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STRENGTH AND PORE STRUCTURE OF TERNARY BLENDED CEMENT MORTARS CONTAINING BLAST FURNACE SLAG AND SILICA FUME

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ABSTRACT

Blended cement mortars with fixed workability and incorporating blast furnace slag and silica fume, were tested for compressive strength and mercury intrusion, with a view to comparing their performance with that of plain Portland cement mortar and/or slag-cement mortar. The obtained results showed that with high portions of slag and silica fume in the binding system, the mortars reached relatively satisfactory level of compressive strength and contributed to the significantly denser pore structure. *© 1998 Elsevier Science Ltd*

Introduction

The use of siliceous by-products such as fly ash, blast furnace slag, and silica fume in making mortars and concretes modifies the strength, pore structure and permeability of hardened material. Incorporation of blast furnace slag and fly ash in Portland cement concrete was common practice recently, due to technological, economic, and environmental benefits. These ternary blends exhibit concretes with substantially greater resistance to water and harmful ions and acceptable strength (1–3).

It is well known that pozzolanic reaction with silica fume occurs more rapidly than with fly ash due to the extreme fineness and higher portion of reactive silica. Several research contributions have demonstrated the suitability of the use of combination of slag and silica fume, because it provides a possible means for further impermeability and durability improvement while achieving acceptable strength (4–7). The majority of these studies deals with the behaviour and properties of pastes or mortars with fixed w/c ratio, but little work has been done on strength and structural changes of those under constant workability.

The results of several laboratory tests on the use of mixes with slag and silica fume as a cement replacement in mortars with constant workability, with respect to its effects on strength, pore structure, and calculated values of permeability coefficient, are described.

Materials and Experimental Methods

The materials used were siliceous sand of continuous granulometry according to STN 721208 (grading 0–2 mm), ordinary Portland cement (C), blast furnace slag (S), and silica fume (SF). The slag used to make mortars can be characterized with 28-day slag-activity index of grade

TABLE 1
Chemical analysis and properties of cement and mineral additives.

	Cement	Slag	Silica fume
Moisture	0.27	0.52	—
L.O.I.	1.24	2.82	—
SiO_2	21.06	38.69	97.10
CaO	61.78	38.92	0.50
Al_2O_3	5.23	6.88	0.21
Fe_2O_3	3.32	1.08	—
MgO	2.64	8.73	0.40
SO_3	2.93	2.42	—
Density (kg/m^3)	3133	2785	2154
Specific surface area:			
BET (m^2/kg)	—	—	14400
BLAINE (m^2/kg)	372	203	—

80 (ASTM C 989). Chemical composition and physical properties of cement, slag, and silica fume are given in Table 1. No dispersing agent or superplasticizer was used in the mortars.

The mixes with the sand/binder weight ratio of 3:1 were made and the dosage of the water was adjusted to give a constant flow of 155 ± 5 mm. The workability test according to STN 722441 (equivalent to ASTM C 230) was performed on the Haegermann flow table and was made immediately after mixing.

In practice, the cement composite mix constituents are always batched by weight; however, It is generally accepted (8) that the mortar and concrete properties basically depend on the volumetric concentration of aggregate, cementitious materials, and water. As a rule, silica fume or slag has a lower density than cement and thus the mortar specimens containing the blend of both mineral additives have greater volumetric proportion of solid particles. Thus it is more convenient to express in some cases the composition of the blends in percent by volume than by weight. In this study the specific volume of each mix component was also expressed in percent by volume.

The total number of 12 different mixes was used in experimental program and three series of blended mortars were studied:

Series I. Control and binary system C-SF (samples A0-control, A6, A10, A11);
Series II. Ternary system C-S-SF, comprising fixed content (by weight) of slag and variable contents of C and SF (samples A1, A7, A8, A9);
Series III. Ternary system C-S-SF, which is characterized by the fixed content (by weight) of cement and variable composition of S-SF blend (samples A1, A2, A3, A4, A5, A6).

