

THE STUDY OF ‘DSP’ BINDING SYSTEMS BY THERMOGRAVIMETRY AND DIFFERENTIAL THERMAL ANALYSIS

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Abstract

The so-called DSP (Densified Systems containing homogenously arranged Particles) systems represent a high-performance class of inorganic binders. The hydration and hardening processes of some DSP systems, based on calcium silicates (C_3S and C_2S) or Portland cement/clinker with silica fume additions, were assessed, in this paper, using the thermogravimetry (TG) and differential thermal analysis (DTA). These data permit a qualitative and quantitative study of the formed hydrates as well as the estimation of hydration process kinetics.

Keywords: calcium silicates, DSP systems, DTA, Portland cement/clinker, silica fume, TG

Introduction

The DSP (Densified Systems containing homogeneously arranged Particles) composites are characterized by a very dense matrix due to the presence in the system of a very fine material. Silica fume, a by-product resulted in the metallic silicon production is the most used addition in this type of composites. The high-performance properties of DSP materials (high mechanical strength and very good durability) made them one of the most studied types of binding materials in the last two decades.

For the assessment of the hydrates formed in different cementitious systems, DTA-TG analyses were often utilized and proved to be an excellent technique alone or in combination with other methods like SEM or XRD [1–2].

An extensive study of the hydration and hardening processes in DSP systems, based on mineralogical compounds (calcium silicates, calcium aluminates or ferritaluminates) and cements (Portland or aluminates) with silica fume additions, was performed [3–6]. Different techniques were used to assess the kinetics of hydration and hardening processes and the nature of formed hydrates: X ray diffraction analysis, SEM and EDAX analysis, the molybdate method, mechanical strength determination and others.

Very useful and precise information concerning the hydration could be obtained using thermogravimetry (TG) and differential thermal analysis (DTA). The kinetics

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of hydration process and formed hydrates, in four types of DSP binding systems with silica fume, assessed by means of these two methods, will be presented and discussed in this paper.

Experimental conditions

The DSP systems based on calcium silicates with silica fume admixtures, studied in this work, are presented in Table 1.

Table 1 Composition of binders based on calcium silicates with/without silica fume additions

Binder	C ₃ S/%	C ₂ S/%	Silica fume/%
A	100	–	–
A5S	95	–	5
A10S	90	–	10
A15S	85	–	15
A20S	80	–	20
B	–	100	–
B20S	–	80	20

The C₃S was prepared from CaCO₃ and SiO₂ mixture, with 1% Na₂SiF₆ admixture by repeated (3+3 h) burning at 1400°C. The C₂S was prepared from CaCO₃ and SiO₂ mixture, with 0.5% B₂O₃ admixture (for the stabilization of β phase) by burning at 1400°C for 4 h.

Table 2 Composition of binders based on Portland cement/clinker with/without silica fume and different plasticizers

Binder	Mass/%						
	Clinker	Silica fume	Gypsum	Flubet	Romatan	LSC	Na ₂ CO ₃
G	95	–	5	–	–	–	–
GS	85.5	9.5	5	–	–	–	–
GSL	85.5	9.5	5	–	–	0.8	–
SL12N6	90	10	–	–	–	1.2	0.6
SL15N12	90	10	–	–	–	1.5	1.2
S'L12N6	80	20	–	–	–	1.2	0.6
L12N6	100	–	–	–	–	1.2	0.6
F7	100	–	–	0.7	–	–	–
SF7	90	10	–	0.7	–	–	–
R7	100	–	–	–	0.7	–	–
SR7	90	10	–	–	0.7	–	–

X-ray diffraction analysis and chemical analysis (free lime content) were used to verify the calcium silicates synthesis. The compounds were ground to Blaine specific surfaces of $3475 \text{ cm}^2 \text{ g}^{-1}$ (C_3S) and $3107 \text{ cm}^2 \text{ g}^{-1}$ ($\beta\text{C}_2\text{S}$).

In Table 2 the DSP composition, based on Portland clinker/cements are presented. The chemical composition and specific surface of Romanian origin Portland clinker and silica fume are presented in Table 3.

