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Hydration Process in $3CaO.SiO_2$–Silica Fume Mixtures

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Abstract

The hydration process and hydrate compounds formed in the C_3S–silica fume mixtures, were investigated using thermal analysis and BET specific surface determinations. Polymerization of silicates anions in the calcium silicate hydrates was studied using the molybdate method. The addition of silica fume to C_3S, increases the kinetics of hydration–hydrolysis, for short periods of time (one day). An increase of Type I calcium silicate hydrates proportion was observed. The results of the molybdate complex method confirm that the presence of silica fume in a hydrating system influences the kinetics of the silicate anion polymerization process because of its pozzolanicity. © 1997 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Tricalcium silicate pastes, silica fume, hydration process, thermal analysis, BET specific surface, molybdate method.

INTRODUCTION

The hydration and hardening of silica fume binder systems have been well studied over the last twenty years. However, there is limited information on the influence of silica fume on the hydration process of the main portland cement components.

In a previous paper,[1] the tricalcium silicate hydration–hydrolysis and hardening processes were investigated from the point of view of their physical and chemical characteristics as a function of silica fume content in the system.

New data on the interaction processes and resulting hydrates, obtained by thermal analysis, BET specific surface and silicate hydrates polycondensation degree determinations, are presented and discussed.

EXPERIMENTAL

Materials

Tricalcium silicate was prepared from $CaCO_3$ and SiO_2 mixture, with a 1% sodium fluorosilicate admixture, by repeated burning at 1400°C. The C_3S synthesis was verified by X-ray diffraction and chemical analysis (free lime content). Tricalcium silicate was ground to Blaine specific surface of 3476 cm^2/g.

The physical and chemical characteristics of Romanian origin silica fume used are presented in Table 1.

Methods

C_3S and silica fume were mixed to obtain the samples presented in Table 2.

The binder pastes were prepared in a CO_2 and moisture-free atmosphere, with a water/C_3S+silica fume ratio of 0.4. The pastes were sealed in plastic bags and stored for 1–360 days in a CO_2-free atmosphere. Hydration was stopped at the appropriate times by ethanol-washing and oven-drying at 100°C. The hydration and hardening processes were investigated by differential thermal analysis and thermogravimetry, BET specific surface and polycondensation degree determinations, using the molybdate complex method proposed by Durecovic.[2]

Table 1. Physical and chemical characteristics of Romanian silica fume

Chemical composition	*Components (%)*								
	SiO_2	*Al_2O_3*	*Fe_2O_3*	*CaO*	*MgO*	*K_2O*	*Na_2O*	*MnO*	*TiO_2*
	92.13	2.09	1.52	0.95	1.80	1.08	<0.01	0.46	<0.01
L.O.I. (%)	2.27								
BET specific surface (m^2/g)	22.3								
Density (cm^2/g)	2.52								

RESULTS AND DISCUSSIONS

Thermal analysis of pastes hydrated provide information on the kinetics of the hydration–hydrolysis process in C_3S-silica fume samples, and the nature and proportion of the hydrates formed. The DTA curves, presented in Figs 1–3, show that for all samples, calcium hydroxide (the endotherm from 480 to 511°C) and calcium silicate hydrates (the endotherms from 100 to 120°C and 710 to 797°C) are present. For the silica fume blend samples, the DTA curves show an exotherm at 840–853°C (Fig. 1b–e), which is characteristic of the calcium silicate hydrate CSH(I) with $CaO/SiO_2 < 1.5$. This effect is due to the reorganization of the lattice network, corresponding to anhydrous calcium silicates with a CaO/SiO_2 ratio of about 1.[3] The increase on this exotherm with the increase in the silica fume proportion confirms that, in this system, a higher quantity of the CSH(I) is formed. At later ages (28 and 360 days), on DTA curves of silica fume blended samples, another effect at 295–314°C, characterized by weight loss on TG curves, appears. This can be attributed, in our opinion, to the water loss from the CSH(I) silicate hydrates, which are formed in a greater quantity, at later ages.

From quantitative analysis of TG curves, information concerning the kinetics of C_3S hydration–hydrolysis process in the presence of silica fume and silica fume interaction with calcium hydroxide was obtained (Table 3). Figure 4 shows that a notable quantity of $Ca(OH)_2$ is formed in silica fume blend samples, after 1 day of hydration, as result of a better dispersion of C_3S particles in water, in the presence of ultrafine particles of silica fume (average diameter 0.1–0.2 μm). This phenomenon causes an intensification of C_3S hydration–hydrolysis process.