For these systems the proportioning of the mortar mixtures is summarized in Table 2. For each mix, 20 mm cube specimens were prepared by mixing binder with sand and water. The silica fume and slag powders were put in the mix together with cement.

After 24 h of normal curing in molds (98% RH, 20 ± 0.5°C), the specimens were demolded and stored in water at 20 ± 0.5°C until the test age. Compression tests were

TABLE 2
Mortar mix details.

		Mix proportion						w/c	w/b	
		% by weight			% by volume					
Series	Mix	C	S	SF	C	S	SF	by wt.	by wt.	by vol.
I	A0	100	0	0	100	0	0	0.52	0.52	1.63
II, III	A1	50	50	0	47.1	52.9	0	1.04	0.52	1.53
III	A2	50	40	10	45.6	41.1	13.3	1.12	0.56	1.60
III	A3	50	30	20	44.3	29.9	25.8	1.24	0.62	1.72
III	A4	50	20	30	43.0	19.4	37.6	1.36	0.68	1.83
III	A5	50	10	40	41.9	9.4	48.7	1.84	0.92	2.41
I, III	A6	50	0	50	40.7	0	59.3	2.12	1.06	2.71
II	A7	45	50	5	41.5	51.8	6.7	1.17	0.53	1.52
II	A8	35	50	15	31.0	49.7	19.3	1.71	0.60	1.66
II	A9	25	50	25	21.3	47.8	30.9	3.00	0.75	1.99
I	A10	90	0	10	36.1	0	13.9	0.62	0.56	1.68
I	A11	70	0	30	61.6	0	38.4	1.11	0.78	2.15

performed at 1, 7, 28, and 90 days. Each strength value is an average of three specimens. Dried (105°C) pieces of the test specimens after strength test were used for pore structure analysis by mercury intrusion porosimeter (MIP) Carlo Erba. This device enables the determination of micropores with the radius in range 3.7–7500 nm and of larger pores with the radius up to 0.6mm. The permeability coefficient K (ms^{-1}) was then calculated from MIP data with the use of following equation: $\log K = 1.2634 \cdot \log VM_F + 0.204$, which was derived and fully described in (9).

Results and Discussion

The fundamental question of the study is how the effectiveness of slag and silica fume in the mixture can be approximately characterized with regard to their contribution to strength, pore structure and permeability development in cement mortars with fixed workability. For this purpose it would be desirable to completely separate both S and SF effects from each other. Since in ternary blended mortar both effects superimpose mutually a test of strength or pore structure of mortars generally can only cover the overall effect of whole binding system. In spite of this certain simplification can be accepted from this point of view:

1. The silica fume is more active mineral additive in binding system than slag;
2. The reactions between low active slag and high active silica fume do not take place during the hardening of mortars. This assumption can be accepted because already Berry (1) suggested those recently for another binding system containing slag and fly ash.

From this aspect it can be suggested that the properties of samples will be predominantly affected by the effect of silica fume. It is well known that the influence of SF comprises of physical and chemical processes. The chemical effect is largely due to the pozzolanic

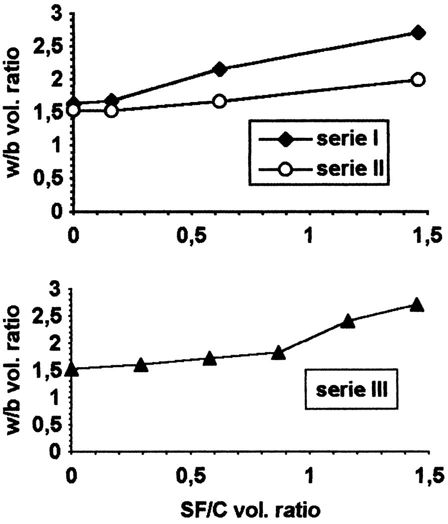

FIG. 1.

