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The properties of Portland cement-limestone-silica fume mortars

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Abstract

This work has studied the influence of the combined action of silica fume and limestone on strength development, porosity, pore structure and morphological features in the system where 15 wt% of cement was substituted by finely ground limestone. Silica fume was added in amounts of 0, 2, 5, 8, 11 and 15 wt% on a cement basis, respectively. It has been established that limestone addition considerably increases the total porosity of mortars. However, if introduced together with silica fume up to 8 wt% of silica, porosity decreases. More than 8 wt% of silica increases the porosity again. The cement mortar containing 8 wt% of silica fume shows the highest compressive strength, the minimum value of the total porosity, and its pore size distribution curve shows a discontinuous pore structure. Limestone is taken up to the system and reacts with aluminate and ferrite phases from cement. Approximately 5 wt% is available for reaction after 120 days hydration of mortars containing no silica fume. The quantity of limestone incorporated is affected by the silica fume content. The replacement of Portland cement by 15 wt% of silica fume causes reduction both in the amount of cement and in the free CH content available for limestone chemical activity, and in this condition limestone acts only as a filler addition. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Microstructure; Silica fume; Limestone; Mortar

1. Introduction

Utilisation of various types of by-product and waste materials such as fly ash, slag, silica fume, and rice husk as additives in concrete results in high- performance concrete, in terms of better chemical resistance, higher strength or better durability [1–5]. The research has confirmed that silica fume addition to blended Portland cement leads to considerable improvements of mechanical properties and sulphate resistance of cement mortars by utilizing special properties such as high pozzolan activity and large specific surfaces. Limestone is used in cement and concrete for various purposes, namely, as a raw material for clinker production and as coarse or fine aggregate. The finely ground limestone (limestone dust) produced in quarrying operations, poses disposal and environmental problems and has been suggested for use as an additive to Portland cement. There exists some controversy with respect to the effect of limestone. Some authors claim that limestone acts as an inert filler to cement, and its effect on cement to be only a physical phenomenon [6], while others consider that limestone acts as an active participant, and that during hydration of Portland cement some $CaCO_3$ is taken into system and reacts with C_3A or ferrite phases to form hemicarbonate, monocarbonate, or a mixture of both [7,8].

The aim of this research was to study simultaneous influence of silica fume and finely ground limestone on properties of mortars. The present work has systematically studied the influence of increasing silica fume additions (2–15 wt%) on the mechanical strength and microstructure development of Portland cement mortars in the system where 15 wt% of cement has been substituted by finely ground limestone.

2. Experimental

2.1. Materials

Commercial, blended Portland cement was produced by grinding Portland clinker and mixing with up to 5% gypsum and 30% of a blast furnace slag, made in Croatian cement works (Dalmacijacement Co., Solin, HR), marked PC 30z 45s, was used.

Silica fume was obtained from filters in production of ferrosilicon (Carbide and Ferroalloys Works, Dalmacija, Dugirat, HR), and contains 89 wt% SiO_2, extremely fine spherical and amorphous particles.

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Table 1
Characteristics of used materials

	Blast furnace slag	PC30z45s	Silica fume	Limestone
Chemical analysis, (wt%)				
SiO_2	36,07	21,03	89,68	0,115
Al_2O_3	10,69	6,58	1,15	0,220
Fe_2O_3	1,18	2,68	1,54	0,230
CaO	41,36	58,10	1,40	55,440
MnO	0,55	–	–	–
MgO	7,20	2,57	1,45	0,970
SO_3	0,98	2,54	0,17	–
P_2O_5	0,20	–	–	–
P	–	–	–	0,011
S	–	–	–	0,034
K_2O	0,82	0,73	–	–
Na_2O	0,45	0,29	–	–
L.O.I. (1000° C)	–	1,04	2,99	42,98
C	–	–	1,83	–
Compound composition (wt%)[a]				
C_3S		62,10		
C_2S		17,60		
C_3A		11,20		
C_4AF		8,20		
CaO free		0,90		

[a] Calculated according to Bogue for the neat cement.

Limestone dust, produced in quarrying operations of a commercially available limestone, which is usually used as aggregate to concrete mixture, contains 99.00 wt% of $CaCO_3$.

The specific surface area of the cement, silica fume, and limestone used is in order of 1.10, 18.00, 1.30 m^2/g, respectively, measured using the nitrogen adsorption method according to BET.

Table 1 shows chemical analyses of used materials and the potential mineralogical composition of the used blended Portland cement, PC30z45s, calculated according to Bogue for neat cement.

Particle size distribution of cement, silica fume and limestone used was determined using the Coulter Counter method (methanol-LiCl solution), as shown in Fig. 1.

2.2. Mortar mixes

Two series of mortar specimens were prepared. The P-series was prepared out of Portland cement, marked PC30z45s with different additions of silica fume. The PK-series represented the Portland cement-limestone-silica fume system. The specimens were prisms having dimensions of 4 × 4 × 16 cm.