At later hydration periods of time (28 and 360 days), the pozzolanic reaction of $Ca(OH)_2$ with silica fume predominates. The results indicate lower values for experimentally obtained $Ca(OH)_2$-CHe (by processing the TG data) compared with that theoretically calculated on the basis of hydrolysis of existing C_3S fraction within the sample (CHt).

The evolution of chemically bound water in CSH provides new insight on the influence of

Table 2. Composition of C_3S+silica fume mixtures

Sample	*C_3S (mass %)*	*Silica fume (mass %)*
E	100	0
5S	95	5
10S	90	10
15S	85	15
20S	80	20

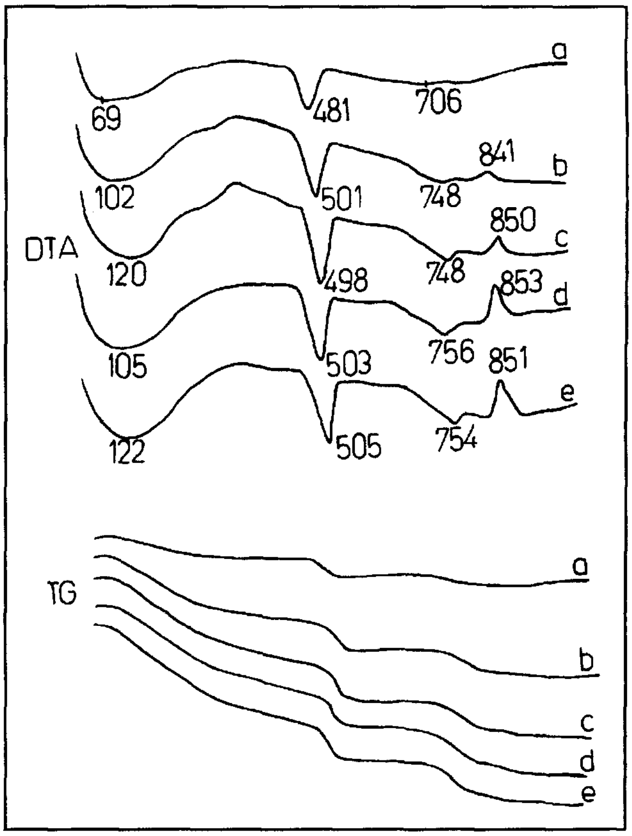

Fig. 1. DTA and TG curves at 1 day of hydration for samples: (a) E; (b) 5S; (c) 10S; (d) 15S; (e) 20S.

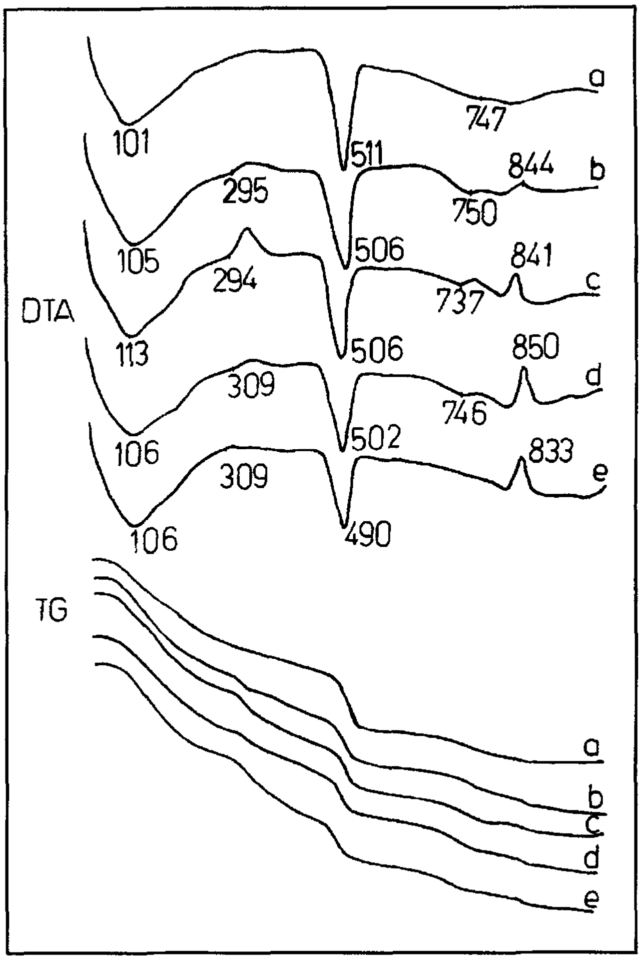

Fig. 2. DTA and TG curves at 28 days of hydration for samples: (a) E; (b) 5S; (c) 10S; (d) 15S; (e) 20S.