The plasticizer admixtures used in this study were:

- calcium ligninsulphonate (LSC), by-product resulted in paper fabrication process, alone or associated with Na_2CO_3 ;
- Flubet – naphthalene formaldehyde sulphonate type plasticizer;
- Romatan – naphthalene formaldehyde sulphonate type plasticizer with tanate content.

Table 3 Physical and chemical characteristic of raw materials

Characteristics	Composition/%	
	Portland clinker	Silica fume
L.O.I	0.9	2.27
SiO_2	21.9	93.13
Al_2O_3	4.5	2.09
Fe_2O_3	3.92	1.52
CaO	65.41	0.95
MgO	1.59	1.80
SO_3	1.37	–
Na_2O	0.26	0.01
K_2O	0.33	1.08
Specific surface/ $\text{m}^2 \text{ g}^{-1}$	0.3080 (Blaine)	22.3 (B.E.T.)

Pastes with 0.4 water to binder ratio were used for TG and DTA analysis. The pastes were sealed in plastic-bags and stored for 1 day up to 2 years in CO_2 -free atmosphere. Hydration was stopped at the appropriate times by ethanol washing and oven-drying at 100°C for the system containing C_3S and 60°C for the other studied systems. The analyses were performed with a heating rate of $10^\circ\text{C min}^{-1}$ on a derivatograph MOM type C equipped with computer data acquisition and processing.

Results and discussion

Hydration and hydrolysis processes in calcium silicates (C_3S , C_2S)–silica fume–water systems

The thermogravimetry (TG) and differential thermal analysis (DTA) made on samples hydrated 1 day up to 2 years, provided us qualitative and quantitative data about

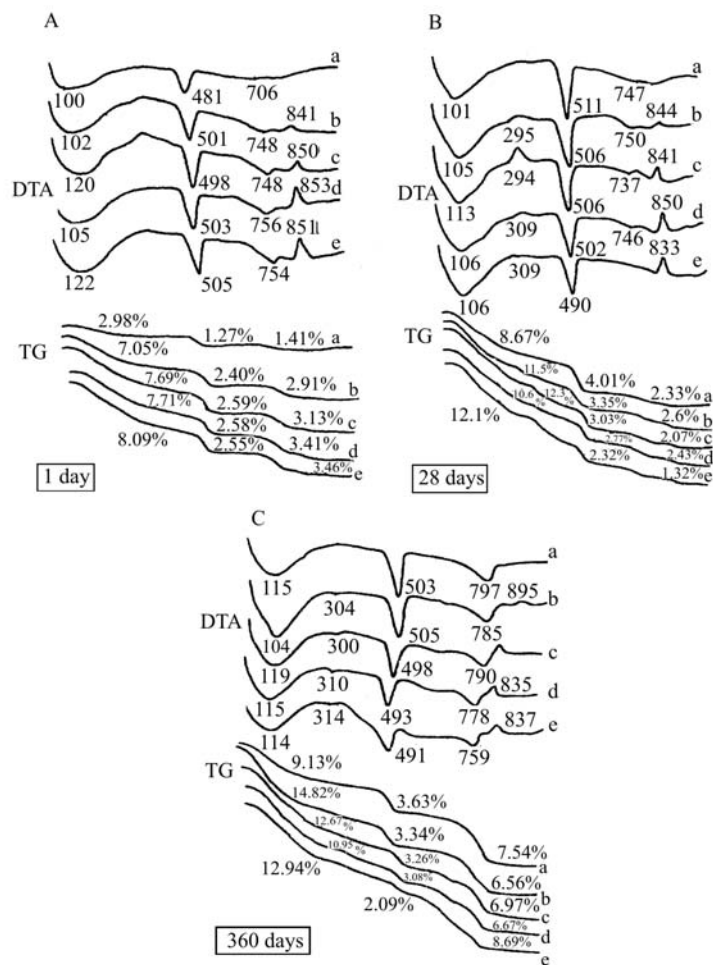


Fig. 1 DTA and TG curves for samples with C_3S and: a – no silica fume; b – with 5% silica fume; c – with 10% silica fume; d – with 15% silica fume; e – 20% silica fume hydrated for one day up to one year

the kinetics of calcium silicates hydration–hydrolysis process in the presence of silica fume, as well as the nature and quantity of formed hydrates.

The TG and DTA curves recorded for these systems are presented in Figs 1 and 2.

