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On the hydration of water-entrained cement–silica systems: Combined SEM, XRD and thermal analysis in cement pastes

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ABSTRACT

The work described in this document focuses on the hydration of low water and low porosity SF-modified cement-based materials. The hydration of the clinker compounds was followed by X-ray diffraction (XRD), differential thermal analysis (DTA) and also by means of the thermo-gravimetric technique (TGA). This study was performed in three systems, each with a different composition namely a plain cement paste, a silica fume (SF)-modified cement paste and a water-entrained SF-modified cement paste with superabsorbent polymers (SAPs). In addition to the previous experiments, the microstructure of the systems was accessed by means of the scanning electron microscopy technique (SEM). This was primarily done with the purpose of supporting some ideas that have emerged when determining the hydration of these complex systems using the former techniques. However, in this manuscript only the results found through the TGA/DTA technique will be shown. Thus, in respect to the quantification of the CH phase developing in the system, the results taken by the TGA/DTA technique enable a more feasible description of the hydration of low water and low porosity SF-modified cement systems, including systems with water-entrainment by superabsorbent polymers. The results show that for cement-based materials with the physical nature of the systems that have been studied in this work, the pozzolanic activity is limited due to lack of water and/or space to accommodate additional hydration products, and as a consequence, a surplus of silica fume is to be found in the mature material. Due to either physical or chemical constraints, the system is not able to fully convert the calcium hydroxide into calcium silicate hydrate during the first month of hydration in sealed conditions. Additionally, in systems with water-entrainment by means of superabsorbent polymers, it is possible to observe the internal curing activity being promoted by this addition, which is translated by enhanced hydration of cement reactants. A model has been constructed from the empirical knowledge developed on the previous framework, which may be used in further research activities to study different formulations of SF-modified cement systems and also water-entrained cement-based systems.

1. Theoretical

Hydration of combined Portland cement with silica fume is a topic that involves intensive research work. Due to the complexity of the multi-phase reactions between clinker compounds and water, the studies on hydration are often restricted to the analysis of pure substances in controlled environments [1]. The phase development of Portland cement compounds may be studied by combined TGA and DTA/DSC analysis [2,3]. While the latter gives information about phase transformations due to energy change with a reference standard, the first can be used to estimate hydration degree and isolate the specific quantities of CH species in the system. Studies on the differentiation of adsorbed and chemically combined water are well documented in the literature. In addition, TGA/DTA profiles were also used to study the pozzolanic activity of mineral additions such as silica fume, fly ash and slag [4,5]. However, all these tests are usually performed using cement-based materials with a relatively high water to cement ratio, which enables the full hydration of the system, since the non-hydrated parts may easily access to the water sources. The existence of insufficient water to fully hydrate the cement compounds leads to relevant uncertainties in respect to the "performance" of the silica fume addition in low water to cement ratio cement pastes. Some ideas that were brought into question include: Is a sealed system cured enough for any given quantity of pure SiO_2 in the system? Is the contribution of silica fume to form additional calcium silicate hydrates efficient at any given low-water content? In practice, silica fume content is restricted to strictly low amounts, typically within 5–10% per gram of cement. It is stated in a number of scientific documents that above this dosage, few benefits are to be expected [6]. Thus, if all of the CH phase is converted to a CSH hydrate, the alkaline environment would be depleted, as the result

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Table 1
Cement phase composition by Bogue method.

Cement type	C_3S [wt.%]	C_2S [wt.%]	C_3A [wt.%]	C_4AF [wt.%]	CS [wt.%]	CaO [wt.%]	Na_2O equiv. [wt.%]
CEM I 52.5_DK	66.1	21.2	4.3	1.1	3.5	1.96	0.17

of the decrease of the PH value, which is attributed to the presence of CH species [7]. On the other hand, in the case of high strength and high performance concrete, the formula often includes higher silica to cement ratios in order to either enhance pore refinement or strengthen the interfacial transition zone (ITZ) regions [8]. Thus, the ingress of hazardous substances is limited by extremely fine pore connectivity with improved material durability.

On the other hand, the XRD technique may be also used to track the development of individual clinker compounds over time. This is done by monitoring the consumption of the mineral phases as they loose their crystal nature upon hydration. For standard cement-based systems ($w/c = 0.50$), Parrot et al. [9] have found a good correlation between XRD and the non-evaporable water measurements, an indirect way to describe the degree of hydration of the system. However, it is found that the quantification of the CH phase through this method is controversial, since it is thought that a poor crystalline phase is expected to occur within this particular hydration product, thus inducing relevant uncertainties in the full hydration profile as taken by XRD. A similar perspective is found elsewhere, further sustaining that the TG/DTA methods may be more reliable, especially in the case where small phases are present in the system and to distinguish between products with similar XRD patterns [3]. In either case, a combined XRD/TG/DTA analysis may prove valuable in order to develop a better understanding of the hydration phenomena. The analysis of various techniques to characterise hydration of high performance cement-based materials with mineral additions was one of the primary objectives of this study.

It is well known that the mineral additions show different kinetics, the nature and the particle size being of major importance in both rate and extent of secondary reactions. It follows that the pozzolanic reaction is primarily dependent from the formation of calcium hydroxide, and secondly, from the microstructure of the system, in particular from the pore network system, both being time-dependent. Ono et al. [10] have conducted studies on the evaluation of the pozzolanic activity in cement pastes with silica fume addition. In a low water system with $w/c = 0.23$ and at moderate rate of silica fume addition (10%), 50% of the CH is consumed during the first month. However, as reported by the ACI committee 234 [11], the exact constituents of Portland cement and silica fume that determine the extent of pozzolanic reaction have not been well defined, although it is generally recognised that higher purity silica promotes the secondary reaction in blended systems. In sum, if the full hydration is not attainable due to lack of water, the development of the main phases will be restricted, resulting in both limited pozzolanic activity and limited extension of the primary reactions. The main objective of this study is to comprehend the nature of the hydration in low water and low porosity SF-modified systems. Furthermore, since silica fume reacts with $Ca(OH)_2$, it should be possible to derive the onset and subsequent behaviour of the pozzolanic activity by thermal analysis of the CH-phase de-hydration. Thus, by comparing the SF-modified system with the plain cement system, it may be possible to model the pozzolanic activity of silica fume for a given water to cement ratio. This was the second major objective of this work. In addition, the effect of adding the superabsorbent polymers on the hydration of SF-modified systems, which is poorly documented so far, is further analyzed by the same procedure. Although it is accepted that the introduction of internal curing water via superabsorbent leads to an increase in the amount of hydrated phases, no study on the differentiation of the hydrates or on the microstructure of water-entrained cement pastes can be found in the literature so far.

