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Influence of the microsilica state on pozzolanic reaction rate

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Abstract

Silica fume is generally supplied as an ultrafine powder in its original state, densified or in suspension. The difference in states should not influence the pozzolanic behaviour of this by-product in a cementitious matrix. In the present work, experimental results relating to pozzolanic reaction have been obtained by different methods: a chemical method, in which lime fixed by pozzolanic material through time is quantified, and a physicochemical method based on the Langavant calorimeter. By the second method, information regarding silica fume is obtained from the value of heat of hydration released by a mortar containing this by-product. These results show that the silica fume in its densified state considerably decreases its chemical reactivity with calcium hydroxide (pozzolanic activity).

Keywords: Hydration; Heat of hydration; Pozzolanic activity; Silica fume; Mortar

In a previous work the authors demonstrated the effect of different pozzolanic materials on heat of hydration developed by blended cements compared to a control cement. These results showed that pozzolanic materials do not cause a reduction in heat equivalent to the amount of cement substituted [1]. Thus, when silica fume (SF) reacts with calcium hydroxide from the hydration of portland cement, there is an increase in the heat of hydration, particularly in the early stages [2,3], which is not witnessed in the case of fly ash or other materials of low activity at early ages. Reaction rate of pozzolanic materials depends on various factors, such as the origin, chemical and mineralogical composition, morphology, fineness, and other factors [4].

SF is now commercially sold in densified form in order to make its transport and management easier. This produces changes in the original state of the material. As a result, important properties such as specific surface and particle size are varied. Although it was originally believed that densified SF can maintain the original material characteristics, some authors have expressed doubts concerning whether agglomerate particles are totally desegregated in the bulk of mortar or concrete [5].

This research is aimed at studying the influence of the decrease of specific surface on the pozzolanic reaction rate.

1. Methods

1.1. Materials

The materials chosen for this study are: cement, sand, and SF in its original state and in a densified form.

According to the Spanish UNE 80 301 standard [6], the cement was a CEM I/42,5R cement with a clinker content equal to or above 95% and could have up to 5% additional components. The sand used was of siliceous origin with a silica content of more than 98% and maximum particle size of less than 2 mm. SF powder was SF in its original state. The main chemical constituent is silica (91.22%) and 6.6% loss of ignition (LOI). Densified SF (DSF) had a silica content of 92.35% and 4.9% loss on ignition.

The high amorphicity of both products is evident from the hump in the X-ray diffraction pattern (Fig. 1), although peaks of quartz, silicon carbide, and trydimite can be seen. Thus, both materials show similar chemical and mineralogical compositions.

The fineness of SF was studied by scanning electron microscopy (SEM). Aggregation of particles is observed in both cases (Fig. 2), although this effect is intensified with densification process. In this way, whereas SF presents particles with a diameter about 10–20 μm formed by aggregated microparticles, in the case of SFD the densification produces spheres with a diameter higher than 100 μm, although it is formed by small particles of less than 1 μm of diameter (Fig. 2). This is also confirmed by the specific surface values, 15,000 cm^2/g Blaine unity for original SF and 5400 cm^2/g for densified SF.

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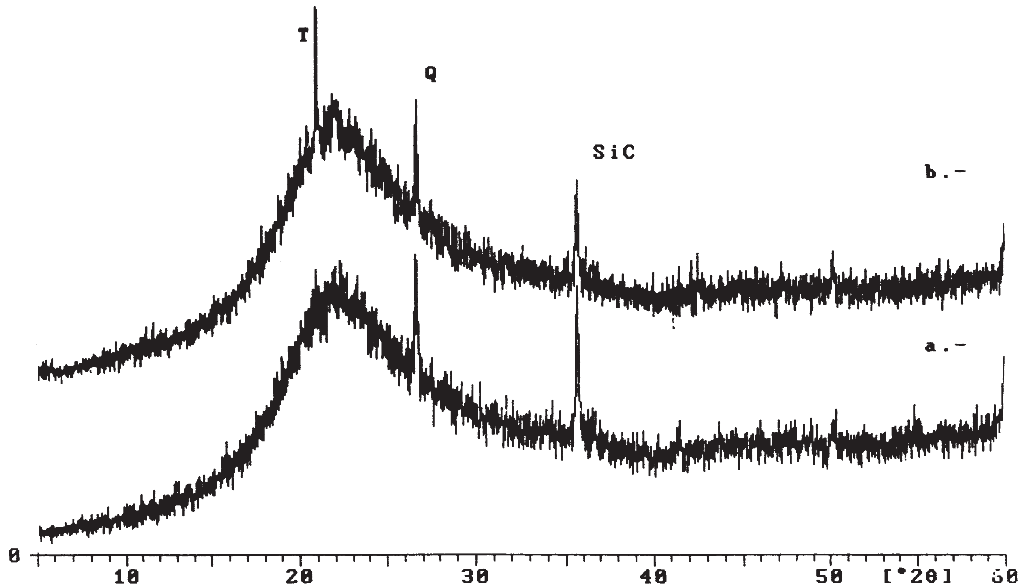