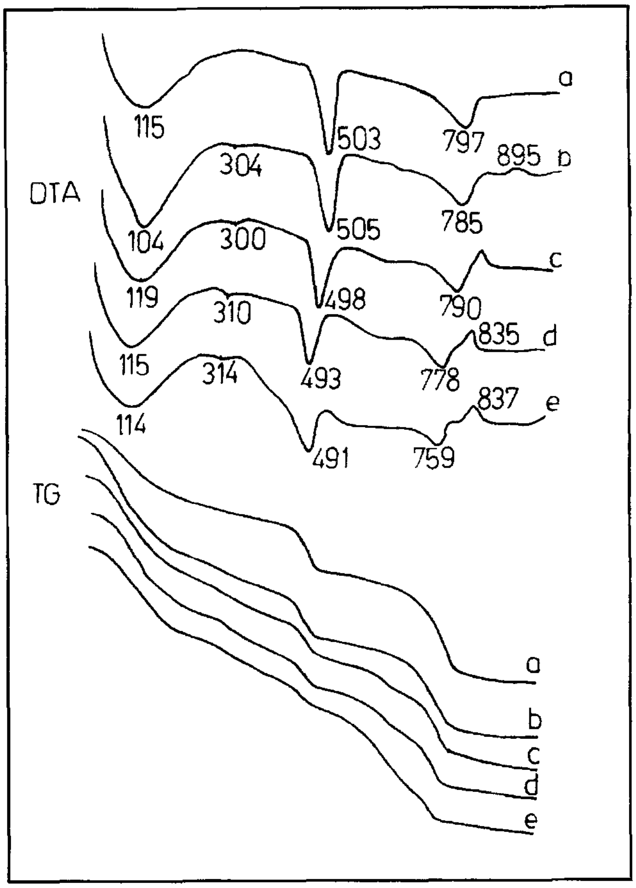

Fig. 3. DTA and TG curves at 360 days of hydration for samples: (a) E; (b) 5S; (c) 10S; (d) 15S; (e) 20S.

Table 3. Calculated data from TG curves

	Calculation mode	*1 day*					*28 days*					*360 days*				
		E	*5S*	*10S*	*15S*	*20S*	*E*	*5S*	*10S*	*15S*	*20S*	*E*	*5S*	*10S*	*15S*	*20S*
Chemically bound water PT (%)	Total weight loss between 0 and 1000°C	5.6	12.2	13	13.7	14.1	15.1	17.5	17.4	15.4	15.8	20.3	25.7	22.9	21	21.7
Water loss from experimentally obtained $Ca(OH)_2$ We (%)	Weight loss between ≈450 and 550°C	1.27	2.40	2.59	2.58	2.55	4.01	3.35	3.03	2.77	2.32	3.63	3.34	2.38	2.08	1.75
Experimentally obtained $Ca(OH)_2$ CHl (%)	Stoichiometric calculation	5.22	9.86	10.64	10.61	10.48	16.48	13.77	12.46	11.38	9.54	14.92	13.73	9.78	8.55	7.19
Theoretically calculated $Ca(OH)_2$ CHt (%)	$Ca(OH)_2$ formed by hydrolysis of C_3S fraction within the samples	5.22	4.93	4.69	4.44	4.19	16.48	15.66	14.8	14.02	13.20	14.92	14.14	13.40	12.66	8.59
ΔCH (%)	CHe − CHt	0	4.93	5.95	6.17	6.29	0	−1.89	−2.34	−2.64	−3.66	0	−0.41	−3.62	−4.11	−1.40
Chemically bound water in CSH phase (%)	PT − We	4.33	9.8	10.41	11.12	11.55	11.09	14.15	14.37	12.63	13.48	16.67	22.36	20.52	18.92	19.95
Rate at which the water is bound in CSH phase v (%)	$\frac{(PT-We)i}{(PT-We)360} \times 100$	26	43	50	58	58	66	63	70	66	67	100	100	100	100	100

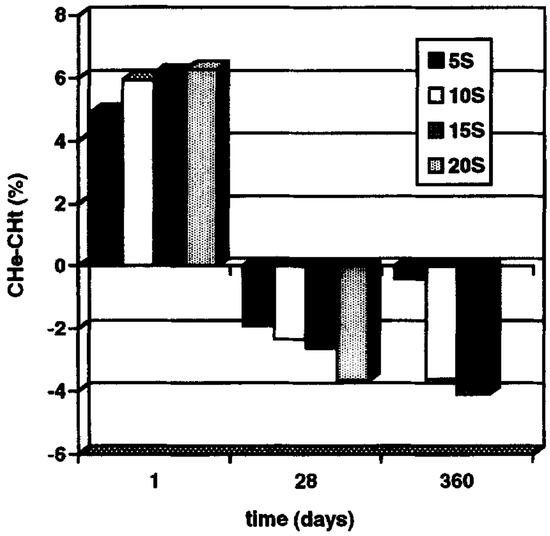

Fig. 4. ΔCH versus time.