2. Materials and methods

A Danish white Portland cement Type I, with a nominal strength of 52.5, was used in the study. The density was 3150 kg/m^3 with a specific surface of 3150 m^2/kg as measured by Blaine. The phase composition as determined by Bogue procedure is presented in Table 1.

Silica fume (SF) was added as a dry powder at a rate of 15% of the wt. of cement. The specific surface of the silica fume is 17.5 m^2/g, as measured by the BET method. The chemical composition is the following, in wt.%: SiO_2: 94.1, Fe_2O_3: 1.00, Al_2O_3: 0.13, MgO: 0.71, SO_3: 0.43, and Na_2O equiv.: 1.09. A naphthalene-based superplasticizer was added at a rate of 1% of the wt. of cement in all mixtures.

Three systems are analyzed here: a plain cement paste (system P0), a cement–silica paste (system P1) and a water-entrained cement–silica paste (system P2). The basic water to cement ratio is 0.30 in all mixtures. The water-entrained system included superabsorbent polymers at a rate of 0.4%, as a function of the wt. of cement, and an additional water to cement ratio of 0.05, following the equation for water-entrained cement-based materials proposed by Jensen and Hansen [12]. The specimens were kept in sealed conditions at a constant temperature of 20 °C until each curing age was achieved.

TG/DTA profiles were obtained with samples from the same batches as the XRD specimens in a Setaram Labsys DTA–TG/DSC. A total quantity of 50–100 mg of sample was heated at 10 °C/min up to 1050 °C. The tests were performed in argon atmosphere at 1.5 bars. Alumina crucibles were used in the experiments. From the energy exchange with Corundum (Al_2O_3), used as internal reference, the phase transformations were recorded. The heat transfer was monitored by a thermocouple Pt/Rh with 10% platinum. In order to calculate the calcium hydroxide content, a separate test was performed with pure $Ca(OH)_2$ to check the enthalpy of this compound. Hence, the amount of $Ca(OH)_2$ in the system was then derived from Eq. (1):

$$Ca(OH)_2[\text{wt.\%}] = k \cdot A_{Pk450} \tag{1}$$

where $Ca(OH)_2$ is the wt.% of calcium hydroxide in the sample, k is the calibration constant of the pure compound and A_{Pk450} is the peak area taken from the DTA profile in μV. A k-value of 8.01×10^{-4} is found in the measurement of pure $Ca(OH)_2$, which is slightly lower than the value 8.23×10^{-4}, as found in Ref. [13]. The TG method does not require any calibration procedure since the mass can be directly derived from the stoichiometry of the $Ca(OH)_2$ de-hydroxylation, hence:

$$Ca(OH)_2 \overset{450\ ^\circ C}{\longrightarrow} CaO + H_2O \tag{2}$$

From the molar ratio between reactants and products of the chemical reaction, a coefficient of 4706 is found, which may be directly applied to derive the wt.% of the $Ca(OH)_2$ phase in the system.

3. Results

The results from the TG/DTA tests performed to the system P0 (plain cement paste) are shown in Fig. 1. The DTA profiles show the typical reactions occurring in the cement-based paste when

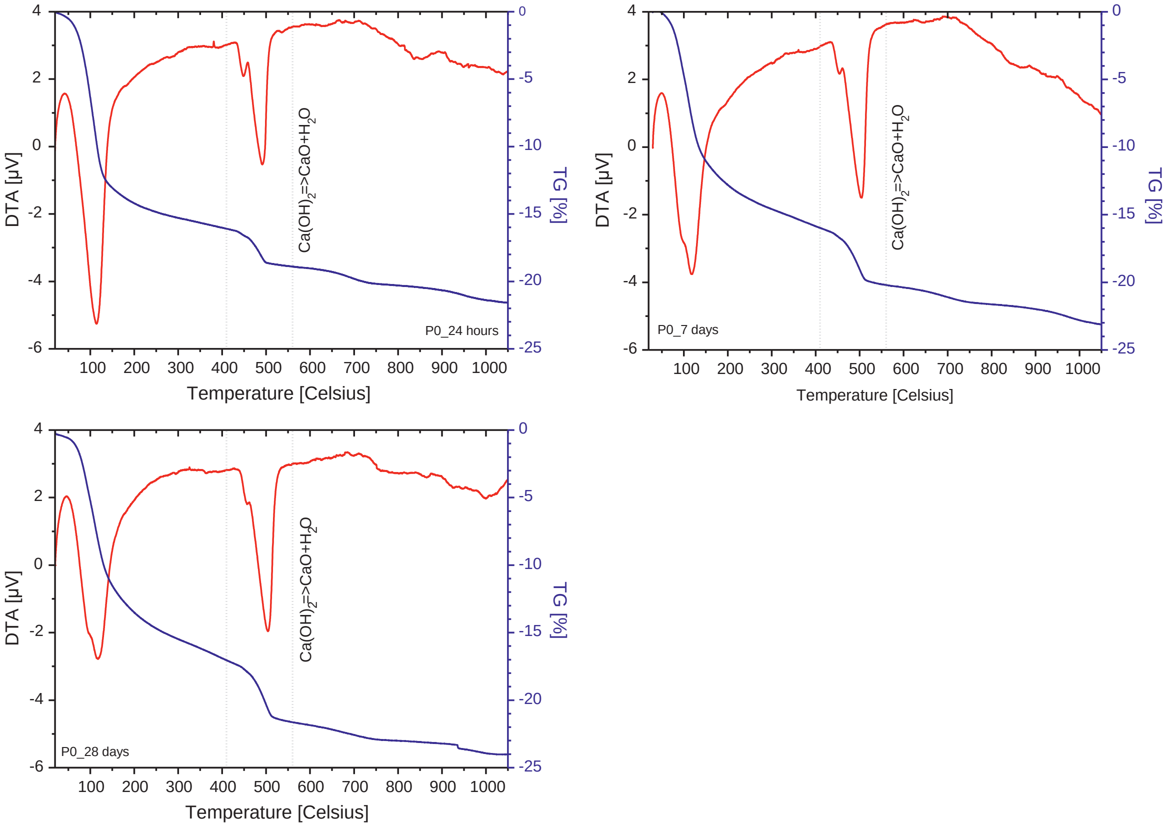

Fig. 1. TG/DTA profiles of cement paste (system P0) after 24 h, 7 and 28 days in sealed conditions. The TG measurement is scaled in the right *y*-axis and DTA in the left *y*-axis.