Variation of w/b ratio with SF+C volume content of blended mortars with constant workability.

reactivity between SF and $Ca(OH)_2$ and the physical effect probably related to the extreme fineness of SF particles might be considered as a filler effect. This microfilling of SF may be more significant than the pozzolanic effect (10,11).

Because of the high specific surface area of SF, its tendency to adsorb water will result in an increase of water demand to attain a desired consistency, and this effect then partially offsets the sum of both filler and pozzolanic effects of silica fume. However, at higher w/c ratio the higher degree of cement hydration is being reached, and a greater amount of $Ca(OH)_2$ is formed which is available for pozzolanic reaction. This may lead to an additional reduction in capillary porosity during hydration and hence to partial repressing of negative effect related to the higher w/c ratio.

The main effect on the worsening of pore structure quality (a considerable increase of total porosity) seems to prevail over the both pozzolanic and filler effects. Thus, the w/b (water/binder) ratio appears to be the most important parameter determining the blended mortar pore structure. The net effect of SF addition on water demand depends on several factors, especially on the volume content of SF and C (SF/C vol. ratio) in the blend. Figure 1 shows the effect of SF+C volume content in mortar on the increase of w/b ratio.

It is apparent from Table 2 that the replacement of 50% (by weight) of cement by slag (sample A1) causes a decrease of the w/b volume ratio, while the w/b weight ratio remains just the same. Because the specific surface of slag is relative low, the total amount of mixing water is changed slightly.

However, for the blends containing silica fume the total water amount and of course w/b ratios increase with increasing content of silica fume. If the SF is added in small portion (up to 10 wt. %) it has not surprisingly an expressive effect on the water demand. At higher portions of SF (more than 30 wt.%) a large portion of total water amount is consumed to wetting of silica fume particles and therefore the water demand significantly increases. This effect is then reflected negatively in the compressive strengths of mortars, in particular early-age strengths.

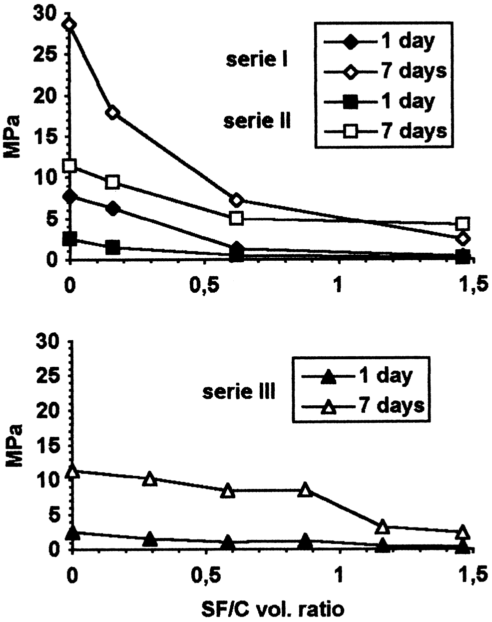

FIG. 2.

Effect of SF to C (by volume) ratio on the early compressive strengths of mortars.

Compressive strength

The main factor which affects the early compressive strength of blended mortars is w/b ratio. In mortars under fixed workability containing SF w/b ratio predominantly depends on the SF to C (by volume) ratio. Thus, where early strengths are concerned, the rate of strength change depends generally to the amount of silica fume in the blend. Figure 2 illustrates the effect of the SF/C ratio on the early compressive strengths of mortars.

The comparison of the compressive strength shows that the strength value of mortars containing S+SF is generally smaller, as are the corresponding ones for control mortars A0 or A1. It is evident that the silica fume in the binary mixes (Series I) caused the more expressive decrease of 1-day compressive strengths than in mortars with S+SF blends (Series II).

As is assumed, the effect of silica fume on strength changes is smaller in mortars with fixed content of cement (Series III); however, this tendency was observed only for silica fume content up to 30% by weight, or approximately 38% by volume (sample A4 with SF/C vol. ratio of 0.87).

