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Microstructural investigation of a silica fume–cement–lime mortar

P.J.P. Gleize [a,*], A. Müller [b], H.R. Roman [a]

[a] Civil Engineering Department, Federal University of Santa Catarina, Caixa Postal 476, 88040-900 Florianópolis, SC, Brazil
[b] Materials Engineering Department, Federal University of Santa Catarina, Caixa Postal 476, 88040-900 Florianópolis, SC, Brazil

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Abstract

Several additions, minerals and organic, are used in mortars, such as pozzolanic materials, cementicious materials and polymers. Literature about the use of additions in masonry mortars (cement/lime/sand mixes) is scarce; usually, studies are about concrete mortars. The purpose of this work is to study the microstructural effects of the substitution of 10% of Portland cement by silica fume in a 1:1:6 (cement/lime/sand mix proportion by volume) masonry mortar. Scanning electron microscopy with energy dispersive X-rays analysis (SEM/EDX) shows that, with silica fume, the C–S–H formed is type III at early ages and that type III and type I coexist at later ages. Silica fume lowers the total porosity and increases compressive strength only at later age and, as expected, the pore structure of mortar with silica fume is found to be finer than of non-silica fume mortar.

Keywords: Cement–lime mortar; Microstructure; Silica fume

1. Introduction

Masonry mortar can be defined as a mixture of Portland cement, hydrated lime and mineral aggregates (sand) with water, which presents hardening capacity and adherence. Masonry mortar functions are: (i) bond units of masonry; (ii) distribute loads; (iii) absorb deformations; (iv) seal joints. Masonry mortars can be employed for joining bricks/blocks, rendering and grouting.

Hydrated calcium silicate, commonly designated C–S–H, is the main compound produced by hydration of Portland cement. In ordinary Portland cement (without additives) the C/S ratio is about 1.5 [1,2]. According to the literature [2–4], in Portland cement mortars, C–S–H gel can exhibit three morphologies: fibrous-acicular form (type I), reticuled or honeycomb form (type II) and denser-almost spheres form (type III). Lime improves plasticity and, consequently, workability, of masonry mortars. It hardens mainly by carbonation.

The microstructure of Portland cement based materials is complex due to: (i) the presence of several hydrated phases, with composition and microstructure characteristics varying locally; (ii) the presence of an aqueous phase of variable composition in a pore net with sizes varying over a large range; (iii) the change of the microstructure with the passing of time and with the environmental conditions (relative humidity, temperature) and; (iv) that the physical and mechanical behavior of the material is often controlled by zones with special microstructures, that occur in specific places in the system, instead of the prevalent general microstructure (example: aggregate–cement paste interfacial zone) [3].

Microstructure has an interdependence with physical and mechanical properties of these materials, such as workability, water retention, compressive and tensile strength, Young's modulus and Poisson's ratio.

Pozzolanic materials and fillers can substitute Portland cement in mortars. These materials change the microstructure of mortars and, consequently, modify some of its properties. Literature about the use of additions in masonry mortars (cement/lime/sand mixes) is scarce; studies are usually about concrete mortars.

Silica fume, which is a very fine pozzolanic material, is commonly used in Portland cement mortars and concretes in order to improve mechanical strength and reduce porosity [4]. The effects of Portland cement partial substitution by silica fume in lime–cement mortars microstructure are not fully established.

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[*] Corresponding author. Tel.: +55-48-331-5176; fax: +55-48-331-5191.

E-mail address: ecvlphg@ecv.ufsc.br (P.J.P. Gleize).

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The aim of this work is to investigate microstructural changes of 10% substitution of Portland cement by silica fume in a 1:1:6 (cement/lime/sand mix volume proportion) masonry mortar through the use of scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and non-evaporable water content.