subjected to a progressive temperature increase (from room temperature up to 1050 °C). The first endothermic peak is attributed to the de-hydroxylation of CSH phase, corresponding to the mass loss on the TG profile up to 150 °C. The main weight loss in this stage is due to the loss of weakly bind water on the gel solid, which is physically adsorbed, and is taken at about 110 °C. The second major peak is also endothermic and corresponds to the de-hydration of calcium hydroxide, resulting in a new loss in mass starting at about 410 °C. In addition, a smaller endothermic peak, is noted at the same temperature level. No other representative peaks were found in the DTA profile, although curves present minor instability around 800 °C, which may be related to minor uncontrolled carbonation of the sample.

As expected, the absolute weight loss occurring in the samples increases with the curing age. The value at the 28th day is 24% by weight. This is an indirect indication about the degree of reaction of the main clinker compounds. The evolution of the second peak also supports that further hydration took place, as the CH phase is one of the by-products of silicate reaction with water.

Fig. 2 shows the TG/DTA thermal analysis of the cement–silica paste. The 24 h plot for this system indicates a stronger first peak in respect to the plain cement paste. The total weight loss is lower than the value measured for the plain cement paste, indicating that the system hydrated to a smaller extent. However, the second peak, related to the CH formation, seems slightly smaller in respect to the same peak measured for the plain cement paste.

As the temperature increases towards 1000 °C, a new exothermic peak can be observed on the DTA profile, without a significant mass change. The reactions occurring at this temperature level may be related to the formation of new silicate compounds, brought out by crystallization of certain types of CSH within a specific molar ratio between the main elements present on the system, SiO_2 and CaO [14]. This occurs at the specific temperature of 900 °C. The evolution of this peak over time suggests that the reaction is time-dependent, as a function of the decrease in the $Ca(OH)_2$ content. This observation may be related with the pozzolanic activity of silica fume and will be discussed further on this document.

3.1. $Ca(OH)_2$ de-hydroxylation

Calcium hydroxide reacts with pure silica fume to further create a CSH (amorphous/poorly crystalline) phase. This secondary reaction has been reported since early research work [14,15]. The evolution of calcium hydroxide in the studied systems is shown in Fig. 3. The analysis of the peak areas in the DTA profiles indicate the growth of CH phase during sealed hydration. As the hydration process proceeds, the peak position is translated towards a higher temperature, suggesting that different enthalpies may exist for the crystallites and that the phase abundance of this substance is increasing. This may be related to the growth of the hydration products, which is translated in higher energy needed for the activation of the chemical process. As noted by Midgley [13], the grain size affects the peak position of pure calcium hydroxide. The TG measurements are consistent with DTA results. The rate of CH production is maintained until the third-day sealed curing in both systems, accompanying the rate of hydration found for the CSH phases. In the case of the plain cement paste, a marked increase of $Ca(OH)_2$ species occurring during the first week is registered, from where no significant change is seen. Inversely, in both SF-modified systems, there is a decrease in the observed species between the 7th and the 28th day, which indicates activity of the silica fume in a secondary reaction.

In particular, the 24 h up to 7 days DTA-profiles show representative peaks of two endothermic reactions, occurring at 460 and 490 °C. The later was previously attributed to the de-hydroxylation of calcium hydroxide. The evolution of this peak is influenced by a