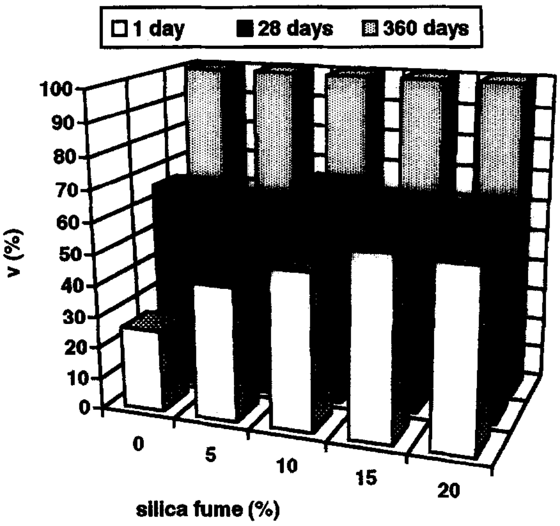

Fig. 6. Rate at which the water is bound in CSH phase versus time.

silica fume on C_3S hydration–hydrolysis process, and on the pozzolanic reaction that occurs in these systems. Figure 5 suggests the formation of a higher calcium silicate hydrates quantity in the silica fume blended samples, compared to the standard sample (E), for all periods of time. For samples with different silica fume proportions, after 28 and 360 days of hydration, the discontinuous variation of the chemical bound water in CSH is observed. This is a consequence of the changes in the resulting CSH(I): it is well known that a decrease in CaO/SiO_2 ratio in CSH results in a decrease of the H_2O/SiO_2 ratio.[4] In the first phase (after 1 day), the rate at which the water is bound in CSH (Fig. 6), when correlated with the $Ca(OH)_2$ data, suggests enhanced C_3S hydration–hydrolysis in the presence of silica fume. After 28 days, the increase in silica fume quantity has a negligible influence on the reaction kinetics.

The evolution of BET specific surface in time (Fig. 7) for silica fume blended hardened samples, leads to the same results as those obtained from thermal analysis. The increase of the silica fume proportion in these samples causes an increase of BET specific surface (for 1 day of hydration) due to silica fume's dispersion action and formation of a large quantity of

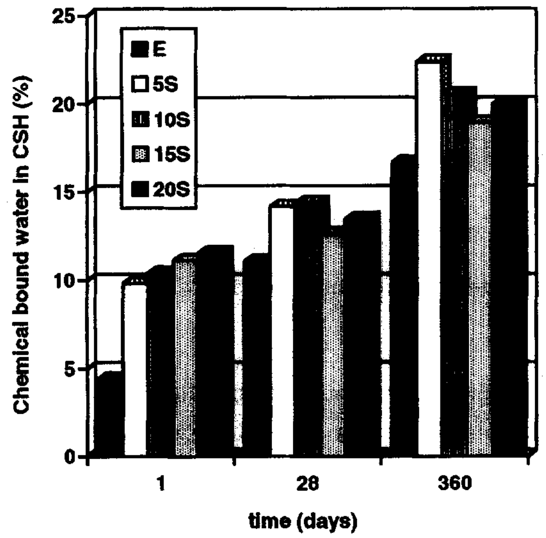

Fig. 5. Chemically bound water in CSH phase versus time.

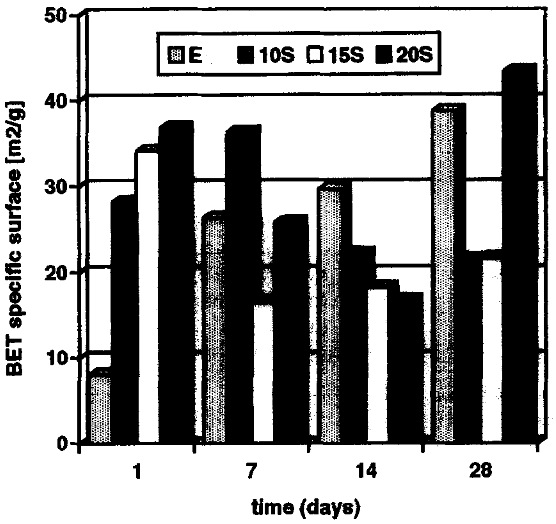

Fig. 7. BET specific surface versus time.