It is known that in mortars or concretes with the same w/c ratio the addition of SF increases the compressive strength. In SF mortars with fixed workability, however, SF simultaneously increases the water demand, and more water may have to be added to achieve the desired level of workability. Such water addition then partially offsets the strength enhancement by silica fume. Figure 3 then illustrates that there is an optimum portion of silica fume that can be used to replace cement to achieve maximum 90-day strength improvement in mortar series: <10% (A10 in Series I), 5% (A7 in Series II), and 30% (A4 in Series III) by weight, respectively. The filler effect of SF is in these cases very significant.

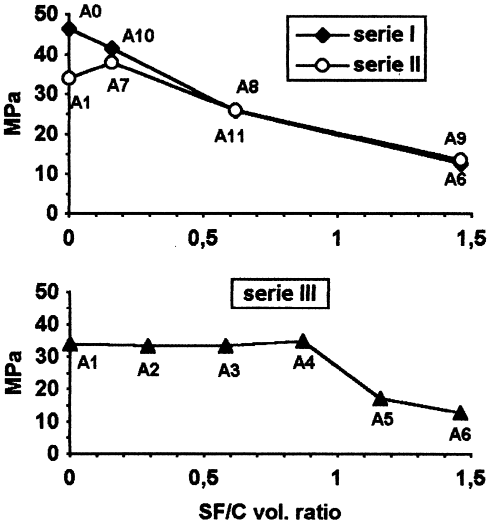

FIG. 3.
The relation between 90-day compressive strength and silica fume content.

The replacement of 50 wt.% cement by slag (sample A1 in Series II and III) caused significant reduction in the 90-day compressive strength of mortar with regard to those of control mortar A0. When the silica fume was added instead of slag (A6 in Series I and III), the total volume needed of mixing water was considerably increased. As is expected, this fact seems to be the prior reason of the strength decrease of mortars with high SF content.

In Series III, as can be seen from Figure 3, the 90-day compressive strengths of mortars are approximately similar to control mortar A1 without silica fume.

This trend, however, can be observed only up to portion 30 wt.% SF in the blend (sample A4). This was thought to be due to the fact that there was not enough water for the cement hydration in both A5 and A6 mortars with the highest contents of silica fume.

Time development of compressive strengths presented in Table 3 shows that in contrast to the reference mortar A1, which develops the bulk of its ultimate strength by 28 days, with a further smaller increase up to 3 months, strength development in mortars with SF (A7, A4, and A5) continues for much longer. It indicates that sufficient lime is probably available at these ages for the cementitious pozzolanic reaction to continue.

Between the test of 7 and 28 days there is also an indirect evidence of a pozzolanic reaction between the mineral additive (mainly the SF) and $Ca(OH)_2$ liberated by the cement hydration and filler effect, because the differences in the strengths of mortars without silica fume (A0, A1) are smaller than those of mortars with silica fume.

Pore Structure

The results of the pore structure analysis of mortars by MIP at 90 days' test age are summarized in Table 4 and show an example of how silica fume influences the mercury intrusion in mortars at a fixed workability. The pore structure becomes finer (filler effect) and total porosity TP available to mercury is increased (higher w/b ratio).

TABLE 3
Time development of compressive strength.

Mortar	Series	Compressive strength gain (%) for belonging test-age range (days)		
		1–7	7–28	28–90
A0	I	270	39	16
A10		185	95	18
A11		442	193	22
A6		623	324	22
A1	II	351	139	25
A7		530	163	53
A8		869	236	57
A9		2376	171	18
A1	III	351	139	25
A2		534	145	34
A3		682	194	34
A4		589	162	56
A5		519	219	64
A6		623	324	22

It is believed that the mixing water dosage expressed as w/b ratio is closely related to TP while the filler effect of SF is related to the pore median. As is shown from Figure 3, the compressive strength is inversely proportional to the increase of SF content (or w/b ratio) in blended mortars. Thus, the similar relation is assumed between compressive strength and

TABLE 4
Pore structure parameters (from MIP) of blended mortars.