The following effects are present on DTA curves:

- the endotherm effect from 472–505°C is assumed to be due to calcium hydroxide dehydration;
- the endotherms from 100–122 and 706–797°C, are assumed to be due to the water loss from calcium silicate hydrates, the high temperature effect can be due also to the $CaCO_3$ (eventually formed during the sample handling and storage) decomposition;

- the exotherm from 819–853°C, present only on the DTA curves registered for the samples with silica fume admixtures, is characteristic for the calcium silicate hydrate CSH(I) with $\text{CaO}/\text{SiO}_2 < 1.5$. This effect is due to the reorganization of the lattice network of the anhydrous calcium silicate [7].

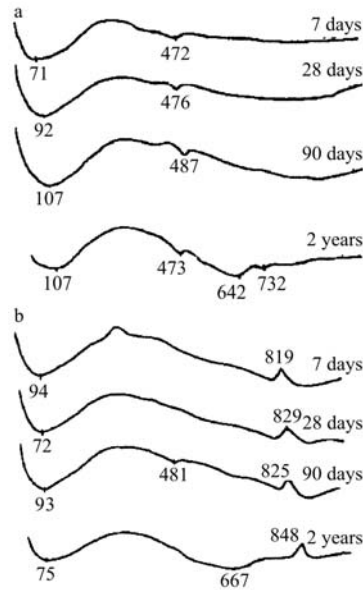


Fig. 2 DTA curves of $\beta\text{C}_2\text{S}$ samples: a – no silica fume; b – with 20% silica fume, hydrated for 7 days up to 2 years

The data obtained from quantitative analysis of TG curves of C_3S samples, with/without silica fume are presented in Figs 3, 4. For the assessment of the chemically bound water in CSH (with a certain degree of approximation) only the mass loss between approximately 20–400°C was considered, in order to avoid the eventual errors determined by the possible presence of CaCO_3 and mass loss induced by its decomposition at higher temperatures (around 800°C).

These data suggest an increase of the chemically bound water in samples with silica fume additions, especially for early ages (1 day). In this way the formation of a higher amount of CSH type of hydrates through C_3S hydration process as well as through the pozzolanic reaction, is obvious.

For longer hydration periods (28–360 days) the discontinuous evolution of chemically bound water in calcium silicate hydrates, in the samples with different amounts of silica fume, can be due to the formation of a higher amount of calcium silicate hydrates with different CaO/SiO_2 ratios and consequently different $\text{H}_2\text{O}/\text{SiO}_2$ ratios.

A confirmation of this hypothesis is the evolution of $\text{Ca}(\text{OH})_2$ content vs. time. After one day of hydration, higher quantities of $\text{Ca}(\text{OH})_2$ are formed in samples with silica fume additions as a direct consequence of the intensified calcium silicate hydration process (Fig. 3).

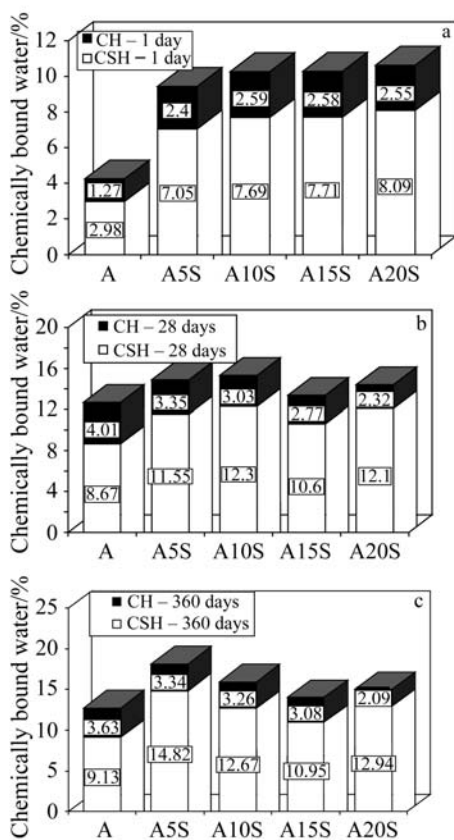


Fig. 3 Chemically bound water in calcium silicate hydrates (CSH) and calcium hydroxide (CH) in C₃S samples with 0–20% silica fume hydrated: a – 1 day; b – 28 days; c – 360 days