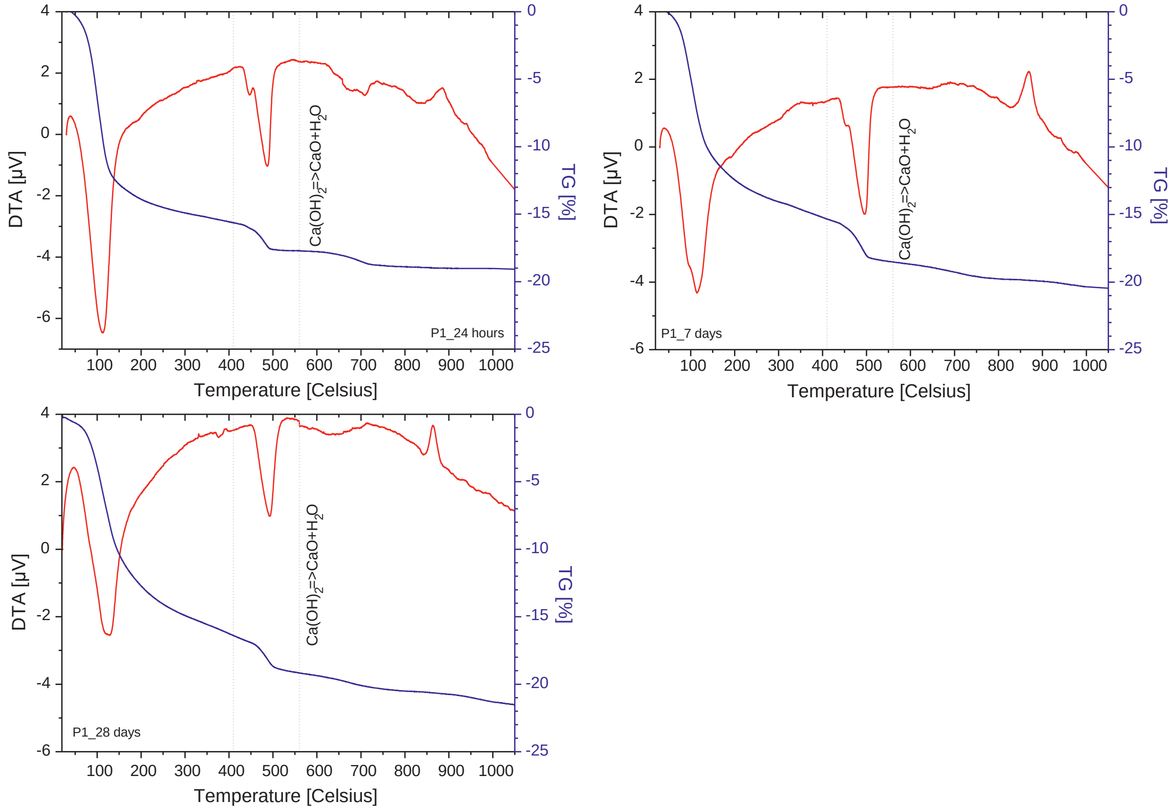

Fig. 2. TG/DTA profiles of cement–silica paste (system P1) after 24 h, 7 and 28 days in sealed conditions. The TG measurement is scaled in the right *y*-axis and DTA in the left *y*-axis.

weaker endothermic peak, which is increasingly broader as hydration progresses. According to work by Nocun-Wczelik [16], there is evidence that the existence of disordered crystals is influencing this particular reaction. Thus, a more stable and ordered $Ca(OH)_2$ crystal phase will appear with the development of hydration.

The production of calcium hydroxide in the studied systems is shown in Fig. 4. The area calculated in the DTA-profile was taken by de-convolution between both peaks through a *Lorentz* multi-peak function, and thus, is excluding the small endothermic peak.

A good correlation factor is found in both TG and DTA techniques. In the first 3 days of sealed curing, the variation of CH content between the systems is not significant, the registered values ranging between 15 and 17%. Thereafter, the behaviour between the plain cement paste and the systems with silica fume is opposite: the effect of silica fume is evident in reducing the amount of $Ca(OH)_2$. Although a higher amount of calcium hydroxide is found in water-entrained paste, it is interesting to note that the addition of superabsorbent polymers do not substantially influence the rate of depletion of calcium hydroxide. This is an indication that the microstructure is not significantly altered in regards to diffusivity of the paste.

The inversion in the growth tendency of the amount of $Ca(OH)_2$ occurs within the first 3 days of sealed curing. However, this should not be seen as a complete depletion of this phase. As seen in the plain cement paste, the rate-production of crystalline CH is severely diminishes after the third-day as well. This may suggest that the rate of pozzolanic activity surpasses the rate-production of CH in the system. Another interesting observation is that the difference in the amount of calcium hydroxide in the systems does not vary more than about 5% at the end of 28 days. If the results are normalised by weight of cement, the differences practically disappear, leaving only the inverse tendency in respect to the rate-production of CH phase.

3.2. Crystallisation of SiO_2–CaO following CSH de-hydroxylation

In the section dedicated to DTA analysis, one of the ideas presented to explain the exothermic peak at the end of the DTA-profile (at about 900 °C) was the degree of crystallization between Ca and Si. It is evident that this peak is growing with the curing age. Taylor [17] supported the idea that the different types of CSH can co-exist in cement-based systems. In his work, is proposed that the type of CSH may be differentiated by the C/S ratio. Accordingly, a higher C/S shall be preferably found in a cement-based reaction and a low C/S ratio in the secondary reactions, viz. pozzolan-based reaction [15].

Fig. 5 shows the evolution of CaO–Si_2O crystallization with time in the SF-modified cement paste, as obtained by baseline-subtraction of the DTA-profiles shown previously. The peak area measured at 24 h hydration is considerably lower in respect to the measured values at the subsequent testing ages: the peak position shifted by 20 °C with curing age. This may be explained by different crystallite sizes within the sample preparation procedure or the growth nature of this phase related with the state of equilibrium of the structural units within the amorphous phase that leads to longer delay in the heat response by the reactants when subjected to the heat ramp, or a combination of both, the latter assumption being more probable.

The assumption of crystallisation occurring upon decomposition of the CSH-type I at the DTA peak at 900 was further confirmed by XRD testing on the burned sample. A higher amount of *larnite* was registered within a highly amorphous material, in respect to the non-burned sample at the same curing age.

It is noteworthy that the source reactants of the reaction may be found within two events occurring when the sample is subjected to the temperature ramp. The first event is related to the de-hydroxylation of calcium hydroxide into free calcium oxide,