Series	Mortar	Pore structure parameter*				
		V_{MP} mm^3 g^{-1}	V_{TP} mm^3 g^{-1}	M_{MP} nm	M_{TP} nm	TP % vol.
I	A0	44.58	46.38	45.15	47.69	10.39
II, III	A1	54.98	63.33	45.55	63.66	12.59
III	A2	72.46	78.84	43.35	75.77	14.68
III	A3	87.42	98.60	42.85	141.23	16.95
III	A4	98.76	124.62	41.62	350.82	21.22
III	A5	145.06	153.90	33.66	42.34	23.05
I, III	A6	171.90	183.43	30.01	35.98	27.75
II	A7	73.23	83.22	34.42	60.81	15.96
II	A8	112.04	125.38	30.58	41.55	20.96
II	A9	146.44	166.83	26.55	37.17	24.73
I	A10	71.85	83.11	36.22	57.54	15.28
I	A11	109.91	123.53	35.85	46.65	17.60

* V_{MP}, volume of micropores (3.7–7500nm); V_{TP}, total pore volume; M_{MP}, micropore radius median; M_{TP}, total pore radius median; TP, total porosity.

TABLE 5
Pore size distribution of blended mortars.

Mortar	Series	SF content (wt. %)	Pore content (%) in the radius range, nm				
			<10	10–100	100–1000	>1000	F_x
A0	I	0	9	56	19	16	29
A10		10	13	44	16	27	33
A11		30	23	31	18	28	39
A6		50	24	37	25	16	36
A1	II	0	12	44	18	26	35
A7		5	20	41	17	22	29
A8		15	22	29	21	28	31
A9		25	22	37	19	24	39
A1	III	0	12	44	18	26	35
A2		10	20	31	23	26	44
A3		20	22	26	24	28	42
A4		30	21	22	22	35	38
A5		40	21	38	21	20	38
A6		50	21	37	25	17	36

total porosity (TP) of mortars, because the effect of porosity is greater than the filler effect of SF in mortars at constant workability.

Hence, in these mortars structural parameter TP seems to be more important parameter influencing strength than pore median.

As is shown in Table 4 by MIP structural analysis, the SF addition of 30% by cement weight caused the micropore radius median drop in opposite to the reference mortar in Series I (45.15 nm–35.85 nm); however, the greater drop in M_{MP} value is generally observed in ternary blend A9 in Series II: (45.55 nm–26.55 nm).

In mortars of Series III, the replacement of slag by the silica fume results in two different effects in the pore structure. Firstly, the increase of water demand is closely related to increase of total porosity; secondly, the filler effect of silica fume is related to decrease of mean pore radius (median). The pore size distribution expressed in Table 5 as the percentage of pore volume with the respect to their radii indicates the usually finer pore structure in mortars with silica fume. It is also shown from Table 5 that the addition of silica fume of over 30% by weight changed the pore size distribution more markedly than did amounts up to 30%. The volume of pores in range 3.7–100 nm considerably increases as the silica fume content rises above the critical level of 30 wt.%. The volume of pores greater than 1000 nm, however, simultaneously decreases.

In general, the silica fume addition to Portland cement/slag mixes in mortars with the same workability leads to the formation of finer and discontinuous pores or to increase in the fraction of the finer pores.

In order to trace changes in pore structure of mortars with silica fume additive, the pore volume (in mm^3/cm^3) of pores having radii smaller than 100 nm (PV_{100}) was chosen. Figure 4 shows the variation of PV_{100} values. It can be seen for a given mortar series, a significantly finer pore structure exists in blends with silica fume. However, the results plotted also indicate that this fine pore structure is not reflected in an increase in strength.