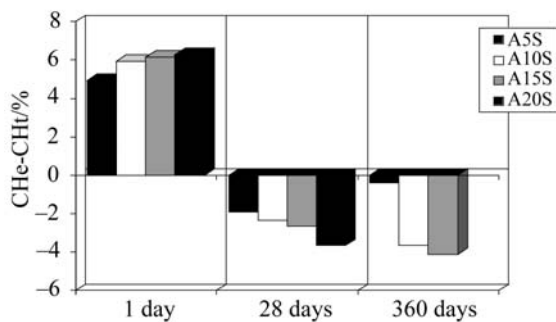


Fig. 4 The difference between experimentally determined Ca(OH)₂ – CHE and theoretically calculated Ca(OH)₂ – CHt vs. time for C₃S samples with different amounts of silica fume

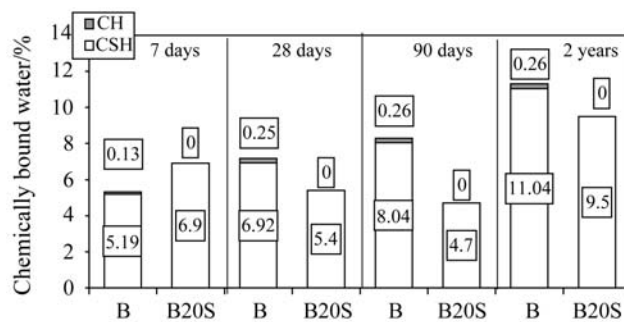


Fig. 5 Chemically bound water in calcium silicate hydrates (CSH) and calcium hydroxide (CH) in $\beta\text{C}_2\text{S}$ samples with 0 and 20% silica fume hydrated from 7 days up to 2 years

After longer periods of time (28–360 days), the pozzolanic reaction of silica fume with $\text{Ca}(\text{OH})_2$ predominates. The results indicate lower values for experimentally obtained $\text{Ca}(\text{OH})_2$ -CH_e (by processing the TG data) compared with the $\text{Ca}(\text{OH})_2$ theoretically calculated on the basis of hydrolysis of existing C_3S fraction within the sample (CH_t) (Fig. 4).

A slower rate of hydration processes is noticed in the samples based on $\beta\text{C}_2\text{S}$ with/without silica fume. In the samples with 20% silica fume (B20S), the DTA curves presented in Fig. 2 and the information obtained by TG data processing (Fig. 5), do not show the presence of $\text{Ca}(\text{OH})_2$ but only the existence of calcium silicate hydrates regardless the hydration period. The smaller values for the chemically bound water in CSH determined at later ages (28 days up to 2 years) in the samples with silica fume (B20S) compared with those recorded for the reference (B), can be explained by the formation and presence of mainly CSH(I) type hydrates; as mentioned before these calcium silicate hydrates have lower values of $\text{H}_2\text{O}/\text{SiO}_2$ ratio.

Based on these data and on some previous literature hypothesis [8–11], the increase of calcium silicate hydration–hydrolysis rate in the presence of silica fume can be explained by the following complex mechanism:

- a better dispersion of $\text{C}_3\text{S}(\text{C}_2\text{S})$ grains in water, in the presence of ultrafine particles of silica fume (average diameter 0.1–0.2 μm);
- a higher value of Ca^{2+} concentration gradient, between the surface of calcium silicate grains and solution, due to the consumption of these ions through the pozzolanic reaction with silica fume;
- the hydrates with low values of CaO/SiO_2 ratio formed in the systems with silica fume, permit an easier diffusion of Ca^{2+} ions from anhydrous grain surface into solution.

Hydration and hydrolysis processes in Portland clinker/cement–silica fume–water systems

Beside the obvious practical interest of the study of the systems with silica fume based on Portland cement, we considered also justified the study of gypsum free ce-

ments with silica fume additions. The major feature of gypsum free cements is the possibility of their processing at low water to binder ratios (approx. 0.2), which is based on the strong synergetic liquefying action of lignin sulphonate–alkali carbonate mixtures used as plasticizer and retarding admixture. Because of low water to binder ratios used, these hardened cements have a very compact structure, which explains their very high mechanical strengths and high resistance to aggressive mediums [3, 4, 12–14]. The addition of silica fume increases once more the compactness of hardened gypsum free cements and consequently improves some of their properties.