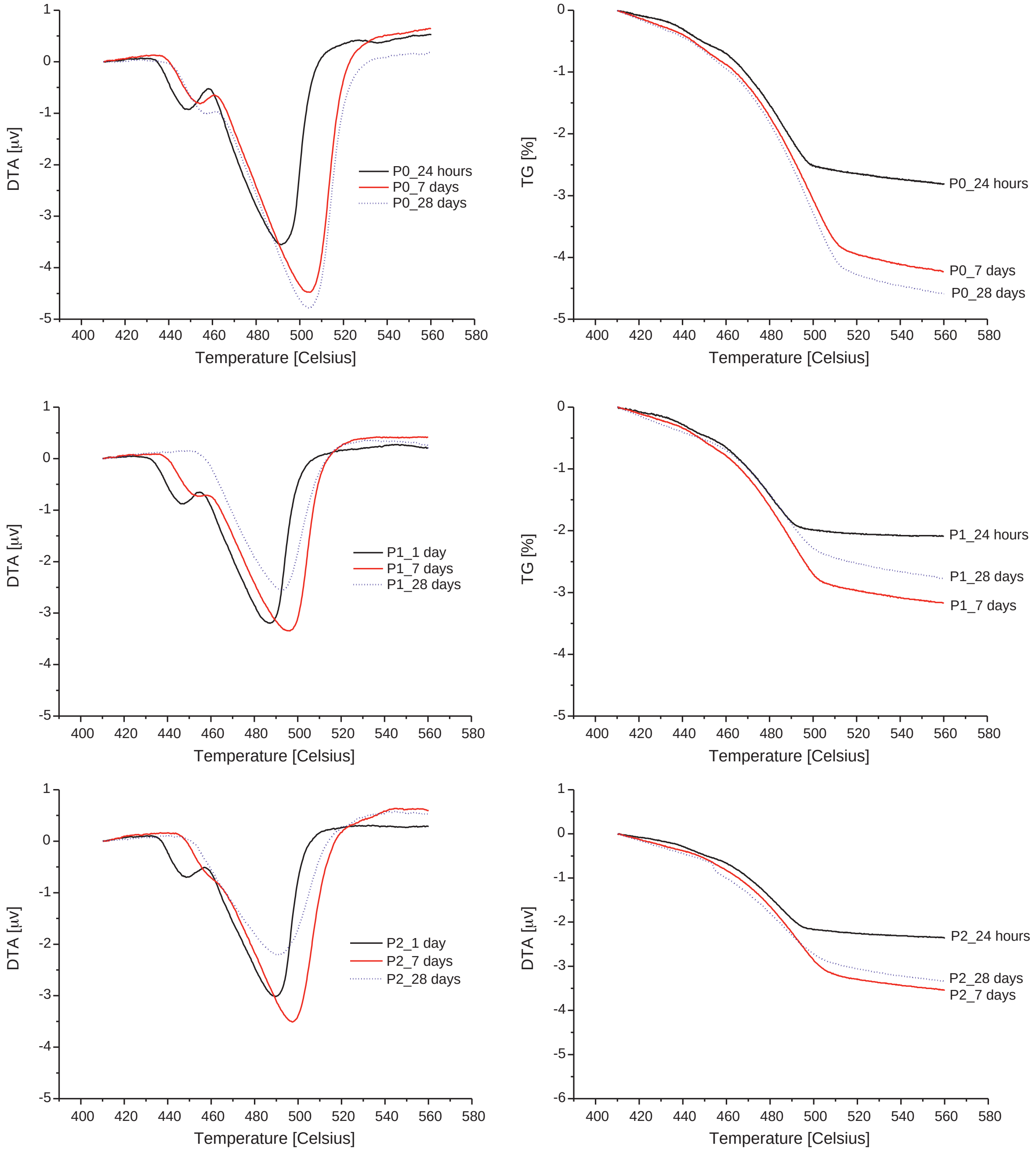

Fig. 3. TG/DTA profiles of cement pastes after 24 h, 7 and 28 days in sealed conditions. The data was normalized at the temperature of 410 °C.

which is known to be highly reactive since it shows poor stability. It follows that the free CaO may react with the remaining SiO_2, which have not been dissolved or reacted at the instant *t*. A second possibility is connected to the de-hydration of CSH to form physically bound CS. It is known that the crystallization in the C–S system requires a given energy and a specific C/S ratio, to which a different nature of crystalline C_xS, as defined by *x*, corresponds. Since the type of CSH formed in the secondary reaction may be poor in *calcium*, the energy and time, viz. power needed to decompose the system C–S–H is lower, in respect to calcium-rich CSH structures. According to the ratio between both reactants, the product may be more or less rich is calcium. In the present case, it seems that the major product forming is *larnite*, as shown by XRD analysis. In comparison, Abo-El-Enein et al. [14] suggested Wollastonite ($CaSiO_3$) forming at 900 °C. This is seen in pure lime-silica pastes.

4. Hydration model of cement–silica systems: including water-entrainment

Hydration is defined as the reaction of water and clinker minerals into hydrated phases. In the case of XRD, hydration degree of the clinker minerals is derived directly from the mineral consumption. However, this technique may be overestimate the quantities of minerals that have been effectively consumed, as the non-hydrated cores may be covered with CSH forming at the core-surface and thus, affecting the real reading of crystalline material. SEM technique may be also used to follow the development of the amount of non-hydrated cement. Despite the intrinsic measurement artifacts, the previous techniques have the advantage of directly tracking the existence of non-hydrated material. However, hydration of Portland cement is more often expressed by the ratio between the water of constitution at time *t* and an infinite value, which corresponds