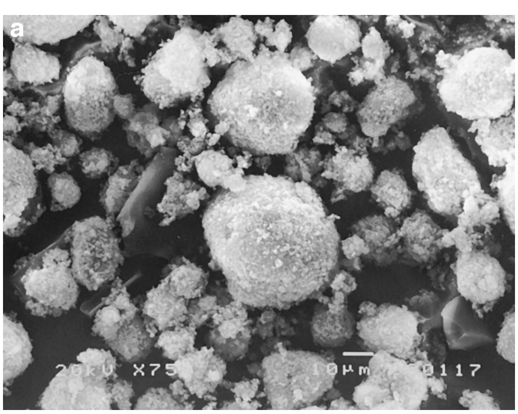
Fig. 1. X-ray diffraction patterns: *(a)* SF; *(b)* DSF.

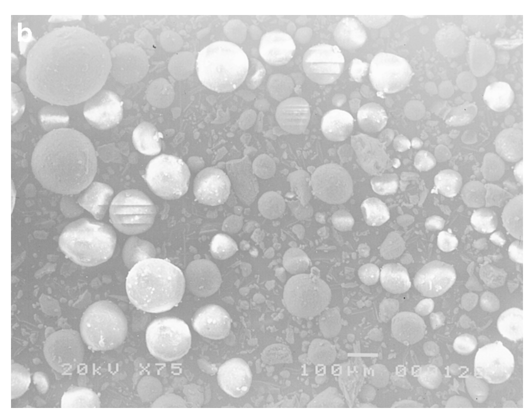
1.2. Blended cements

The blended cements were prepared in a high-speed powder mixer to guarantee their perfect homogeneity and safeguard their granulometry. Mixtures were prepared by weight in the following proportions: cement/silica fumes (SF, DSF): 100/0; 90/10. These cements were used to prepare mortars whose sand/cement proportion was 3/1 and water/cement ratio was 0.5.

1.3. Methods

Pozzolanic activity of materials is a well-studied field [7–10]. There are a great number of test methodologies, but





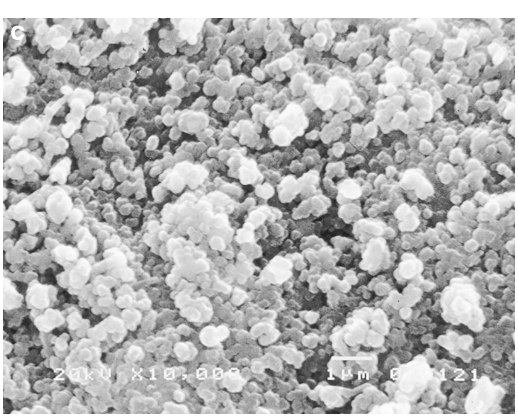
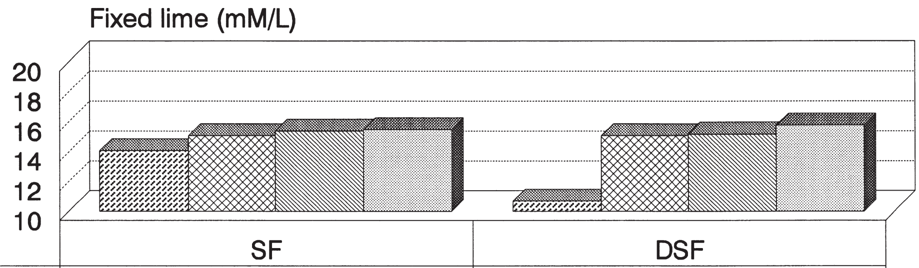


Fig. 2. SEM: *(a)* SF; *(b)* DSF; *(c)* DSF.



	SF	DSF
1 Day	14,1	10,7
3 Days	15,1	15,1
7 Days	15,4	15,2
28 Days	15,5	15,8

Samples

1 Day 3 Days 7 Days 28 Days

Fig. 3. Pozzolanic activity: fixed lime over time.

they are all based on the ability of reaction with the calcium hydroxide in aqueous medium to form hydraulic compounds [11].

