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HYDRATION AND MECHANICAL PROPERTIES OF WATER-ENTRAINED CEMENT-BASED MATERIALS

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Abstract

In this work, the relation between compressive strength and the hydration of water-entrained silica fume modified cement-based materials is analysed. A model developed in previous research is used to determine both pozolanic and internal curing activity. This is done taking as base-input the thermal decomposition of SF-added and plain cement-based systems. It is found that the addition of superabsorbent polymers enhances both primary and secondary reactions within hydration. There is also a clear indication that the physical properties of the cement paste influences the course of the secondary reaction. Furthermore, the compressive strength of the composites was analysed in non-restrained and in restrained systems, referring to cement pastes and cement mortars respectively. The measured compressive strength is lower in the case of water-entrained unrestrained cement-based materials. However, in restrained systems, the addition of superabsorbent polymers is beneficial. The relation between hydration degree and strength development is discussed for water-entrained cement-based materials. Further research is required to verify the degree of cracking of these systems.

1.   INTRODUCTION

Hydration of combined Portland cement and silica fume is a topic that comprehends intensive research work. While the complete description of the hydration products within hydration of cement itself constitutes a still-on-going investigation, the mineral additions brings additional difficulties in to the characterisation of new multi-phase reactions, either by providing new sites for the nucleation of cement minerals, or by influencing the nature and rate of a particular reaction. In a previous work [1], a new method was proposed in order to describe the pozolanic activity of blended systems. This method takes into account the interpretation of different thermal decomposition profiles, such as plain and mineral-added cement systems.

The characterisation of mechanical properties in cement-based materials still is a sensible topic within scientific community. The fragile nature of the cement pastes often introduces a high degree of uncertainty in the description of the real strength that is developing within a

particular system. There are only few studies on the mechanical properties of water-entrained cement-based materials, the first example being found in work by Lura et al. [2].

In this work, the matter of strength development is further analysed supported by the hydration behaviour of the same systems. In addition, the applicability of classic approaches to model strength in cement-based composites is discussed.

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/m3 with a specific surface of 3150 m2/kg as measured by Blaine. The phase composition as determined by Bogue procedure is presented in Tab.1.

Table 1: Cement phase composition by Bogue method

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

Silica fume 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 m2/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 eq.: 1.09. A naphthalene-based superplasticizer was added at a rate of 1% of the wt. of cement in all mixtures.

Three paste systems were analysed: 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 systems 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 [3]. The specimens were kept in sealed conditions at a constant temperature of 20 ˚C until each curing age was achieved, where measurements took place. In addition, either water-entrained and standard silica-added cement-based mortar systems were casted. These essentially consists in a cement paste and a fine aggregate, the later existing in a fraction of 35 vol.-%. All the other components were kept accordingly.

TG/DTA profiles were obtained with samples from the same batches than XRD specimens in a Setaram Labsys DTA-TG/DSC. A total amount of 50 to 100 milligrams of sample is heated at 10 ºC/min up to 1050 degrees Celsius. 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 the calculation of the calcium hydroxide content, a separate test was performed with pure Ca(OH)2 to check the enthalpy of this compound, which enables the calculation of the wt.-% of calcium hydroxide. A 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 the literature [4]. The TG method does not require any calibration procedure, the mass being directly derived from the stoichiometry of the $Ca(OH)_2$ de-hydroxylation.

Compressive strength and the modulus of elasticity in compression were determined in a fully automated INSTRON testing machine with a load capacity of 250 KN. Early-age tests

were done according to the hydration peaks of each system, as measured by temperature evolution, taken by calorimetric measurements in the cement pastes [5]. In the case of cement-silica pastes, cylindrical specimens with diameter of 14 mm and length to diameter ratio of 2 were tested at the first 24 hours. The strength properties at 1, 3, 7 and 28 days in sealed conditions were examined. In addition, a careful procedure was taken in the sample preparation procedure. Samples were casted individually to avoid microcracking during the cutting of longer cylinders, as an alternative method reported in Ref. [2]. The tests were performed according to the procedures described in ASTM standard number C39-86.

