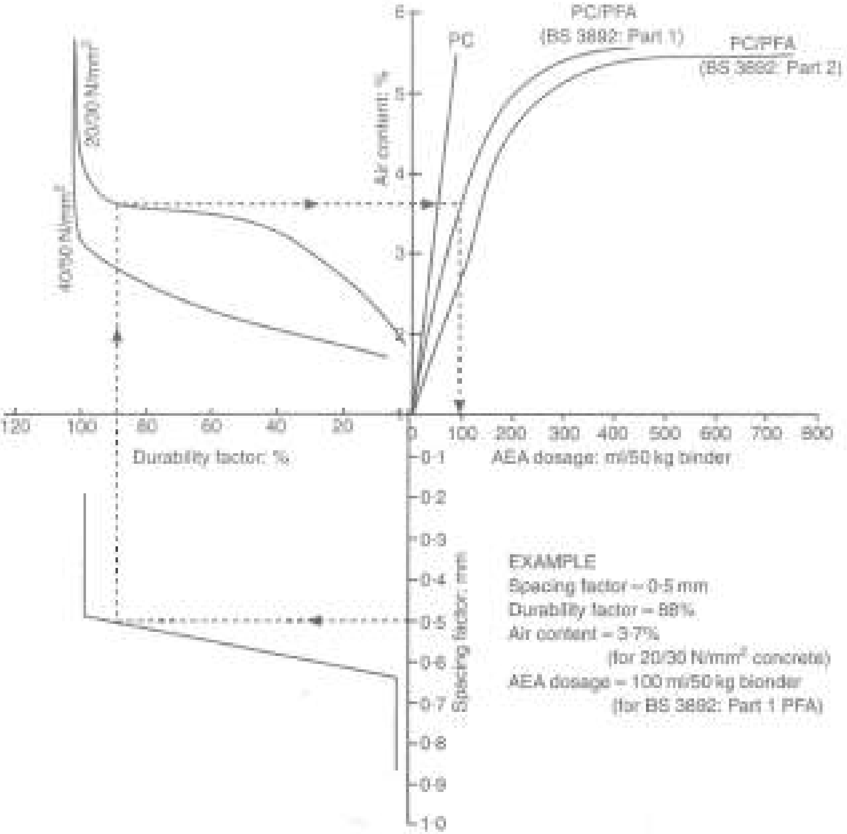
Fig. 11. Influence of (a) PFA quality and (b) spacing factor on durability performance of PFA concrete exposed to freeze/thaw conditions

quent resistance to freeze/thaw conditions. In addition, air entrainment is a more effective route to achieving frost resistance than the use of high-strength concrete. Moreover, for all concretes tested, air contents of 3·5% or a spacing factor of 0·5 mm will produce concrete of very good frost resistance (durability factors in excess of 90%). While this study has considered internal deterioration due to freeze/thaw, there is evidence to suggest that with the use of an air-entraining admixture and the resulting air void system, good scaling resistance should also be achieved.[39]

Using the results of the study, a nomogram has been developed (Fig. 12). This demonstrates how enhanced durability for freeze/thaw exposures may be achieved. Starting from a required durability or spacing factor, a suitable combination of air content and design strength can be obtained. As indicated in the study and in the figure, these are material-independent. The final quadrant provides an indication of the variation in dosage requirements depending on the characteristics of the binder material used. Clearly, as mentioned, the relationships between air content and dosage requirements are dependent on the materials used, and adjustments for individual material characteristics will be necessary in this quadrant for the use of the nomogram in practice.

Conclusions

It was found that at air contents of up to 4·5% and with suitable admixtures (vinsol resins), concretes con-



EXAMPLE
Spacing factor – 0·5 mm
Durability factor – 88%
Air content – 3·7%
(for 20/30 N/mm^2 concrete)
AEA dosage – 100 ml/50 kg bionder
(for BS 3892: Part 1 PFA)

Fig. 12. Nomogram for estimating freeze/thaw durability of PC and PFA concrete

taining BS 3892: Part 1 PFA showed an increase in the admixture demand by a factor of 2·0. This increased at higher air contents and with PFAs of high LOI. The design strength had little or no influence on the admixture requirement for a given concrete type.

It was found that for cements from different sources, the variability in air content for a given admixture dosage reduced when PFA was included. It was also found that the rate of air loss through extended mixing/handling was unaffected by the inclusion of PFA in concrete.