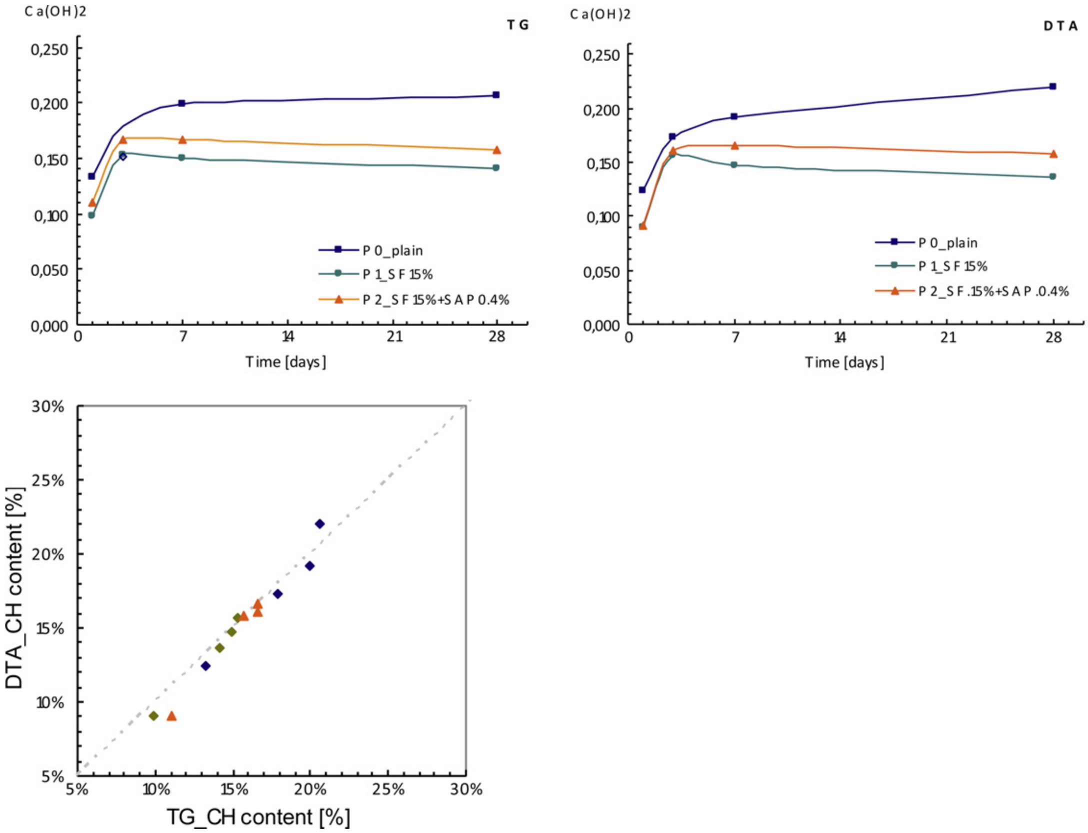

Fig. 4. Upper-plot: $Ca(OH)_2$ content of high performance cement pastes as measured by DTA and TG techniques. Down-plot: correlation of data between TG and DTA techniques.

to the maximum value of water-reacted to complete the hydration of the original reactants. The clinker compounds may achieve complete hydration when the chemically bound water (meaning that no hydrates may further be formed) equals the values presented in Eq. (3), as evidenced in the literature [18,19]:

$$w_n = \begin{cases} C_3S = 0.24\,\text{g/g} \\ C_2S = 0.22\,\text{g/g} \\ C_3A = 0.40\,\text{g/g} \\ C_4AF = 0.16\,\text{g/g} \end{cases} \tag{3}$$

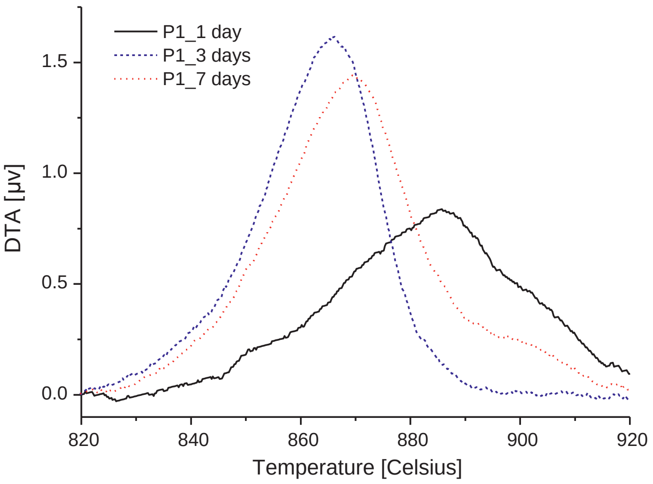

Fig. 5. Crystallization of calcium and silica to form crystalline C_2S from the CSH-type I phase at about 900 °C.

The latter values may be combined with the chemical formula of cement to derive the infinite value of water of constitution, as defined by Eq. (4), where w_i represents the individual water-combined amounts, the clinker compounds appearing as weight percentage.

$$W_n = w_1(C_3S) + w_2(C_2S) + w_3(C_3A) + w_4(C_4AF) \tag{4}$$

By equating the values from the Bogue analysis given in Table 1, a global maximum value of 0.224 g/g is found. The water-combined values in time may be easily determined by any of the techniques referred to in the preceding sections.

In the case of blended cement-based systems comprising mineral additions, the previous equations need to be re-arranged to include the fraction resolving the pozzolanic activity, which requires the knowledge of the time-dependent amounts of both silica fume-reacted and calcium hydroxide formed. Thus, neither SEM or XRD techniques are straightforward when attempting to isolate the pozzolanic activity by silica fume as TG/DTA.

The activity of a pozzolan may be defined by the stoichiometry of the chemical reaction with $Ca(OH)_2$, which takes the general form translated by Eq. (5):

$$x \cdot S + y \cdot CH + z \cdot H \rightarrow C_yS_xH_{y+z} \tag{5}$$

A first problem with balancing Eq. (5) is that one must know the ratio of C/S in the hydrated structure of the CSH_{SF} phase. According to El-Shimy et al. [15], this ratio may be about the unit, for low molar ratios between lime and silica. In this respect, it is further referred in work by Burkes [20], who showed, by means of XRD, that the main hydration product between the pure substances mainly consists in CSH type I. It follows a second uncertainty, which is connected to the amount of water that is being consumed in the reaction. According to Sellevold et al. [21] and also Papadakis [22],

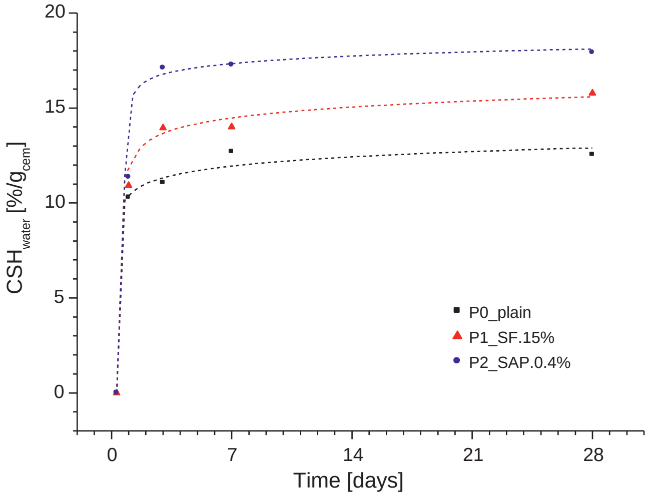

Fig. 6. CSH water in the studied systems, as found by TG method. The dashed lines corresponds a three-parameter approximation by a logarithmic function of the type: $y = a - b \cdot \ln(x + c)$.