2. Materials and methods

The Portland cement used is type CPI-S-32 according to Brazilian Standards (ASTM Type I). Table 1 gives its chemical characterization. Lime used is class CH-III according to Brazilian Standards (ABNT). Its chemical composition is given in Table 2. Silica fume has a specific surface area of approximately 26 m^2/g and its main chemical component is SiO_2 (Table 3). Sand was washed, and oven dried for 24 h (105 °C). Sand grading (Table 4) fits in the interval fixed by the BS 1200 (1976) [5]; it has a specific gravity of 2580 kg/m^3 and an organic matter content of less than 300 ppm.

Proportion of components was 1:1:6 (cement or cement + silica fume:lime:sand), by volume. Good workability (255 ± 10 mm measured by the flow table test [6]) was enhanced with a water/cement ratio of 1.85 for the reference mortar (without silica fume). Portland cement was partially substituted by 10% silica fume, according to Table 5. The use of a 0.3% (wt% binder) superplasticizer additive (melamim type) was necessary to maintain constant the water/binder (cement + silica fume) ratio due to the high finess of the silica fume. Volume proportion of components were converted in weight to avoid measurement imprecision on mixing process: 1:0.71:8.61 (cement:lime:sand) for the reference mortar and 1:0.08:0.79:9.57 (cement:silica fume:lime:sand) for the mortar with 10% silica fume.

The mixer used was a 10 l vertical ax type. Mixing was done according to Brazilian Standard NBR 13276 [6] recommendations. Sand and lime were blended for 2 min. Water was then added and mixed for 4 min in low speed. The lime mortar was weighted and left in a covered plastic recipient. After 48 h, the lime mortar was weighted again and the quantity corresponding to the water lost by evaporation was added. The lime mortar was introduced in the mixer and the binder (cement or cement + silica fume) was added and mixed for 4 min. For the cement–silica fume mortar, the superplasticizer was added 1 min later. Consistency was measured by the flow table test [6]. The mortars were cast in forms and demolded 48 h later. Curing was made in laboratory ambient (to allow lime carbonation) until the test day (RH 80% and 23 °C).

Table 1
Cement composition

Compound	wt%
Al_2O_3	4.31
SiO_2	19.81
Fe_2O_3	2.60
CaO	61.47
MgO	5.09
SO_3	2.51
Ignition loss	3.26
Free CaO	1.78
Insoluble residue	0.63

Table 2
Lime composition

Compound	wt%
Ignition loss	20.0
$Fe_2O_3 + Al_2O_3$	0.99
CaO	40.0
MgO	28.0
SO_3	0.04
CO_2	$\leqslant 15.0$
CaO + MgO	$\geqslant 88.0$

Table 3
Silica fume composition

Compound	wt%
SiO_2	95.10
Al_2O_3	0.09
Fe_2O_3	0.10
CaO	0.24
MgO	0.43
Na_2O	0.23
K_2O	0.93

Table 4
Sand grading

Sieve size (mm)	% Retained
0.15	97.8
0.3	80.4
0.6	49.6
1.2	20.7
2.4	6.1
4.8	0

Following the recommendations of Brazilian Standards (ABNT), three cylindrical samples (5 × 10 cm^2) were prepared for compressive strength [7]. The adopted rate of loading was 1.5 MPa/min due to the low strength of mortars.

For SEM observations, and non-evaporable water content, samples were extracted from the core of compression test samples at the age of 7 and 28 d. For SEM observations, samples were covered with a thin gold layer and C/S ratio were measured by energy dispersive X-rays analysis (EDX) as the average of four measurements of the same zone. Non-evaporable water content was measured by the weight loss between 105 and 1000 °C as described elsewhere [8].

Table 5
Volume proportions between constituent materials of mortars

Mortar	Cement	Lime	Silica fume	Sand	Water/cement or water/ (cement + silica fume)
Reference	1.0	1.0	0.0	6.0	1.85
10% Silica fume	0.9	1.0	0.1	6.0	1.85

For mercury intrusion microscopy (MIP), samples were extracted from the core of cylinders crushed at a relatively high rate of load application (approximately 25 MPa/min). Under short term loading the chance of micro crack propagation is minimum [9]. Small fragments (2–3 g) were immersed in acetone to arrest further hydration. This was followed by oven drying for 24 h at 105 °C before MIP measurement. The pressure was applied from 0 to 240 MPa. A constant contact angle of 130° and a constant surface tension of mercury of 485 dyn/cm were assumed for the pore size calculation.