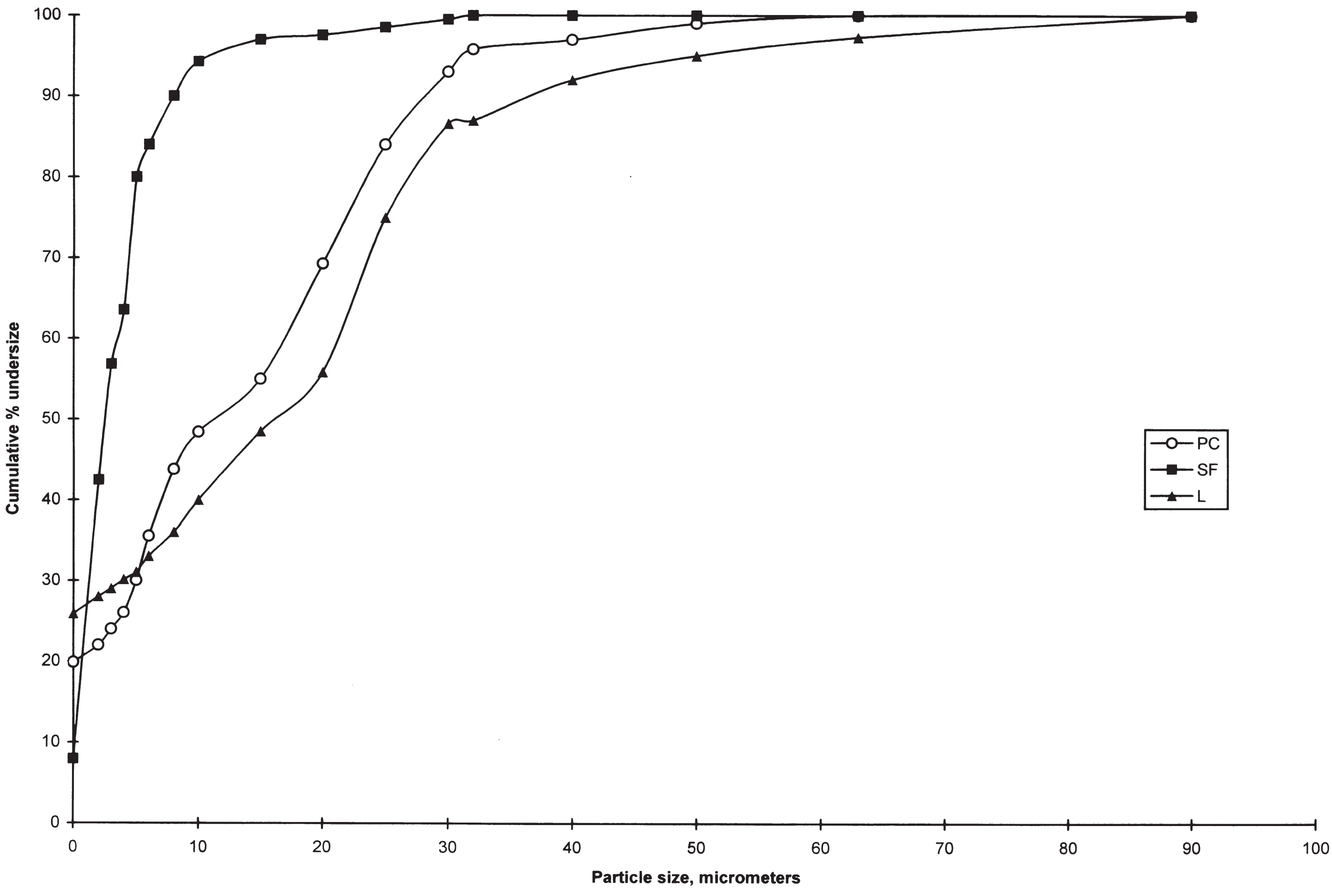

Fig. 1. Particle size distribution of Portland cement (PC), silica fume (SF), and finest ground limestone (L).

The mix proportion of the control mortar corresponded to 450 g cement content, 1350 g of fine aggregate (standard, natural quartz sand) and 0.5 water-to-cement (W/C) ratio. In mortars containing silica fume (P-series) the amount of 0, 2, 5, 8, 11 and 15 wt% of Portland cement was replaced by an equal weight of silica fume. The samples were designated P-0, P-2, P-5, P-8, P-11, and P-15, respectively. In mortars containing silica fume and limestone (PK-series), 15 wt% of cement was always replaced by the equal weight of limestone. Silica fume in the amount of 0, 2, 5, 8, 11, and 15 wt% on a cement basis was added. Designations used for the PK-series were PK-0, PK-2, PK-5, PK-8, PK-11, and PK-15, respectively. The W/C varied from 0.50 to 0.67 by increasing the silica fume addition. The samples having been prepared to have the same flow table consistency, formed the pats of 12.2–13 cm in diameter. The air content of freshly mixed mortars was determined by the pressure method, according to ASTM C231-68. The specific gravity of the Portland cement, aggregate, silica fume, and limestone used were 3.18, 2.62. 2.26, and 2.70, respectively. The weight ratios of mixture's composition were calculated into the volumetric ratio [9]. In each of these mixes the weight (and volumetric) ratio both of cement to limestone, and of cement to silica fume were fixed. The specimens were demoulded at an age of 24 hours after casting and were then cured in water at 20°C until testing.