1.3.1. Pozzolanic activity test

To study the pozzolanic activity of these materials, an accelerated method was used that measured the evolution of the material-lime reaction as a function of time. The test consists of putting the different pozzolanic materials in contact with the saturated lime solution at 40 ± 1°C for 2 h, 1, 7, and 28 days. At the end of that time, the CaO concentration in the solution was measured. The fixed lime (mM/L) was obtained from the difference between the concentration in the saturated lime solution and CaO in solution in contact with the sample at the end of the given period. The lime fixed value is a good indicator of pozzolanic activity of the materials. This is larger as the lime fixed amount increase.

1.3.2. Heat of hydration test

The method used for determining hydration heat in the Spanish standard [12] is based on the Langavant calorimeter [13]. This semiadiabatic method consists of quantifying the heat generated during cement hydration using a Dewar flask, or, more exactly, a thermally isolated bottle. Since the exterior conditions have a strong influence, the test is carried out in a perfectly climatized room at 20 ± 2°C. The measurements were made over 5 days, since the heat increase is very low at later times, and the relative error of the measurement increases beyond that time.

2. Results and discussion

2.1. Pozzolanic activity of the materials

The results obtained are shown in Fig. 3. After 24 h the SF has fixed 14.1 mM/L of lime in comparison to 10.7 mM/L by the DFS. Thus, pozzolanic activity is higher in the case of undensified SF although they are equal at 3 days.

However, studies carried out on SEM samples in contact with saturated lime solution for 28 days show a very different morphology of the resultant product. Whereas dense masses of hydration products are formed with SF (see Fig. 4), hydration products joined to unreacted or partially reacted silica particles are seen with DSF, which shows a matrix with a different morphology.

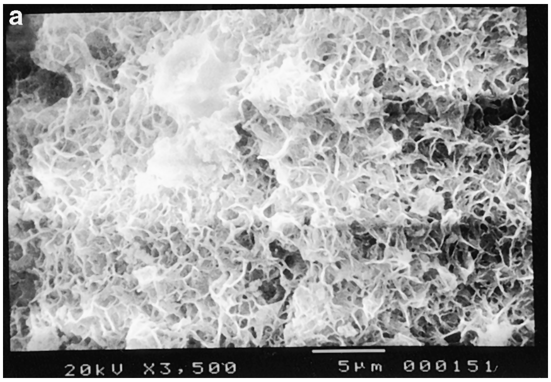
2.2. Heat of hydration

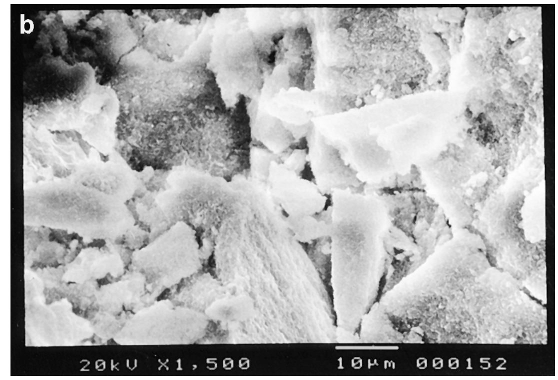
The mortars that have pozzolanic material incorporated in them usually have decreased heat of hydration compared to cement during the first hours of the test, depending on the pozzolanic activity of the material; the reaction taking place with the lime also gives off some heat. However, between 5 and 12 h of the test, reactions due to portland cement are strongly exothermal, which makes the ascending slope of the curves very steep; after 48 h the temperature begins to stabilize and the heat given off is of little significance.

Fig. 5 shows positive and negative heat increments where plain cement mortar is considered as zero. As can be seen, the mortar with SF undergoes a positive increment with respect to base mortar while it is the opposite when densified SF is incorporated. This shows that SF activity [2] that increases heat of hydration at early ages, decreases notably when this material is in densified state.

3. Conclusions

This study confirms the direct relationship between pozzolanic activity of materials (expressed as fixed lime) and heat of hydration. The results show that densified SF partially affects the characteristic properties of the original material.





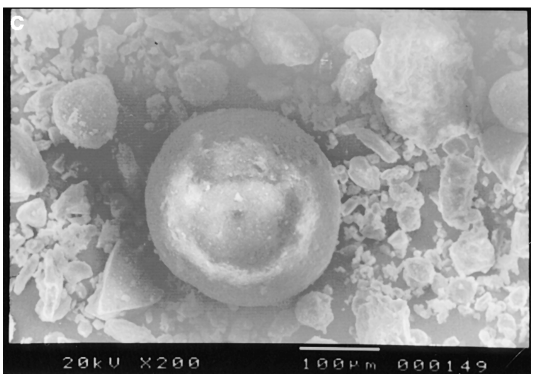


Fig. 4. SEM: SF in the saturated lime solution for 28 days. *(a)* Dense masses of hydration products formed with SF; *(b* and *c)* hydration products joined to unreacted or partially reacted silica particles (DSF).