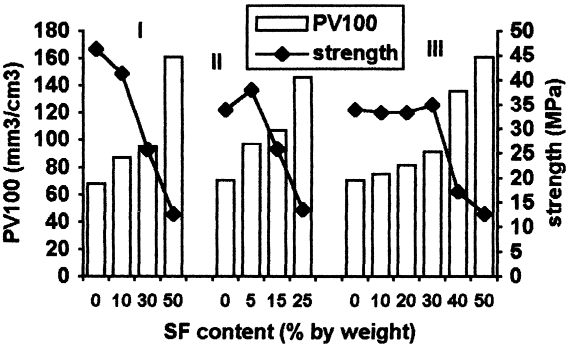

FIG. 4.
Relation between pore volume in range 3.7–100 nm (PV_{100}), 90-day compressive strength and silica fume content.

The observed effects on pore structure by cement substituents suggest that more consideration should be given to this aspect of mortars permeability evaluation. Figure 5 presents the importance of the volumetric expression of both silica fume content and porosity of mortars in Series I and II.

Part B of Figure 5 shows that if the intruded pore volume is expressed as a per unit volume of binding paste basis and is then plotted against the silica fume content expressed in volume %, the relationship is not linear. This result gives an important conclusion that SF/C vol. ratio

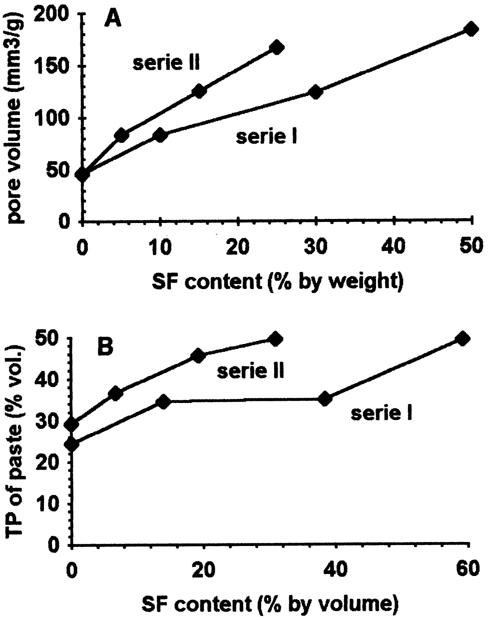

FIG. 5.
Relation between silica fume content and porosity parameters.

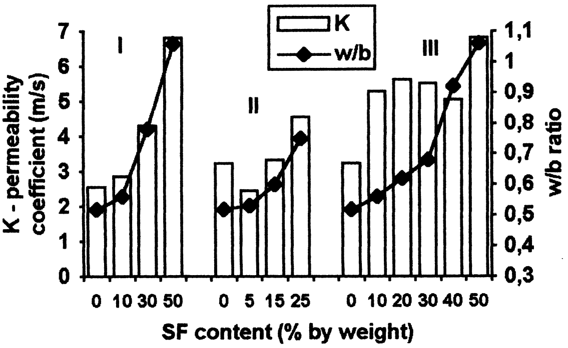

FIG. 6.
Relation between permeability coefficient $K\cdot 10^{-10}$ (ms^{-1}), w/b ratio and silica fume content.

can only be increased to a limit value to form a good pore structure in blended mortars. This critical level seems to be about 50–60% by volume of silica fume.

Permeability

The compressive strength is not the single significant physical parameter of blended mortars, because SF also affected the resistance of mortars against aggressive waters by improvement of their permeability

Decrease of water permeability, however, can be assumed in silica fume blends with constant water-to-cement ratio. In mortars with fixed workability the permeability is more affected by water demand (w/b ratio) rather than filler effect of silica fume. At present, information on the permeability of cementitious materials is usually obtained from the results of measuring of water permeation through the sample in the special laboratory devices. In several cases (samples with denser structure), however, it has not been possible to measure permeability with sufficient accuracy and speed.