2.3. Test methods

Compressive strength measurements were carried out at ages of 3, 7, 14, 28, 120, and 360 days. The strength value was the average of three specimens.

The microstructural changes of mortars during hydration were determined in mortars at age of 28 and 120 days. At the given age, the mortar specimens were crushed, washed thoroughly with acetone to stop hydration, and vacuum dried at room temperature for 24 hours.

The quantity of calcium hydroxide (CH), non-evaporable water content, and CO_2 content in the 28- or 120-day-old hydrated Portland cement mortars was determined by the differential thermal analysis, DTA-DTG-TG (Derivatgraph-MOM, Budapest, Hungary, with Pt-crucibles and corundum inert substance), and calculated on a constant cement weight basis. All mixing was done and cured in an evacuated chamber to minimize the amount of entrapped air to prevent carbonation.

The morphology of the hydration phase was studied by scanning electron microscopy, (SEM Leitz AMR 1600 T, Germany). The fracture surface of mortars was gold coated.

The pore volume and the pore size distribution in the range 7.5 to about 0.001 micrometer radii of 28-day-old hydrated Portland cement mortars were determined by a mercury intrusion porosimeter (Carlo Erba series 200, Milano, Italy). The contact angle was taken to be 140°. The volume of mercury intrusion at the maximum pressure was considered to be the total porosity.

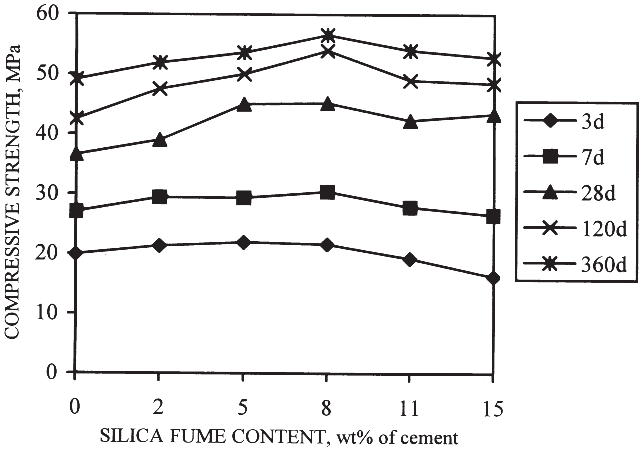

Fig. 2. Development of compressive strength of the PK-series mortars as a function of silica fume content and hydration time.

3. Results and discussion

Development of compressive strength as a function of hydration time of PK-series mortars containing different silica fume content is presented in Fig. 2.

Compared to the sample without limestone (0 wt%) the mortars containing both limestone and more than 8 wt% of silica fume show lower strength at earlier ages of hydration. After 28 days, however, these samples show a considerable increase in compressive strength. The strength development is obviously related to the silica fume content. The cement mortars containing 8 wt% of silica fume show the highest compressive strength after 120 and 360 days of hydration. Silica fume increases the compressive strength in the same

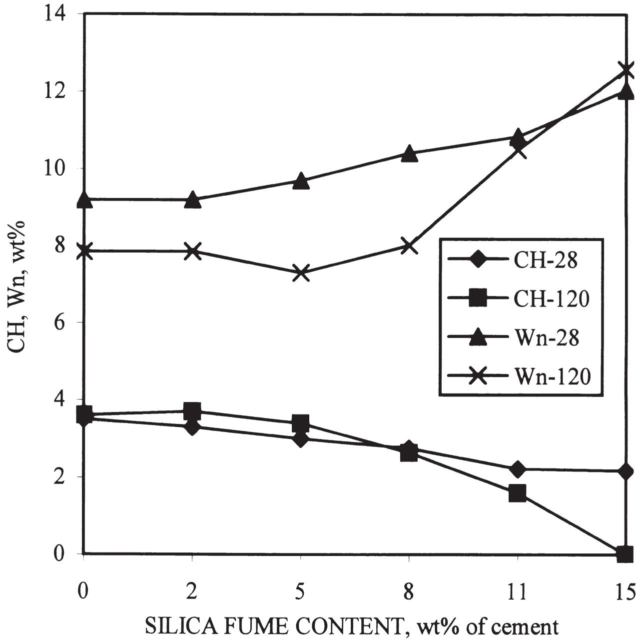

Fig. 3. Effect of silica fume addition on the free calcium hydroxide (CH) and on the non-evaporable water content (Wn) for 28- and 120-day-old mortars. The results are computed based on constant cement content of 25 wt%.

way as in analogous P-series mortars, although they are lower than those for samples of mortars containing no limestone [5].