Pozzolanic activity for nondensified silica fumes is higher in the first setting stages in comparison with other pozzolanic materials (natural pozzolans, fly ashes, etc.) and hence, mortar with this product has positive heat increment. However, when SF is densified, the material shows a normal pozzolanic activity during the first hours, decreasing heat of hydration due to the effect of cement substitution and then losing the most interesting characteristic of SF—its high activity at early ages.

Thus, precautions must be taken when SF is used to obtained the desired performance. It is necessary to reach a good dispersion of particles before and during their incorporation in the mortar or concrete mass. This factor becomes important when low water/cement ratios are used to obtain high performance concrete in which a bad dispersion of SF particles may have a negative effect, mainly at initial stages.

Acknowledgments

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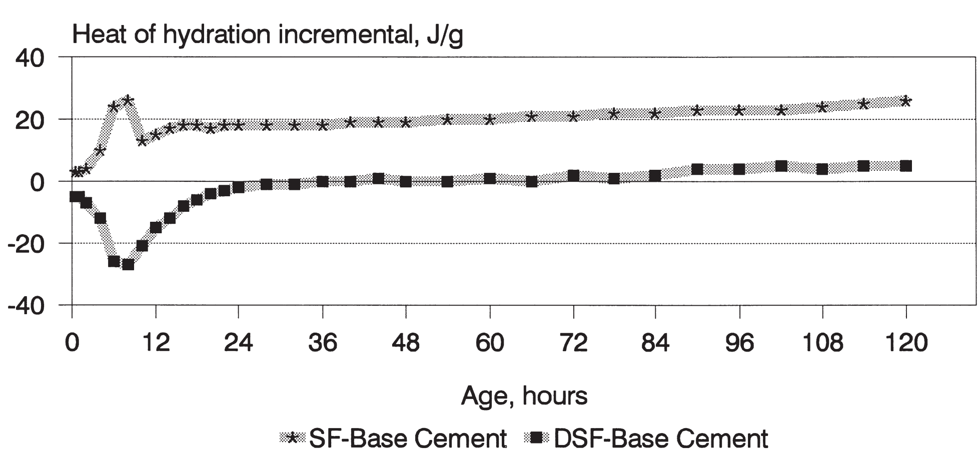

Fig. 5. Heat of hydration incremental over time.

References

[1] M.I. Sánchez de Rojas, M.P. Luxan, M. Frías, N. García, Cem Concr Res 23 (1) (1993) 46–54.
[2] M.I. Sánchez de Rojas, M. Frías, Fifth CANMET/ACI Int. Conf. Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Vol. 2, Milwaukee, WI, USA, 1995, pp. 829–843.
[3] M.I. Sánchez de Rojas, M. Frías, Cem Concr Res 26 (2) (1996) 203–213.
[4] A. Traetteberg, Il Cemento 3 (1978) 369–376.
[5] L. Sarkar, Advances in Concrete Technology, CANMET, V.M. Malhotra (ed.), Canada Communication Group, Ottawa, Canada, 1992, pp. 123–158.
[6] Norma Une 80 301, Cementos. Definiciones, Clasificación y Especificaciones, 1996.
[7] J. Calleja, Ion, Nos. 340, 341, 343, and 344, November and December 1969, January and February 1970, 623-38, 700-13, 81-90, 154-60.
[8] F. Soria, Materiales de Construcción, 190–191 (1983) 69–84.
[9] R. Sersale, 7th Int. Congr. Chem. Cem., IV-1/3-21, Paris, 1980.
[10] K. Takemoto, H. Uchikawa, 7th Int. Congr. Chem. Cem., I, IV-2/1-29, Paris, 1980.
[11] M.P. Luxan, M.I. Sánchez de Rojas, Materiales de Construcción, 35 (200) (1985) 3–13.
[12] Norma Une 80 118, Métodos de Ensayo de Cementos. Ensayos Físicos: Determinación del Calor de Hidratación por Calorimetría Semiadiabática (Método del Calorímetro de Langavant), 1986.
[13] R. Alegre, Revue des Matériaux 547 (1961) 218–229, 548 (1961) 247–262.