3. Results and discussions

3.1. SEM/EDX observations

In mortar without silica fume (reference mortar), at 7 and 28 days old (Fig. 1), morphology of C–S–H gel appears as type III [3] (denser-almost spheres); it is intimately mixed with lime as EDX analysis (Table 6) shows C/S ratios between 2.2 and 2.5 (C/S ratio is commonly 1.5 in Portland cement composites without lime [1]). Large plates of calcium hydroxide are present as showed in Fig. 1 (C/S ratio $\cong$ 8.7).

At 7 days old, observations of mortar with 10% silica fume (Fig. 2(a)) shows that the paste is denser than that C–S–H appears as type III and C/S ratio decreases (nearly 1.6) due to the presence of silica fume. No calcium hydroxide plates were observed. At 28 days old, the presence of two C–S–H morphologies was noted: type III (C/S ratio nearly 2.0) as observed for 7 days old samples, and a new feature as C–S–H type I, with fibrous-acicular morphology and a higher C/S ratio, nearly 3.6 (Fig. 2(b)) [3]. Paste densification due to silica fume is not evident.

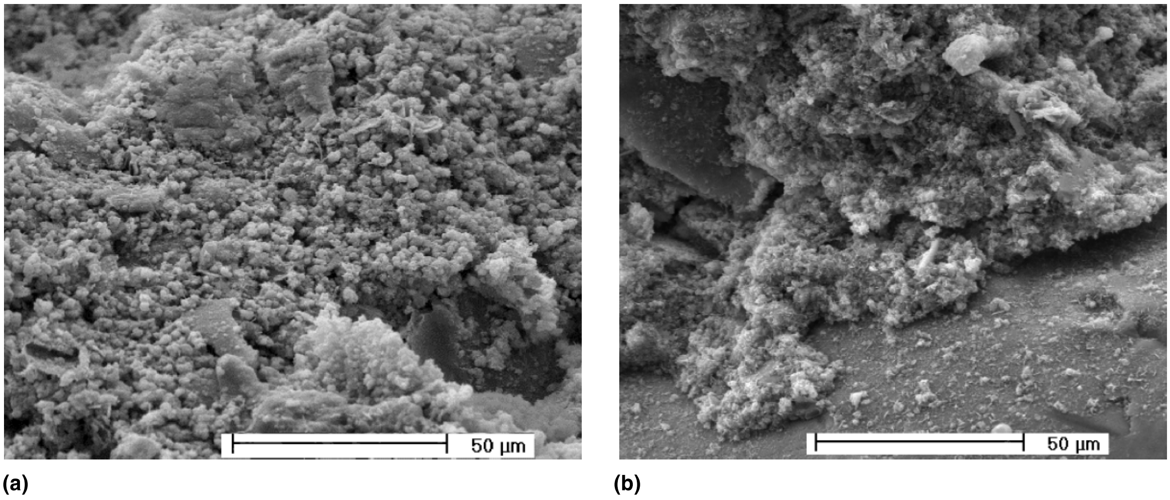
Table 6
C/S ratios of C–S–H gel

	7 days old	28 days old
0% Silica fume type III C–S–H	2.2	2.5
10% Silica fume type III C–S–H	1.6	2.0
10% Silica fume type I C–S–H	Not observed	3.6

Table 6 summarizes C/S ratios of C–S–H gel for masonry mortars with 0 and 10% silica fume at 7 and 28 days old.

As observed in Portland cement mortars and concretes (without lime) [1], C–S–H becomes richer in silica with silica fume addition in masonry mortars (with lime).