The quantity of free CH, determined as weight loss in the temperature range of 460–560°C, the loss of weight due to loss of CO_2 from $CaCO_3$ in the temperature range of 720–920°C, and total loss of weight due to the non-evaporable water content in the temperature range of 20–1000°C have been determined by thermal differential analysis after 28 and 120 days of hydration. Fig. 3 shows the effect of silica fume addition on both the free calcium hydroxide (CH) content and the non-evaporable water content (Wn), respectively.

As shown in Fig. 3, a replacement of up to 5 wt% of silica fume indicates a relatively stable content of free calcium hydroxide for 28 days and 120 days. The quantity of free CH is almost the same as in sample without silica (0 wt%) perhaps indicating that the CH liberated by cement hydration has been consumed by limestone more rapidly than by the pozzolanic reaction. In mortars containing more than 5 wt% of silica fume, the CH content decreased more rapidly during the period of 28 to 120 days, indicating the effect of the CH–pozzolanic reaction. At a 15 wt% replacement, approximately all of CH was consumed after 120 days. It is interesting to note that non-reacted amorphous particles of silica fume are detected by TEM only in the 28-day-old mortars containing 15 wt% of silica. Free silica fume particles were not detected in the same samples aged 120 days, which confirms retardation of the pozzolanic reaction in comparison to the reaction of hydration [5]. The amount of CH, formed by hydration of cement containing no silica fume, is not changed significantly by the age of hydration. This is attributed to the reaction of limestone with constituents of cement, which consumed some CH [8].

Total loss of weight in the temperature range of 20–1000°C represents the non-evaporable water content, the amount of chemically bound water in the CH and CSH phases. The CO_2 content of limestone was considered. CSH phases in this context stand for all hydration products in their various compositions except CH. As shown in Fig. 3, in the period of 28 days, the obtained values for the non-evaporable water content, Wn, slightly increase with the increase of the silica fume content, indicating the formation of the hydrated products. With increasing non-evaporated content, the amount of the free lime decreases. Accordingly, the higher amount of water combined is not bound in CH, but in other hydrated phases, which consume CH for their reactions to produce hydration products. The observed non-evaporable water content after 120 days was lower than after 28 days except in mortars containing 11 and 15 wt% of silica fume. For these mortars, the content of the non-evaporable water is highest at the age of 120 days but the CH content is the lowest. This suggests that the pozzolanic reaction produces new CSH phases. It appears that in the first 28 days of hydration, the pozzolanic reaction takes place later than the reaction of hydration, because a certain period of time is needed for the dissolution of silica [10]. From the above results it can be seen that in the presence of silica fume, the non-evaporable water content decreases from the 28th to the 120th day. This is assumed to be due to a release of water during polymerization of silicates, and the non-evaporable water content appears to be reduced with time [11]. The similar effect of decreasing non-evaporable water content from the 28th to the 120th day of hydration is remarkable in the sample containing no silica fume (0 wt%), perhaps indicating the effect of the slag from the used Portland cement [12].

For the PK-series mortars, the loss of weight due to the loss of CO_2 from $CaCO_3$ in the temperature range of 720–920°C has been determined on DTA-TG curves after 120 days hydration. Table 2 presents the changes of limestone remaining in the PK-series mortars as a function of silica fume content. In mortar containing no silica fume (the PK-0) about 5.09% uptake of 17.65% limestone addition was incorporated into a cement system. Therefore, inclusion of limestone as an active participant in the hydration reaction of Portland cement is possible. Recently, the formation of calcium monocarboaluminate hydrate has been detected by XRD in the PK-series samples containing up to 8 wt% of silica fume [13]. The values obtained for remaining limestone in mortars containing both an addition of limestone and different contents of silica fume (Table 2) show that the amount of incorporated limestone has been affected by the silica fume content. The increase in the silica fume content is reflected by the decrease of incorporated limestone. The samples containing 11 and 15 wt% of silica fume show no remarkable limestone reaction. This is compatible with previous reports that the conversion of $CaCO_3$ in cement system sufficient for the formation of monocarbonate depends on the amount of aluminate and ferrite phases available, as well as on the presence of free lime [8,14]. At a 15% replacement of cement with silica fume (PK-15 sample) the level of the amount of aluminate and ferrite phases available in the cement system is the lowest, all of free CH has been consumed by the pozzolanic reaction, and there are no conditions for the limestone reaction.

Scanning electron micrographs of the fracture surface of the mortars with 8 wt% of silica fume without (P-8) and with limestone (PK-8) hydrated to 28 days are given in Fig.