A pilot study established that the data obtained using the ASTM microscopy method for assessing the air void parameters in concrete were reliable.

A study considering the air void parameters of air-entrained PC and PFA concretes indicated that these improved with increasing air content. However, at a given air content in the concrete, PFA of variable fineness and LOI gave slight improvements in these parameters compared to those of PC concrete.

The freeze/thaw durability results showed that for the materials considered, PFA quality had no influence on the freeze/thaw durability of the concrete. Indeed, it was apparent that at a given air content and spacing factor very similar performance was obtained for all concretes considered. Furthermore, it was found, for all concretes, that an air level of 3·5% and spacing factor of less than 0·5 mm provided a concrete of durability factor under freeze/thaw exposure in excess of 90%.

References

1. Wallbank E. J. *The Performance of Concrete in Bridges; A Survey of 200 Highway Bridges.* G. Maunsell & Partners, Beckenham, Apr. 1989, Report for the Department of Transport.
2. Dhir R. K., Jones M. R., Ahmed H. E. H. and Seneviratne A. G. M. Rapid estimation of chloride diffusion coefficient in concrete. *Magazine of Concrete Research*, 1990, **42**, No. 1552, 177–185.
3. Dhir R. K. Pulverised-fuel ash. Cement replacement materials. In *Concrete Technology and Design* (ed. R. N. Swamy). Surrey University Press, Guildford, 1986, vol. 3, pp. 197–255.
4. Dhir R. K., Jones M. R. and Seneviratne A. G. M. Diffusion of chloride ions in concretes: influence of PFA quality. *Cement and Concrete Research*, 1991, **21**, No. 6, 1092–1102.
5. Department of Transport. *Notes for Guidance on the Specification for Highway Works.* HMSO, London, 1998.
6. McCarthy M. J., Dhir R. K. and Jones M. R. Experiments on the effect of binder type, content and air-entrainment on chloride ingress in concrete. *Proceedings of the International Conference on Concrete in the Service of Mankind—Concrete for Infrastructure and Utilities* (ed. R. K. Dhir and N. A. Henderson). E & FN Spon, London, 1996, pp. 29–38.
7. Larson T. D. Air entrainment and durability aspects of fly ash concrete. *Proceedings of the ASTM*, 1964, **64**, 866–886.
8. Ashby J. B. Answers to objections to the use of fly ash in concrete. *Sixth International Ash Utilization Symposium, Reno, Nevada*, 1982, 246–258.