The DTA curves (Fig. 6), show for the sample with Portland cement and 10% silica fume (GS), a large endotherm at $T_{\max} \approx 117\text{--}124^\circ\text{C}$. This effect can be attributed to the dehydration of CSH with a low structured lattice, as well as to the ettringite (AFt) dehydration [3, 15]. The endotherm at $480\text{--}482^\circ\text{C}$ suggests the presence in the hydrated samples of $\text{Ca}(\text{OH})_2$ and the endotherms at $721\text{--}740$ and $751\text{--}765^\circ\text{C}$ can be attributed to the CSH (with a better-structured lattice) dehydration, as well as to the CaCO_3 (eventually formed) decomposition. For the sample with complex plasticizer (SL12N6), the endotherm at $112\text{--}121^\circ\text{C}$ can be due to the dehydration of CSH with low structured lattice and also of some hexagonal calcium aluminate hydrates.

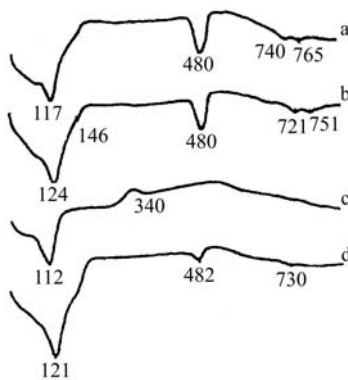


Fig. 6 DTA curves of: a – GS hydrated 1 day; b – GS hydrated 28 days; c – SL12N6 hydrated 1 day; d – SL12N6 hydrated 28 days

If we assume that the hydration processes in systems based on Portland cement/clinker is determined mainly by the hydration of calcium silicates (preponderant in this type of binders), correlated with the data presented in previous section, we can assess the kinetics of hydration processes at early ages (1–2 days) by the quantitative analysis of $\text{Ca}(\text{OH})_2$ formed in samples.

After 2 days, the values calculated on the basis of TG data, presented in Fig. 7, suggest an increase of Portland cement hydration speed when 10% silica fume is added to the binding system (samples G and GS). The use of 0.8% plasticizer (LSC) induce an important decrease of the hydration process speed; for GSL sample the TG data suggest the absence of $\text{Ca}(\text{OH})_2$ in the sample hydrated 2 days. The important delaying effect of this type of plasticizer was also reported in other works [15].

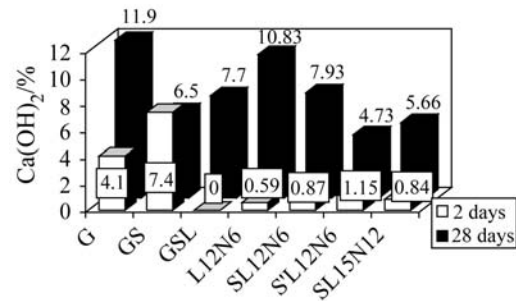


Fig. 7 Ca(OH)_2 content (calculated on the basis of TG data) in samples based on Portland clinker/cement with/without silica fume and plasticizers

In the gypsum free cements, the complex plasticizer ($\text{LSC} + \text{Na}_2\text{CO}_3$) plays a double role: delays the Portland clinker hydration process and increases the workability of fresh mortars (pastes). The data presented in Fig. 7 shows an important delaying effect induced by the complex admixture on the Portland clinker hydration process, i.e. the formed Ca(OH)_2 quantity (after 2 days of hydration) is much smaller in these samples compared with those based on Portland cement (G). The delaying effect was explained by Jawed *et al.* [16] by the inhibition of Ca(OH)_2 nucleation and crystal growth in the presence of LSC and its influence on the calcium silicates hydration, at early ages. This effect was confirmed also by the data obtained using X-ray diffraction analysis [3, 4]. The silica fume addition reduce the plasticizer's delaying effect, and the increase of silica fume content (from 10% – SL16N6 to 20% – S'L12N6) seems to increase the hydration process speed at early ages (2 days).