According to the literature [2–4], it can be found in Portland cement mortars (without lime) the coexistence of C–S–H type I (“acicular”), type II (“honeycomb”), type III (“compact”) and great hexagonal calcium hydroxide crystals. In masonry mortars (without



(a) (b)

Fig. 1. SEM micrograph of reference mortar: (a) 7 days old; (b) 28 days old.

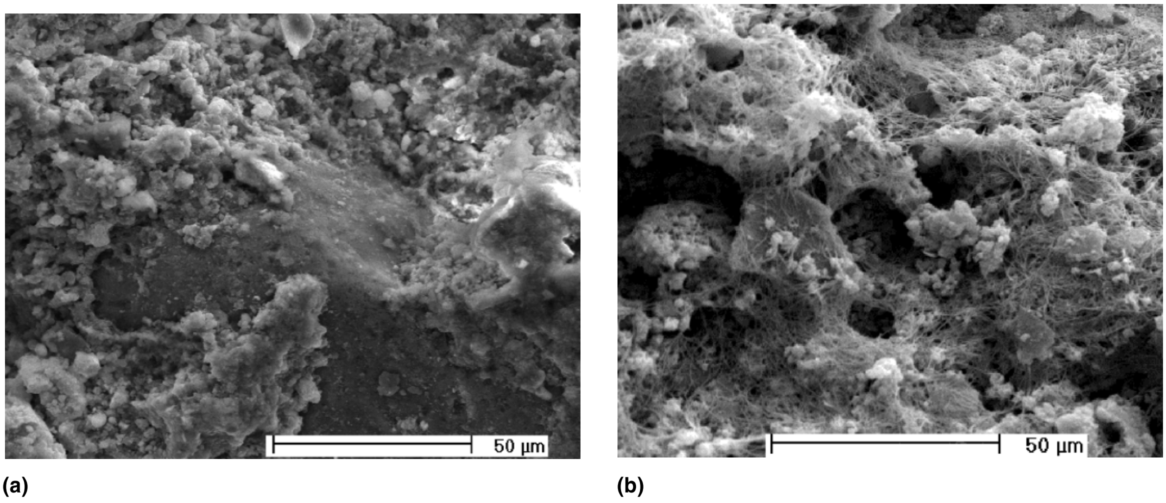


Fig. 2. SEM micrograph of 10% silica fume mortar: (a) 7 days old; (b) 28 days old.

silica fume), only C–S–H type III was observed (Fig. 1), as well as calcium hydroxide, but not well crystallized.

In Portland cement mortars (without lime) with silica fume at any age, literature relates that only C–S–H type III is formed and that hexagonal calcium hydroxide crystals were never observed [2,3]. Similarly, in masonry mortars with lime and silica fume, the presence of hexagonal crystals of calcium hydroxide was never observed. At 7 days old, only the presence of type III C–S–H was noted with a lower C/S ratio. However at 28 days old, type I C–S–H was observed coexisting with type III. EDX measurements showed that C–S–H type I has a higher C/S ratio than C–S–H type III (Table 6). C–S–H type I grows in paste capillary voids and its formation is presumably caused by the pozzolanic reaction between silica fume and hydrated lime at later age (Fig. 2(b)).

3.2. Porosity and pore structure

As can be seen (Table 7) silica fume lowers the total porosity only at 28 days old and as it was expected, the pore structure of mortar with silica fume is found to be finer than of non-silica fume mortar (Figs. 3 and 4). But this refinement in pore size is more pronounced at 28 than 7 days due to silica fume pozzolanic reaction.