Therefore, the use of usable relationship which express the influence of pore structure on permeability seems to be a suitable method how to predict the permeability of cement composites from structural data. From our recently published work (9), it was ascertained that the range of pore radius between 100 and 10,000 nm represents the most significant pore size range having the deciding influence on the permeability. The values of this pore radius range expressed as F_X are shown in Table 5. The permeability coefficients K (ms^{-1}) were calculated according to equation derived in (9):

$$\log K = 1.2634 \log VM_F + 0.204$$

In this equation a new pore structure parameter VM_F (nm) is defined as a product of the micropore radius median and the portion of relevant micropore volume in the total open pore volume: $VM_F = (V_{MP}/V_{TP})\cdot TP\cdot F_X\cdot M_{MP}$.

The Figure 6 then illustrates effect of SF in mortars on the permeability. Only slight changes in the permeability coefficients K were observed in ternary blended mortars of Series III by the SF weight dosage between 10–40%. The K values of these mortars vary from 5.03 to $5.62.10^{-10}$ ms^{-1}. This indicates that the 50% replacement of cement by blend of SF-S (mortar A4, 30% SF + 20% S) renders a material with relatively low permeability and acceptable strength in comparison to corresponding mortar with only silica fume (sample A6, 50% SF).

Conclusions

Based upon the experimental procedure reported in this paper, the following conclusions are made:

1. The basic technical characteristics of the studied mortars containing binding system cement-slag-silica fume are similar to those containing silica fume alone, because the effect of slag in blends is superimposed to the more expressive effect of silica fume. The extent of this superimposing depends mainly on the volume of silica fume. From this aspect, the critical level of silica fume content seems to be 30% by weight or approximately 38% by volume from the total binder amount.
2. The presence of slag in ternary blends guarantees that the increasing of water demand due to the silica fume fineness appears not to be so expressed as in cement-silica fume mortars and hence, the drop in compressive strength due to the increased w/b ratio is significantly lower. Therefore, the silica fume can be added to cement mortars in larger volumes, even if no water reducing admixture is added to the mixture. Also, the mix of slag-silica fume can substitute cement in these mortars in greater amount than silica fume in cement-silica fume blends.
3. The use of slag as the partial replacement of the cement in mortars (sample A1) results in a material with an slightly higher water permeability than similar mortar with only Portland cement (sample A0) by the same workability. The addition of silica fume to such slag mortar (sample A2) further increases the permeability; however, the permeability is not influenced by further higher portions of SF (20–40% by weight; samples A3, A4, A5).
4. The low and medium strength mortars (ultimate compressive strength up to 40 Mpa) cast with optimized level of both active mineral additives and without water reducing admixture is possible to produce with relatively high density and acceptable permeability, even when the slag activity is very low.

Acknowledgments

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References

1. E.E. Berry, Cem. Concr. Res. 10, 1–11 (1980).
2. M.N. Haque and T. Chulilung, Cem. Concr. Res. 20, 120–130 (1990).
3. E. Douglas and G. Pouskouleli, Cem. Concr. Res. 21, 523–534 (1991).
4. V.M. Malhotra and G.G. Garette, Int. Symp. Technology of Concrete when Pozzolans, Slags, and Chemical Admixtures are Used, Monterey, pp. 395–444, 1985.

5. M. Baalbaki, S.L. Sarkar, P.C. Aitcin, and H. Isabelle, Proc. 4th Int. Conf. Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Istanbul, SP-132, Vol. II, 921–942, 1992.
6. C. Ozyldirim, ACI Mater. J. 91, 197–202 (1994).
7. M.G. Alexander, Adv. Cem. Res. 6, 73–81 (1994).
8. T.C. Powers, The Properties of Fresh Concrete, John Willey & Sons Inc., New York, 1968.
9. L. Bágel and V. Živica, Cem. Concr. Res. 27, 1225–1235 (1997).
10. S. Chatterji, N. Thaulow, and P. Christensen, Cem Concr. Res. 12, 781–784 (1982).
11. C. Zhang, A. Wang, and M. Tang, Cem. Concr. Res. 26, 943–947 (1996).