The data presented in Fig. 8 provide information about the hydration process and pozzolanic reaction. The positive values of the difference between experimentally determined Ca(OH)_2 – CHe and theoretically calculated Ca(OH)_2 – CHt suggest an increase of the speed of the hydration process, mainly due to the silica fume dispersing action. The negative values of this difference at longer hydration periods (28 days) are due to the consumption of Ca(OH)_2 through pozzolanic reaction.

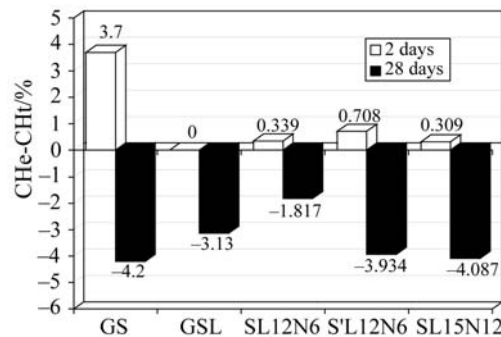


Fig. 8 Silica fume influence on Ca(OH)_2 content in samples with Portland cement/clinker

The important delaying effect of the LSC (alone or mixed with Na_2CO_3) is noticeable even after 28 days of hydration (see samples GS, GSL and SL12N6). The in-

crease of Na_2CO_3 (from 0.6 to 1.2%) together with those of the LSC content (from 1.2 to 1.5%) diminishes its delaying effect, so after 28 days the $\text{Ca}(\text{OH})_2$ quantity consumed through pozzolanic reaction is comparable with the one determined in Portland cement sample (samples SL15N12 and GS).

The substitution of LSC with other types of plasticizers – Flubet and Romatan – in the gypsum free cements with/without silica fume, do not modify the nature of formed hydrates (on DTA curves the same effects are present) [6]. The compositional difference between Flubet and Romatan (the last one contains also some tanate compounds) modify the kinetics of hydration process. The values of bound water in hydrates (calcium silicates and calcium ferrit(aluminate) hydrates) – bwh are smaller in samples with Romatan (R7 and SR7) compared to those with Flubet (F7 and SF7), which means the hydration process is slightly delayed (Fig. 9). The silica fume addition increases, as expected, the rate of hydration process at early ages – see the higher bound water in hydrates (bwh) values for samples GS, SF7 and SR7 compared with G, F7 and R7 respectively (Fig. 9).

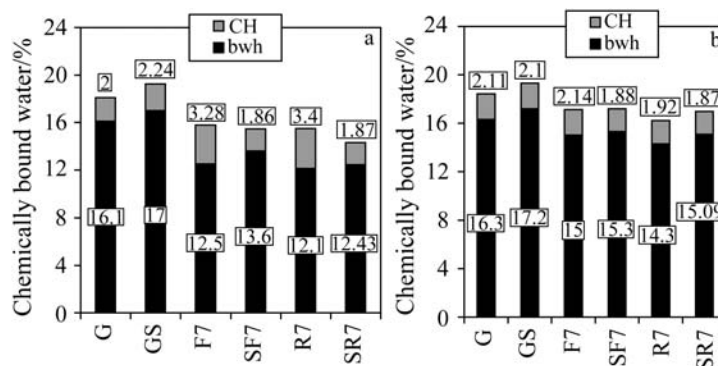


Fig. 9 Chemically bound water in $\text{Ca}(\text{OH})_2$ – CH and calcium silicate/(ferrit)aluminate hydrates – bwh, in Portland cement and gypsum free cement samples, with/without silica fume, hydrated for a – 2 days and b – 28 days

The higher calcium hydroxide content (CH) in samples with gypsum and silica fume confirms the increase of hydration process rate at early ages (2 days); the pozzolanic reaction seems to be more intense for the systems without gypsum (SF7 and SR7 compared with GS) and predominate at longer periods of time (28 days).

Conclusions

Based on the results obtained by DTA and TG analysis (confirmed also by XRD or/and chemical analysis [3]) in DSP systems with silica fume, the following conclusions can be drawn:

- at early ages (up to 7 days) silica fume additions increase the rate of hydration of binders, mainly due to a better dispersion of the anhydrous grains in water;
- at longer hydration periods (28 days and more) the pozzolanic reaction predominates, with the supplementary formation of CSH (I) type calcium silicate hydrates.

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