4.   RESULTS

Fig. 1 shows the TG/DTA profiles taken from the cement pastes after 28 days in sealed conditions. In respect to the typical TG/DTA profile, it is possible to obtain indirect information of the compounds by analysing the reactions occurring in the sample subjected to a temperature increase.
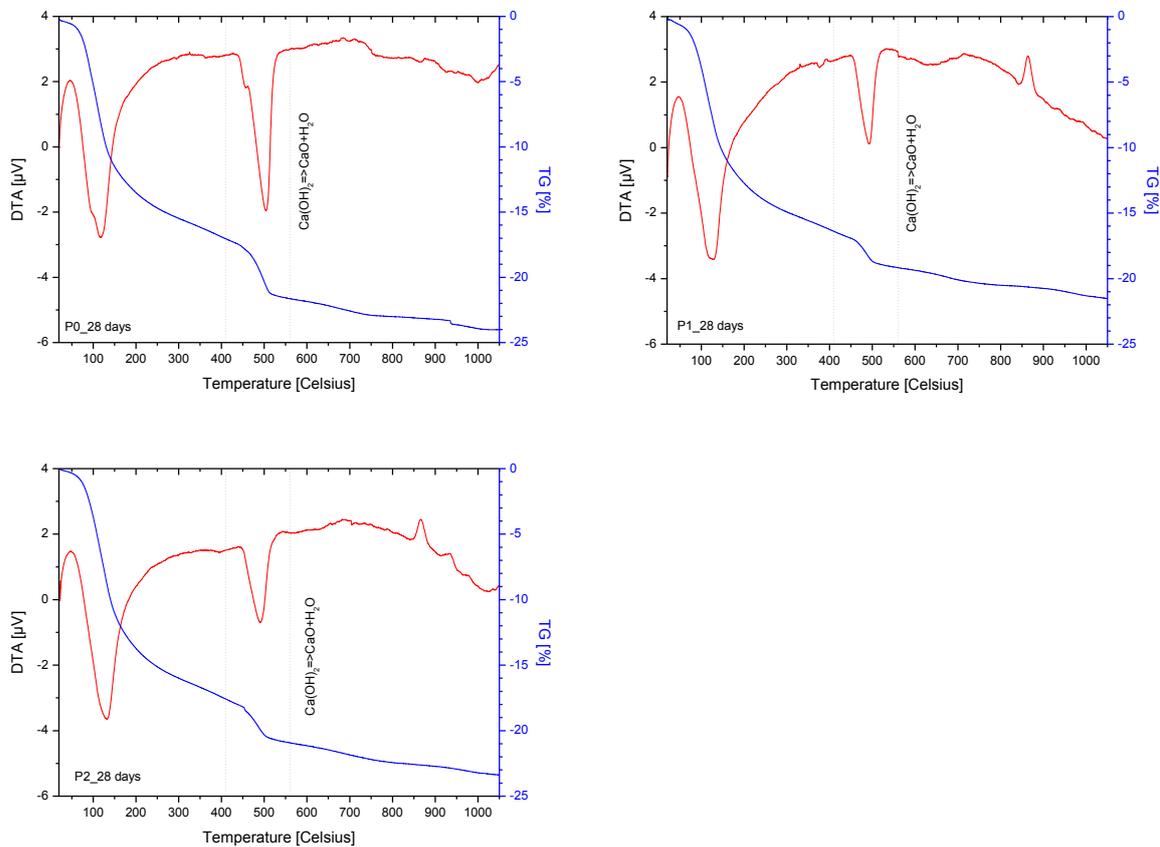

Figure 1: TG/DTA profiles of the cement pastes after 28 days in sealed conditions. The TG measurement is scaled in the right y-axis and DTA in the left y-axis.

The first endothermic peak in the DTA curve is attributed to the de-hydroxylation of CSH phase, corresponding to the mass loss in the TG profile up to 150 ºC. The weight loss on this stage is due to the loss of weakly bind water on gel solid, which is physically adsorbed, taken at about 110 ºC. The second major peak is also endothermic and corresponds to the de-

hydration of calcium hydroxide, resulting new loss of mass starting at about 410 ºC. It is not found any other representative peak in the DTA profile, although curves present minor instability around the 800 ºC, which may be related to a minor uncontrolled carbonation of the sample. However, SF-modified systems show a third characteristic peak located at about 900ºC. 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. The calcium hydroxide may be easily differentiated within 460 and 490 degrees Celsius. In Fig. 1, it is clear that both the peak area and weight loss of the plain cement is lower in respect to the silica-cement paste. This is a clear indication of pozolanic activity via secondary reaction occurring between silica and $Ca(OH)_2$. The data taken from DTA and TG is consistent in respect to the quantification of this phase. Moreover, the CSH produced during both reactions may be obtained by the direct measurement of the water released during the temperature ramp, subtracted from the weight loss attributed to physically-bound water and the weight loss involved in the Ca(OH)2 de-hydroxylation. A hydration model that evolved from this approach may be found in Ref. [1].