Table 7
Total porosity of mortars

Silica fume content (%)	Age (day)	Total porosity (%)
0	7	30.57
10	7	32.31
0	28	28.53
10	28	27.92

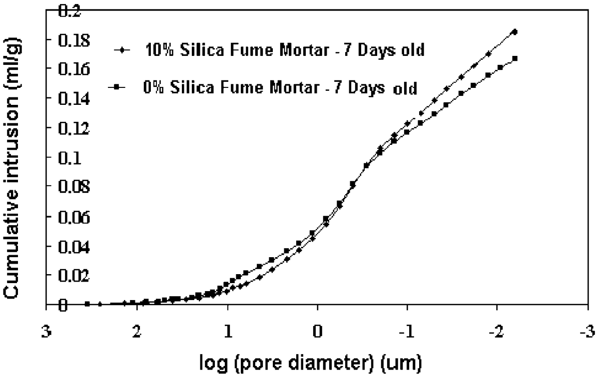


Fig. 3. Pore size distribution of mortars at 7 days old.

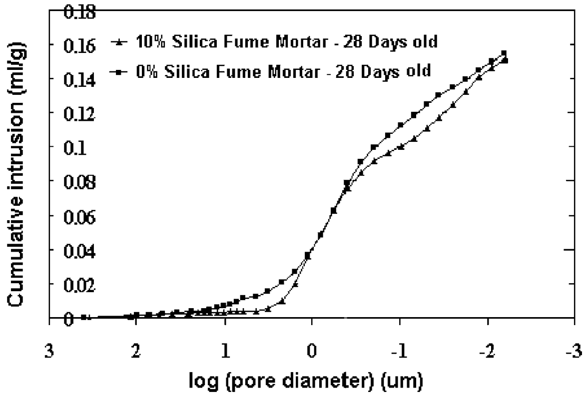


Fig. 4. Pore size distribution of mortars at 28 days old.

3.3. Compressive strength and non-evaporable water content

There is a significant difference between the compressive strength of 28 days old mortars with the in-

Table 8
Mortar compressive strength, MPa

Age	0% Silica fume	10% Silica fume
7 days old	3.26 ± 0.12	2.93 ± 0.13
28 days old	6.58 ± 0.19	7.11 ± 0.25

Table 9
Non-evaporable water content in mortars (percent relative to dry binder content)

Age	0% Silica fume	10% Silica fume
3 days old	10.4 ± 0.3	9.3 ± 0.6
7 days old	11.6 ± 0.7	10.6 ± 0.8
28 days old	14.7 ± 0.5	16.4 ± 1.0

crease of silica fume content (Table 8). Densification of paste can be the explanation for this behavior. Densification is the result of the microfiller effect and high pozzolanic activity of silica fume in the mortar paste. However, it can be noted that this effect only occurs at a later age. Non-evaporable water content results presented in Table 9 are coherent with the evolution of mortars compressive strengths. 10% cement substitution by silica fume decreases non-evaporable water at early age but it increases at later age due to silica fume pozzolanic effect.

4. Conclusions

In Portland cement mortars (without lime) with high w/c ratio, a coexistence of type I C–S–H (“acicular”), type II C–S–H (“honeycomb”), type III C–S–H (“compact”) and large hexagonal calcium hydroxide crystals occurs. In cement-lime mortar (without silica fume) with high w/c ratio, only type III C–S–H was observed, as well as calcium hydroxide, but not well crystallized. In Portland cement mortars with silica fume, literature relates only the presence of type III C–S–H at any age. SEM observations of Portland cement–lime mortars with silica fume show that, after the formation of type III C–S–H at an early age, there is the formation of type I C–S–H at later ages with a higher C/S ratio than type III C–S–H. Type I C–S–H formation is probably due to silica fume pozzolanic reaction with hydrated lime, and it grows in paste capillary voids. As a result, silica fume–cement–lime mortars compressive strength is smaller and porosity is higher than reference mortars at early age (7 days old) but becomes, respectively, higher and smaller at a later age (28 days old).

In Portland cement mortars, silica fume acts mainly at the interface paste–aggregate, where there is a higher concentration of calcium hydroxide and greater porosity than in paste. In Portland cement–lime mortars with silica fume, lime is better distributed in the paste and there is no evidence of concentration of silica fume at the interface paste–aggregate. In this case, silica fume pozzolanic reaction seems to occur mainly in larger capillary pores.

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