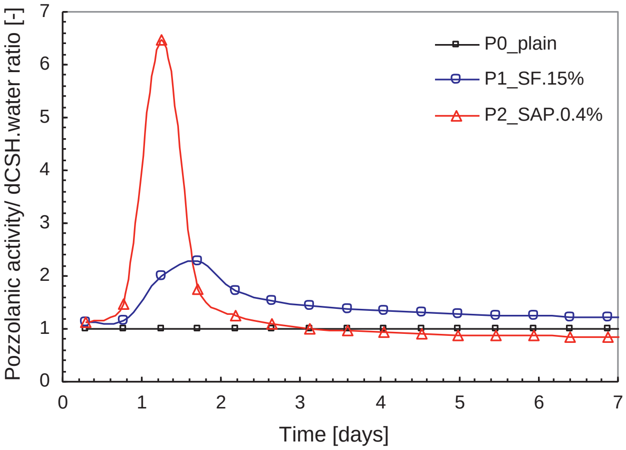

Fig. 7. Pozzolanic activity of SF-modified paste and internal curing activity of water-entrained SF-modified paste, based on the knowledge of bound-water from the correspondent cement paste, according to Eq. (6).

the amount of water bound in the CSH_{SF} is the same as the water present in the CH phase. Fig. 6 shows the calculation of water bound to CSH in the systems, as found by subtracting the water bound to CH in each system. It is found that the water bound per gram of cement is higher in the presence of SF, which means that additional water is to be bound to the CSH formed in the secondary reaction. This is supported in experiments by Diamond [23] and also by Bentz et al. [24]. Thus, both the effects of silica fume and superabsorbent polymer addition are clearly indicating an increase in the amount of water bound per gram of anhydrous cement. It is also clear the course of pozzolanic activity due to the presence of both SF and SAP. In the case of the water-entrained SF-modified cement system, the pozzolanic activity seems to cease earlier in respect to the SF-modified cement system. This is an indication of that the water in the superabsorbent polymer is mainly active during the first 3 days of hydration in sealed conditions.

The pozzolanic activity may be derived from the ratio between the rate of binding water occurring in the SF-modified systems and the rate of binding water in the plain cement paste, which may be obtained by the derivation of each CSH_{water} content as function of time, according to Eq. (6):

$$\alpha_{pozz} = \frac{(dCSH^{Cem+SF}_{water}/dt)}{(dCSH^{Cem}_{water}/dt)} \qquad (6)$$

This is done as an alternative to assume an ultimate value of water consumed by per gram of silica fume, as shown in Fig. 7. It may be seen that the pozzolanic activity of the water-entrained system is significantly different from that of the SF-modified paste. The interpretation of the water-entrained curve is not simple, since the introduction of additional water may be promoting both first and secondary reactions. Therefore, the rate of additional bound-water may not be solely due to the activity of SF, but also due to hydration of clinker minerals. The term internal curing activity should be introduced as an alternative to the term pozzolanic activity in this case.

In either case, the relative rate of reaction corresponding to the development of additional bind water in the water-entrained paste seems to happen very fast in respect to the SF-modified paste, the latter appearing at a later time and taking a longer period, in regards to the plain cement paste. A factor of 6.5 is found for this acceleratory period in the water-entrained system within the second 48 h. It may be that the internal curing activity is promoting the consumption of SF in the system, leading to additional hydrated material, and thus, affecting the diffusivity of the system with a concomitant reduction in additional hydration beyond the third-day. However at the present, this is just a speculation that, not being well supported requires further evaluation. The introduction of 15% of SF also results in an increased relative rate of hydration with a factor of 2 in respect to the rate of hydration expressed by the plain cement paste. The de-acceleratory period may be indicating the onset of a diffusion-controlled reaction, which remains in the subsequent period of hydration. This is consistent with the perception by Yogendran et al. [1], even though silica fume was introduced as cement substitution and not as an addition, leading to a different w/c ratio. On the other hand, this approach systematically leads to lower values of chemical combined water.

The knowledge concerning the water-bound to the hydrates may be further considered to characterise the full hydration of blended systems. This may be done by assuming that the stoichiometric parameters in Eq. (5) are equal to the values presented in Eq. (7), as taken from the literature:

$$\begin{cases} x = 1.1 \\ y = 1.0 \\ z = 2.8 \end{cases} \qquad (7)$$

By computing the initial quantities of phases present in the system, it is possible to describe the consumption of silica fume and the development of CSH type one, as presented in Fig. 8.

It may be seen that about 8% of the total silica fume is consumed in the production of about 7% calcium silicate hydrate (type I). Additionally the water-consumed in the reaction is given by the difference in the water-bound in the SF-modified paste and the water-bound in the plain cement paste. Therefore, it is possible to conclude that in low water and low porosity systems, the pozzolanic activity may not be completed at the 28th day of sealed hardening, and the full consumption of silica fume is physically impossible due to lack of water to sustain either the first reaction and especially the secondary. This may be why the hydration is hampered as early as the 1st 24 h and, in the case of the pozzolan, at the third-day of sealed hardening, the diffusivity of the system playing a major role in this respect.

The previous approach is obviously empirically oriented and is based on the knowledge of the water bound per gram of cement in the systems. Pane and Hansen [25] have proposed a hydration model for blended systems, which is based on the knowledge of the ultimate value of non-evaporable water. For a SF-modified paste with s/c ratio of 0.10 and a w/c ratio of 0.385, the infinite value of non-evaporable water per gram of binder is of 0.256. However,

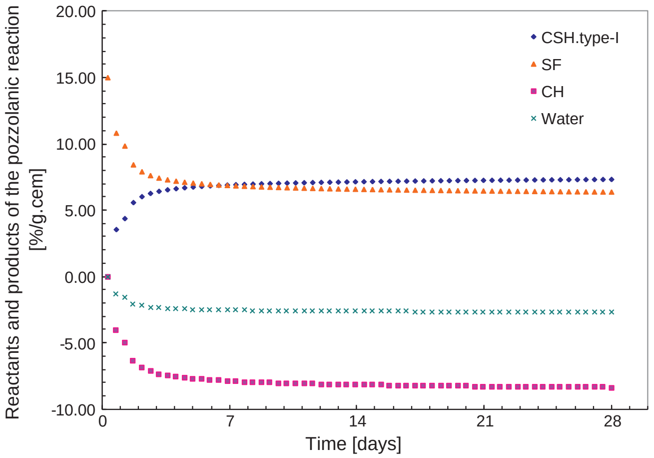

Fig. 8. Pozzolanic activity in SF-modified systems, described by SF-reacted, CH and water consumed, and the development of CSH-type I (reaction product). The negative part of the *y*-axis should be read as material consumption from the original system, and not as absolute value of the mineral in the system.