The compressive strength of both paste and mortar systems in the first month in sealed hydration is shown in Fig. 2. It can be observed the effect of both the introduction of silica fume and the water-entrainment by superabsorbent polymers in a plain cement paste with a w/c ratio of 0.30.
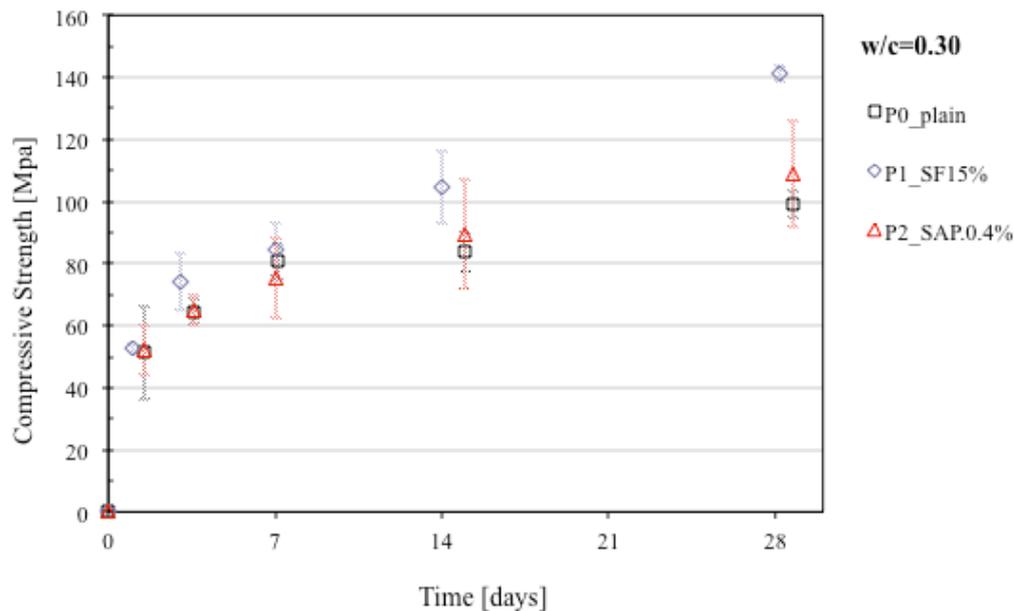

Figure 2: Compressive strength of the composite systems. The samples were kept in sealed condition at 20 ºC. (a) cement pastes

In the former case, referring to the addition of silica fume, a significant increase of the hardened properties is registered in respect to the plain paste, being particularly evident beyond one week. It should be emphasised that the introduction of silica particles was performed as function of the cement weight, the w/c ratio being constant. This method may be a source of criticism, since the relation between water and binder is changed. However, this

approach enables one to see the direct influence of the introduction of silica fume, since it is ideally not reacting on the initial stage of the hydration, thus not playing a major role on the modification of the system within the first reaction. In fact, the one-day strength level is nearly equal for both plain and SF-modified systems. On the other hand, the introduction of both superabsorbent polymers in 0.4% (wt.-% of cement) and the water-entrainment leads to a significant reduction in the compressive strength, in respect to SF-modified cement paste. Fig. 3 shows the effect of the introduction of the aggregate phase in the system. Both mortar systems show lower strength in respect to the SF-modified paste system. However, the water-entrained cement-based mortar system shows a higher strength level in respect to the non-entrained mortar system. In this case, the introduction of superabsorbent polymers in the system is not detrimental in relation with the compressive strength performance.
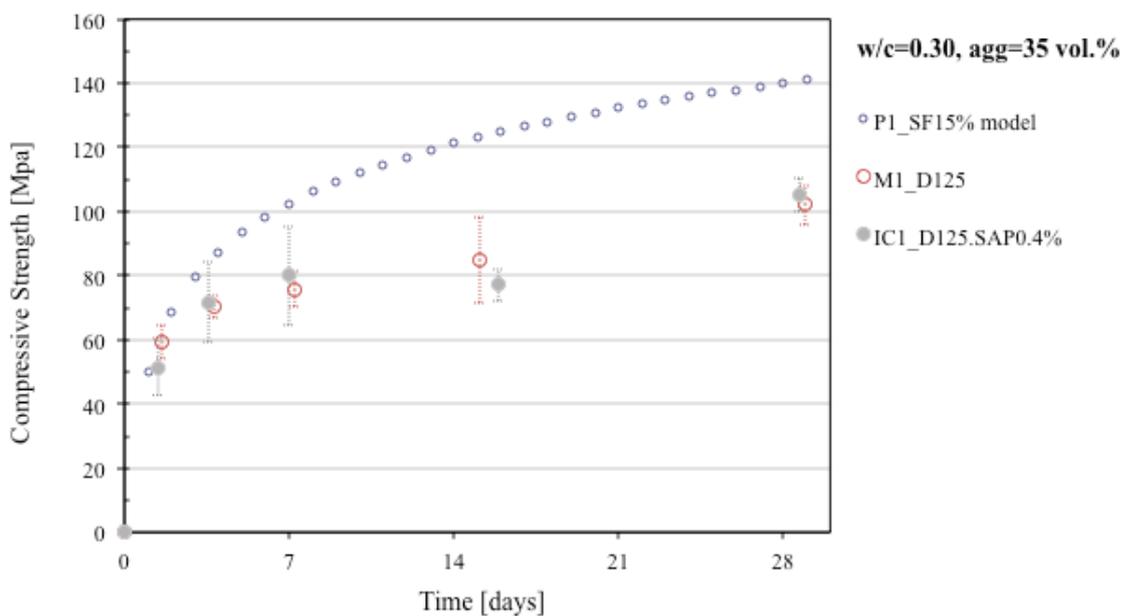