Table 2
Changes in limestone remaining in the PK-series mortars as a function of the silica fume content

Limestone content after 120 days hydration (wt%)			
Mortars	Added	Remaining	Incorporated
PK-0	17.65	12.56	5.09
PK-2	17.65	12.28	5.37
PK-5	17.65	14.72	2.95
PK-8	17.65	14.48	3.17
PK-11	17.65	17.08	0.57
PK-15	17.65	17.60	0.05

Calculated on the 100 wt% cement basis.

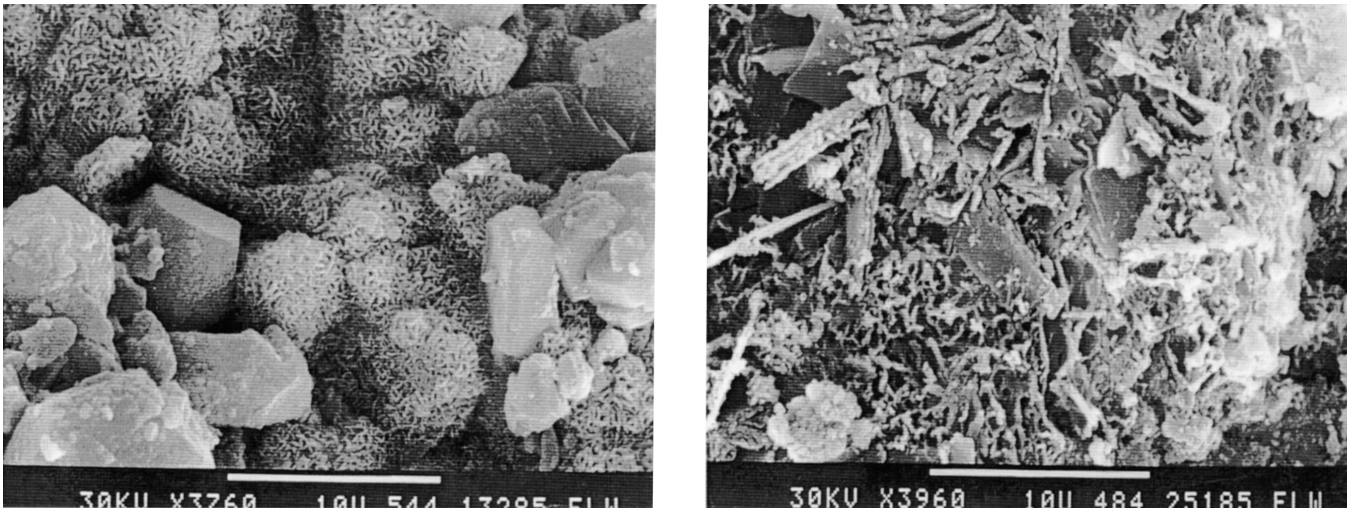

Fig. 4. SEM micrographs of fracture surface of mortars after 28 days of hydration. (a) Sample P-8, (b) sample PK-8.

4a and 4b. The recticular network formation of the CSH layer precipitated on the surface of SiO_2 grains and the CH hexagonal plates is detected for the P-8 samples (Fig. 4a). The sample containing 15 wt% limestone and 8 wt% of silica (PK-8) does not exhibit recticular network features and shows occasional evidence of hexagonal plates (Fig. 4b). A distinct difference between it and the sample without limestone (P-8) is that its surface seems to be consolidated and