it is noted that the basic assumptions are not physically meaningful in order to describe the pozzolanic activity. For example, the model predicts that only 20% of the silica fume reacted at the age of 4 days, which contradicts the well-established idea that most of the secondary reaction happens in the first 3 days. A more consistent and comprehensive approach is found in the work by Yajun and Cahyadi [26]. By assuming that the pozzolanic reaction of silica fume follows the equation based on the stoichiometry of the reaction, as proposed by Bentz et al. [24], they were able to theoretically describe the pozzolanic activity as a diffusion controlled reaction, being expressed by the Jander equation, which as referred by Odler and SchUppstuhl [27], is a well-known equation to explain the reaction between tri-calcium silicate C_3S. A good theoretical review of chemical reaction engineering that may be used to approach this particular problem is given by Levenspiel [28]. Accordingly, in a diffusion-controlled reaction with a changing core in the particle, the rate of reaction is governed by the particle size and the chemical potential of the medium, in this case, being the pore fluid. The basic assumption in the approach by Yajun and Cahyadi [26] is based on work by Bonen and Diamond [29], who have found that the penetration depth of pozzolanic CSH with 35–80 μm, due to the dissolution and subsequent reaction with dissolved cations from calcium hydroxide, is within 20 μm, with the C/S molar ratio decreasing towards the centre of the core (agglomeration of silica fume particles), which was seen to remain Ca-free after 1-year. However, one of the limitations of this approach is that the pozzolanic activity mainly depends on the reaction rate constant and the existence of calcium hydroxide produced in the first reaction. This may not be the case in the system evaluated here, the existence of insufficient water, the pore structure and diffusivity of the system playing a central role in the course of the pozzolanic reaction. Although an approach of this kind would be preferable, at the present it does not seems feasible to be applied further, due to lack of information about the aforementioned parameters. For the purpose of the present investigation, it seems sufficient to draw conclusions about the effect of both silica fume addition and superabsorbent polymers in the course of hydration.

5. Conclusions and final remarks

Hydration of cement–silica systems comprises highly complex phenomena at the microscopic scale. An approach was attempted to isolate the pozzolanic activity by silica fume, which is based on the differentiation of CH and CSH phases through thermogravimetric measurements. In the present study, only qualitative information was possible to take from the measurements of three pastes having distinct nature. However, some important conclusions may be outlined:

1. Techniques

   Fours techniques were used to describe hydration of the studied systems. The TG/DTA technique should be preferably applied to describe the pozzolanic activity of silica fume. In addition, it may be used to differentiate the consumption of SAP-water. A good correlation was obtained by TG and DTA methods on quantifying the CH present in the system. On the other hand, these methods show poor correlation with the XRD technique, which may be underestimate the production of calcium hydroxide due to limitations in identifying poor or hindered crystalline phases. SEM technique may be preferably used to describe the pore structure of low water and low porosity systems. In addition, the SEM technique revealed a poor potential for differentiating hydrated phases. This difficulty is connected with the physical structure of low water systems, which may be hindering sub-microscopic and poorly developed crystal phases. However, the preparation of the samples may be enhanced to overcome this problem, for example by sputtering techniques. A gold coating may provide higher conductibility of the electron beam, enabling differentiation analysis at higher magnifications and potentially amplifying the threshold values in the backscattering.
2. Hydration of clinker compounds

   It is clear that the secondary reaction by adding silica fume into the system makes use of additional binding water. This was demonstrated through the use of three different techniques. The excess CSH forming is related to CH consumption within the pozzolanic activity by silica fume. The total consumption of CH cannot be verified with the current results, although it is not expected that substantial pozzolanic reaction may occur in long-term hydration. Further tests are needed at longer hydration-times to confirm the previous statement. The addition of superabsorbent polymers increases both the formation of CH and rate of secondary reaction, especially during the first week of sealed hydration. From the third-day forward, the activity of silica fume and additional water in the superabsorbent polymers to sustain further hydration is severely diminished. It is concluded that internal curing is mainly active during this period, rather then the whole hydration time.
3. Microstructure and pore structure

   It is found that the systems investigated in this work are highly homogeneous materials at the microscopic scale. Differences in morphology may only be found in sub-microscopic scale, where crystalline phases appear within voids or capillary space. Water-entrainment by superabsorbent polymers dramatically changes the pore structure of the system, which consists of isolated macro-inclusions and little capillary porosity. The latter is also found in SF-modified cement paste in respect with the plain cement paste, which shows higher absolute porosity, although it seems poorly connected as well. Potentially, gel porosity in SF-modified cement pastes may be significantly reduced as well, but a higher resolution is required to corroborate this suggestion. This concept is more evident in the water-entrained system, where additional water may have promoted hydration in pores, leading to the sublimation of fine porosity. It is further seen that superabsorbent polymers are well dispersed throughout the matrix. Furthermore, the evaluation of macro-porosity on 2D sections may be hindering pore depressions or slit-pores, which may have source in measurement artifacts. A 3D approach would be of great interest to describe the pore network system in cement-based materials.

4. Hydration model

A simple approach based on the stoichiometry of the chemical reaction between silica fume and forming calcium hydroxide to model the hydration of blended cement–silica systems was applied. However, it is seen that this modeling approach, which is solely based on the kinetics of the pozzolanic activity is not sufficient to describe hydration in low water and low porosity SF-modified systems. Information about the diffusivity and transport properties of each system seems vital to have a deeper knowledge of the extent of the pozzolanic activity. In order to study this, it is necessary to develop greater knowledge on the physical properties of the system over time, viz. pore structure and diffusivity. However, for a cement paste with $w/c = 0.30$ and at $s/c = 0.15$, it is concluded that the system may not fully convert the calcium hydroxide into CSH via pozzolanic activity. The recognition that the pozzolanic activity is not significant in the long-term hydration is consistent with the experimental results, as the rate of pozzolanic activity is practically negligible after the third-day of sealed hydration. This effect is even more obvious in the water-entrained SF-modified cement paste, suggesting that water movement is primarily dependent on the initial water to cement ratio and the amount of silica fume in the system, the physical properties governing the course of water release from the superabsorbent.

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