CSH with a large specific surface. For longer periods of hydration, the evolution of BET specific surface, however is discontinuous. This is interpreted as result of the simultaneous progress, for different rates of two opposite processes:

(1) the formation of CSH by C_3S hydration–hydrolysis process and pozzolanic reaction of $Ca(OH)_2$ with silica fume that increase the BET specific surface, and
(2) the silicate hydrates polycondensation process, which induces a reduction of the BET specific surface.

Data on the structural evolution of calcium silicate hydrates were obtained using the molybdenic method.[2] Figs 8 and 9 show the time evolution of low mers (LM), polymers from one to five silicate anions in the structure and oligomeric–polymeric fraction (OM), polymers with more than five silicate anions in the structure. A 20% silica fume in C_3S pastes increases the quantity of OM fraction and reduces the quantity of LM for the same hydration period as a direct consequence of an increase in the polycondensation process rate. The intensification of polycondensation process is due to the modification of hydrate silicate basicity, which decreases when the silica fume is present. This fact is clearly shown by the presence on DTA curves of the exothermic effect at 840–850°C.

For E and 20S samples, the growth of LM proportion after 7 days of hydration is due to the increase in quantity of silicate hydrate formed in the C_3S hydration–hydrolysis process and by the pozzolanic reaction.

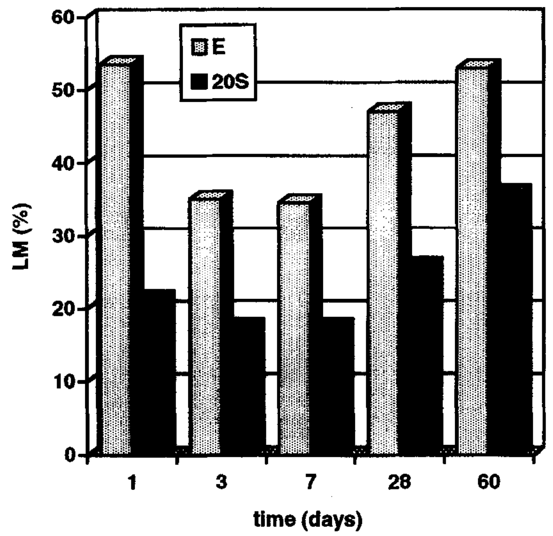

Fig. 8. Low mers fraction (LM) versus time.

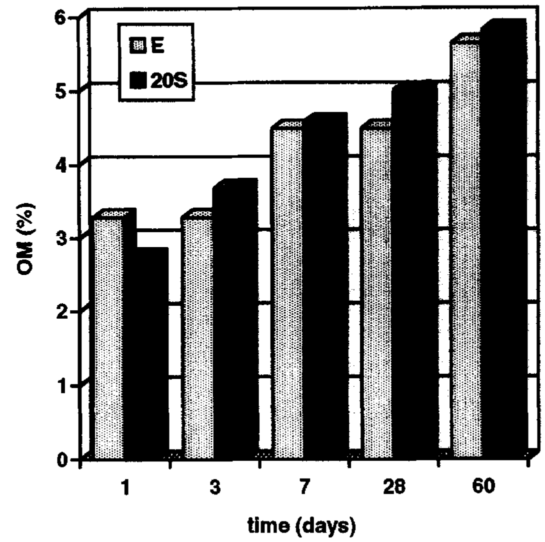

Fig. 9. Oligomeric polymers fraction (OM) versus time.

CONCLUSIONS

(1) The addition of silica fume to C_3S intensifies the kinetics of the hydration–hydrolysis process, especially at early ages (1 day).
(2) The quantity of CSH(I) increases when silica fume is present in the system. This is a consequence of a pozzolanic reaction between $Ca(OH)_2$ and silica fume.
(3) The formation of increased quantity of CSH(I) determines the increase in the degree of polycondensation.

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REFERENCES

1. Georgescu M., Badanoiu A. & Necula L., Processus d'hydratation et durcissement dans systemes liants complexes. *Revue Roumaine du Chemie*, **10** (1997).

2. Durecovic, A., Silicate anions polymerization in the pastes of OPC — silica fume blends during hydration and after action of leaching attack — part II. Study by use of molibdate method. *Cement Concrete Res.*, **18** (1988) 532–538.
3. Tamas F., *Proceedings 6th Conf. Silicate Ind.* Budapest (1961), 423.
4. Brunauer, S., Kantro, D. L. & Copeland, L. E., The stoichiometry of the hydration of β-C_2S and C_3S at room temperature, *J. Am. Chem. Soc.*, **80(4)** (1958) 761