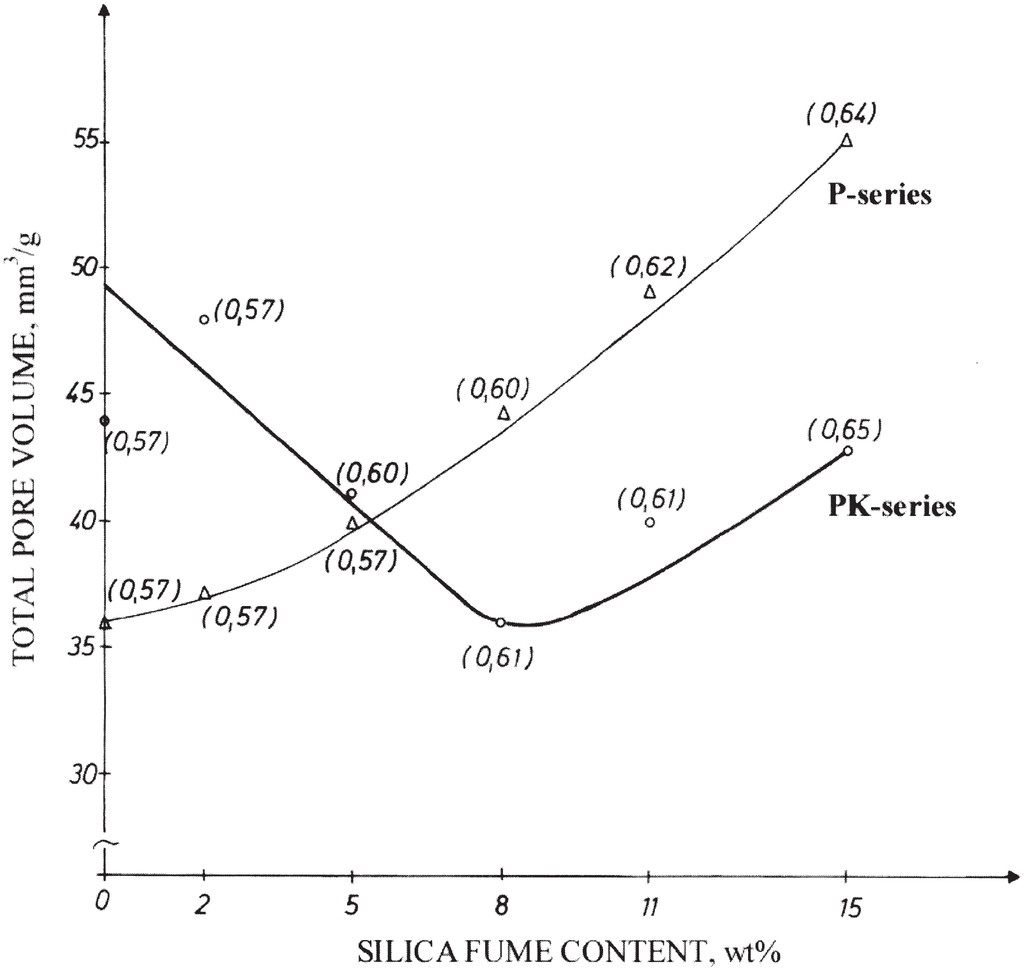

Fig. 5. Total pore volume vs. the silica fume contents in the 28-day-old P- and PK-series mortars. W/C ratios are give in parentheses.

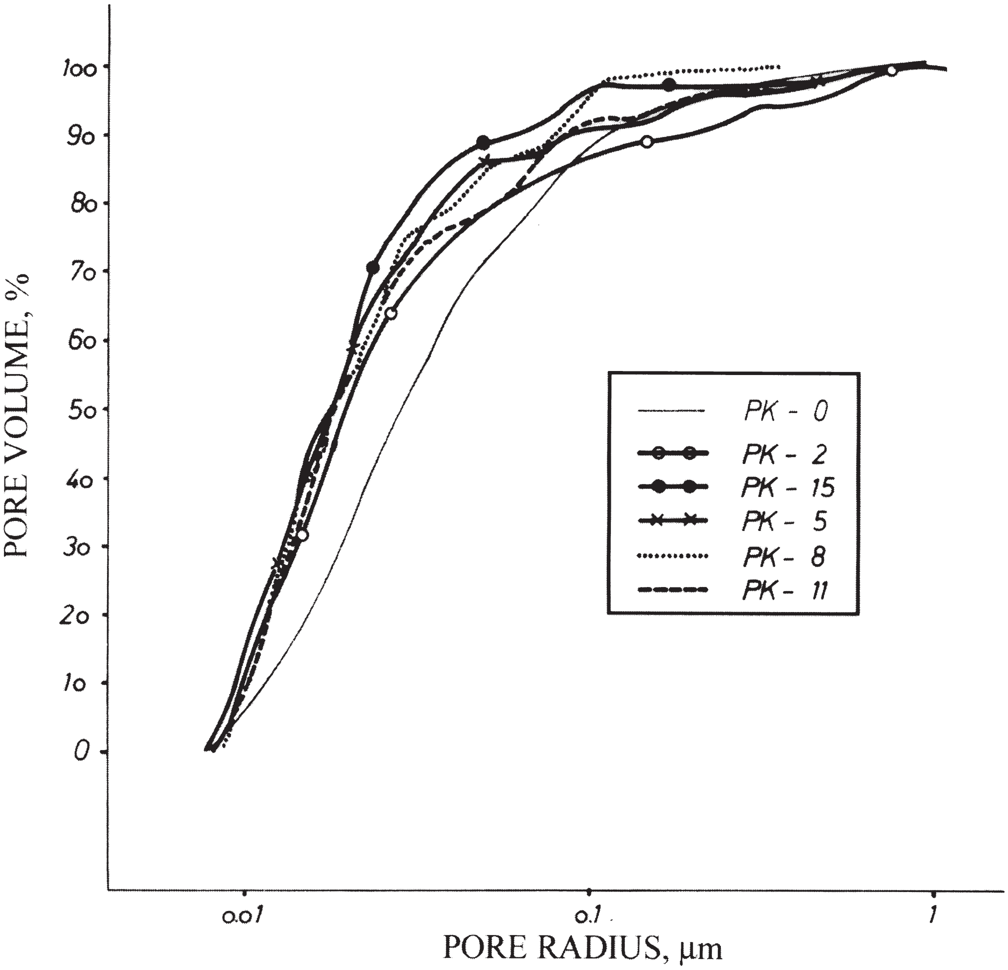

Fig. 6. Pore size distribution curves of 28-day-old PK-series mortars.

uniform, formed as an interconnected network. It is in a good correlation with the work by Ramachandran et al. [7].