9. Sturrup V. R., Hooton R. D. and Clendenning T. G. Durability of fly ash concrete. *Proceedings of the First International Conference on the Fly Ash in Concrete* (ed. V. M. Malhotra). American Concrete Institute, Detroit, 1983, ACI Special Publication SP-79, pp. 71–86.
10. Gebler S. H. and Klieger P. Effect of fly ash on the durability of air-entrained concrete. *Proceedings of Second International Conference on the Fly Ash, Silica Fume, Slag and Natural Pozzolanas in Concrete* (ed. V. M. Malhotra). American Concrete Institute, Detroit, 1986, ACI Publication SP-91, pp. 483–519.
11. Hewlett P. C. (ed.). *Cement Admixtures: Uses and Applications*, 2nd edn. Longman, London, 1988.
12. Brown B. and Anderson R. High strength air-entrained concrete, a survey of supply and acceptance. *Concrete Forum*, 1998, 19–21.
13. British Standards Institution. *Specification for Portland Cement*. BSI, Milton Keynes, 1996, BS 12.
14. British Standards Institution. *Specification for PFA for Use with Portland Cement*. BSI, Milton Keynes, 1997, BS 3892: Part 1.
15. British Standards Institution. *PFA for Use in Grouts and for Miscellaneous Uses in Concrete*. BSI, Milton Keynes, 1984, BS 3892: Part 2.
16. British Standards Institution. *Fly Ash for Concrete—Definitions, Requirements and Quality Control*. BSI, Milton Keynes, 1995, BS EN 450.
17. British Standards Institution. *Specification for air entraining admixtures*. BSI Milton Keynes, 1982, BS 5075: Part 2.
18. Teychenne D. C., Nicholls J. C., Franklin R. E. and Hobbs D. W. *Design of Normal Concrete Mixes*. BRE-Garston, Watford, 1988.
19. Munday J. G. L., Ong L. T. and Dhir R. K. *Mix Proportioning of Concrete with Pulverised Fuel Ash: A Critical Review*. American Concrete Institute, Detroit, 1983, ACI Special Publications SP-79, pp. 267–288.
20. British Standards Institution. *Methods for Determination of Air Content in Fresh Concrete*. BSI, Milton Keynes, 1983, BS 1881: Part 106.
21. Gebler S. and Klieger P. Effect of fly ash on the air-void stability of concrete. *Proceedings of the First International Conference on the Use of Fly Ash, Silica Fume, Slag and Other Mineral By-products in Concrete* (ed. V M. Malhotra). American Concrete Institute, Detroit, 1983, ACI Special Publication SP-79, pp. 103–142.
22. Powers T. C. Air requirement of frost-resistant concrete. *Proceedings of the Highway Research Board*, 1949, **29**, 184–211.
23. Pigeon M., Gagné R. and Aitcin P. C. Frost durability of high performance concrete. *Proceedings of the Second Canadian Conference on Cement and Concrete, Vancouver*, 1991, 160–171.
24. Siebel E. *Air-Void Characteristics and Freezing and Thawing Resistance of Superplasticized Air-Entrained Concrete with High Workability*. American Concrete Institute, Detroit, 1989, SP-119, pp. 297–319.
25. Cordon W. A. and Merrill D. Requirements for freezing and thawing durability for concrete. *Proceedings of the ASTM*, 1963, **63**, 1026–1036.
26. American Society for Testing and Materials. *Standard Test Method for Microscopical Determination of Parameters of the Air-Void System in Hardened Concrete*. ASTM, Philadelphia, 1990, C457.
27. Langan B. W. and Ward M. A. Determination of the air-void system parameters in hardened concrete—an error analysis. *ACI Journal*, 1986, **83**, 943–952.
28. Sommer H. The precision of the microscopical determination of the air void system in hardened concrete. *Cement, Concrete and Aggregates*, 1979, **1**, 49–55.
29. Hover K. C. Analytical investigation of the influence of air bubble size in the determination of the air content of freshly mixed concrete. *Cement, Concrete and Aggregates*, 1988, **10**, 29–34.
30. Gay F. T. The effect of thermal history on air content, chord intercept and spacing factors of hardened concrete mixes, with standardized additions of neutralized vinsol resin air entraining agent. *Proceedings of the International Conference on Cement Microscopy, International Cement Microscopy Association*, Orlando, 1986, pp. 145–160.
31. Pigeon M., Marchand J. and Pleau R. Frost resistance concrete. *Construction and Building Materials*, 1996, **10**, No. 5, 339–348.
32. American Society for Testing and Materials. *Standard Test Method for Resistance of Concrete to Rapid Freezing and Thawing*. ASTM, Philadelphia, 1988, C666.
33. British Standards Institution. *Recommendations for the Measurement of Dynamic Modulus of Elasticity*. BSI, Milton Keynes, 1990, BS 1881: Part 209.
34. Roberts L. R. and Scheiner P. Air-void system and frost resistance of concrete containing superplasticizers. *Development in the Use of Superplasticizers*. American Concrete Institute, Detroit, 1981, ACI 68, pp. 189–213.
35. Kobayashi M., Nakakuro E., Kodama K. and Negami S. Frost resistance of superplasticized concrete. *Development in the Use of Superplasticizers*. American Concrete Institute, Detroit, 1981, ACI SP 68, pp. 269–282.
36. Pigeon M. and Lanchance M. Critical void spacing factors for concretes submitted to slow freeze–thaw cycles. *Proceedings of the ACI*, 1981, **78**, 282–291.
37. Kivekas L. K. *Durability of Concrete in Arctic Offshore Structures*. Nordic Concrete Federation, Oslo, 1984, Nordic Concrete Research Publication 3, pp. 129–139.
38. Dhir R. K., Hewlett P. C. and Chan Y. N. Near-surface characteristics of concrete: assessment and development of *in situ* test methods. *Magazine of Concrete Research*, 1987, **39**, No. 141, 183–195.
39. Lamontagne A., Pigeon M., Pleau R. and Beaupre D. Use of air-entraining admixtures in dry-mix shotcrete. *ACI Materials Journal*, 1996, **93**, No. 1, 69–74.

Discussion contributions on this paper should reach the editor by 27 August 1999