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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:

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

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