The total pore volume and pore size distribution of 28-day-old mortars of P- and PK-series are shown in Fig. 5 and Fig. 6. The increase of silica fume the P-series mortars results with the increase of the W/C ratio and with the increase of the total pore volume (Fig. 5). Comparing the porosity of the P-0 and PK-0 mortars, it can be established that the addition of limestone increases the porosity. When silica fume is added to the mortars containing limestone (PK-series), the total porosity of mortars decrease at first, and the curve has its minimum value at 8 wt% of silica. By adding up to 8 wt% of silica the porosity increases. The results obtained for decreasing total pore volume in mortars containing up to 8 wt% of silica fume are in good correlation with development of compressive strength up to 28 days of hydration (Fig. 2).

Pore size distribution curves of 28-day-old PK-series mortars, as given in Fig. 6, show that the addition of silica fume to the PK-series mortars increases only the portion of smaller pores in the system. Recently, it has been shown that the addition of up to 5 wt% of silica increases the quantity of the small pores, but higher additions of silica (more than of 5 wt%) increase the larger pores in the P-series mortars [5].

The derivate plots of cumulative pore volume of dV/dln r versus pore radius, r for 28-day-old mortars of P- and PK-series were made, and are shown in Fig. 7. Compared to mortar containing no silica fume (P-0) addition of silica up to 5 wt% (P-series) increases the number of small pores from 0.01 to 0.02 μm. The derivate maximum occurrence at about 0.015 μm. With the increase of silica fume content (over 5 wt%) the derivate maximum decreases, and the number of higher pores increases in the range of 0.02 to 0.06 μm. The derivate plots indicate a great difference between the mortars of P- and PK-series. At a 15 wt% replacement of cement by the equal weight of limestone, the derivate plot shows discontinous pore structure with two maximums. As both cement and limestone show similar characteristics (the specific surface area and pore size distribution) their different behaviour perhaps indicating the limestone activity during cement hydration, which is responsible for the development of pore structure, producing size distribution covering many orders of magnitude. In Fig. 7, a de-

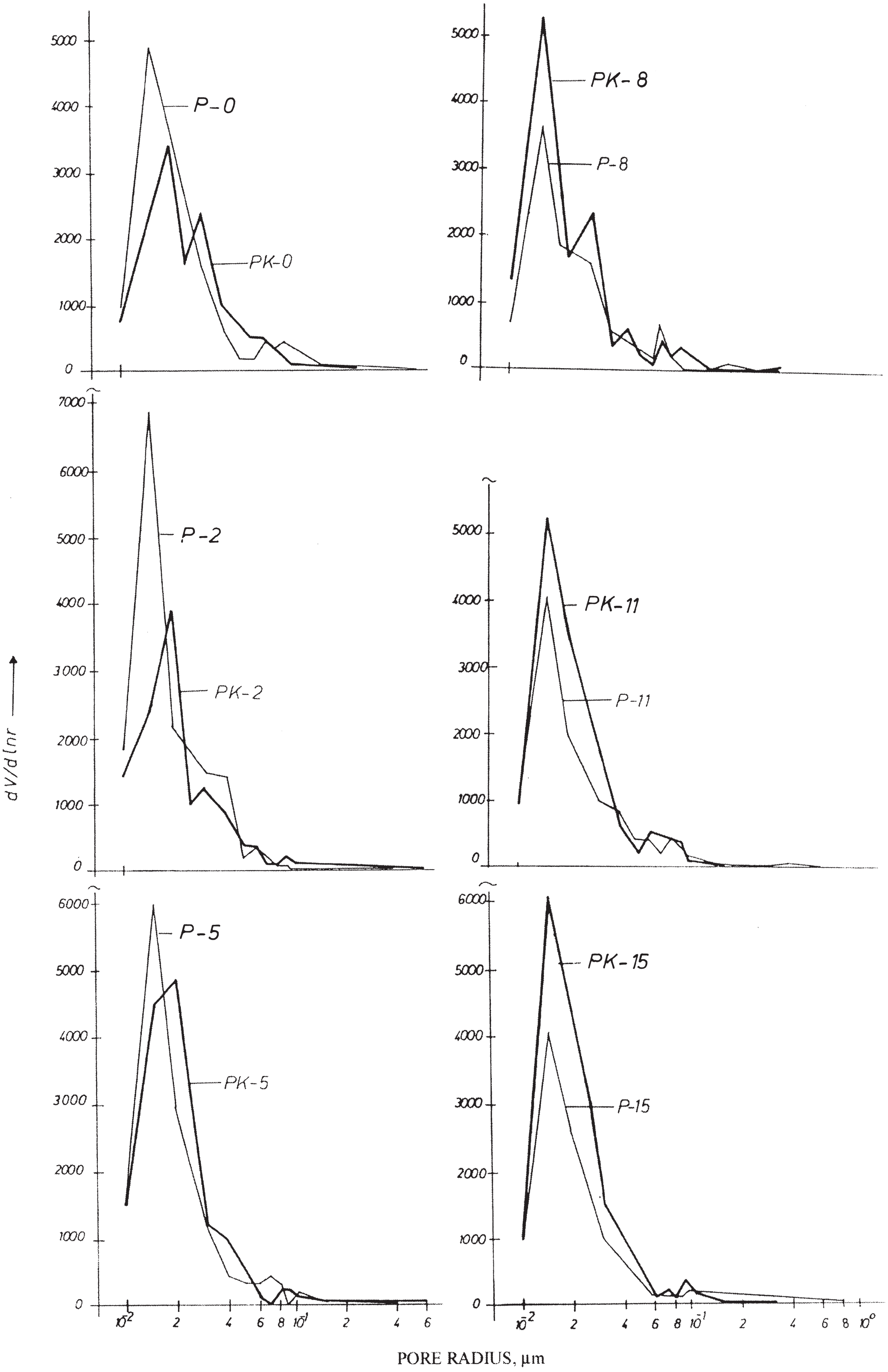

Fig. 7. The derivative plots pore voume vs. pore radius.

crease of the number of small pores and a shift of the radius of pores to higher pores when limestone is added is seen.

The addition up to 5 wt% of silica fume into the system containing limestone decreases the volume of small pores between 0.01–0.04 μm and derivate plots show a maximum occurrence at about 0.02 μm. But, with higher additions of silica fume (over 5 wt%) a greater number of small pores is seen than in analogous samples containing no limestone, and the derivate maximum occurs at about 0.015 μm. The PK-0 and PK-8 samples have a discontinuous pore structure with the first maximum of occurrence of pores at 0.02 μm radii and the second maximum of occurrence at a pore radii of 0.03 μm. The mortar containing 8 wt% of silica fume (sample PK-8) also has the lower porosity and shows the best mechanical properties. According to Feldman [15], a discontinuous pore structure attributes to a lower permeability, and better resistance to sulphate attack. It has been shown that all PK-series samples are characterized by good sulphate resistance and show the lower expansion of mortars than the P-series ones. The P-0 sample disintegrated after only 60 days while the PK-0 endured 150 days immersion in the sulphate solutions before breakdown [13].

4. Conclusions

1. The hydration reaction in the Portland cement-limestone-silica fume system is controlled both by the amount of the non-evaporable water content and by the free CH content. Only a moderate increase in the non-evaporable water content during a period of 28 days was observed. Upon replacement of Portland cement by up to 8 wt% of silica fume, however, the non-evaporable water content decreased from 28 to 120 days. The decrease of the CH content, as result of the pozzolanic reaction, is visible only in the sample containing more than 8 wt% of silica fume. At a 15 wt% replacement, approximately all of the CH has been consumed during a period of 120 days.
2. The replacement of Portland cement by 15 wt% of limestone caused a reduction in the compressive strength. When silica fume was added together with limestone, the mortars containing up to 8 wt% of silica fume showed a considerable increase in the earlier compressive strength. After 28 days hydration mortars containing more than 8 wt% show higher strength than mortar containing no silica fume.
3. Limestone considerably increases the total porosity of mortars. However, introduced together with silica fume up to 8 wt% of silica, it decreases the porosity. When more than 8 wt% of silica is present, the porosity increases again. The cement mortar containing 8 wt% of silica fume shows the highest compressive strength, a minimum value of the total porosity, and its pore size distribution curve shows a discontinuous pore structure. The morphological features of mortars containing limestone is well consolidated with a network-like structure.
4. The measurement of the CO_2 content in limestone remaining after a period of 120 days indicated that limestone is taken up to system. Approximately 5.09 wt% is available for reaction during 120 days of hydration in a system not containing silica fume. Therefore, limestone can be an active participant in the hydration reaction of Portland cement. However, the amount of limestone incorporated is affected by the silica fume content. The increase of silica content is reflected in the decrease of incorporated limestone. Accordingly, the replacement of Portland cement with more than 8 wt% of silica causes reductions both in the amount of cement and in the CH content available for limestone reaction as active participant. Thus, in these conditions, limestone acts as filler.
5. Combined effect of both silica fume and limestone addition affect the hydration process and development of the pore structure. Both silica fume and limestone can act as inert and active participants. Ratio of their effect changes depending both on their individual content and on the hydration time.

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