Figure 3: Compressive strength of the composite systems. The samples were kept in sealed condition at 20 ºC. (b) mortar systems.

5.   DISCUSSION

5.1   Hydration versus strength development

TG/DTA technique reveals the behaviour of a water-entrained SF-modified cement-based system. In addition, it clearly indicates that the secondary reaction occurs within the initial stage of hydration, the pozolanic and internal curing activity being the mechanisms of such kinetics. In either case, there are noted two different hydration stages, which are being governed, aside from the chemical features of each system, by the physics of the system, viz. diffusion-controlled reaction. In this section, the relation between hydration kinetics and the development of compressive strength is discussed. Accordingly, the hydration rate and strength gain rate should be linearly-correlated, see for example the classic work by Powers [6]. In Fig. 4, the relation between the water of constitution, measured by TG/DTA and the

development of compressive strength is shown. Since the SF-modified systems have a lower weight of cement per gram of composite, the water of constitution was normalised by weight of cement to reflect the effect of both pozolanic and internal curing activity (see Ref. [1]).
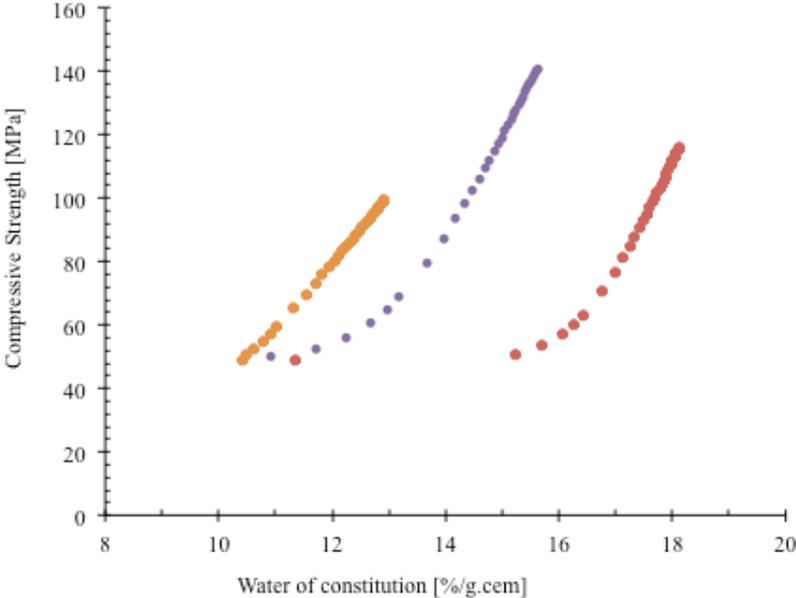

Figure 4: Relation between the compressive strength of the paste systems.

In the plain cement paste system a linear relation between both the development of hydration and strength is found. However, the SF-modified cement paste systems show a non-linear relationship. It may be inferred that a major part of the strength development occurs at a relatively low hydration rate, translated by a relatively lower rate of water reacted, the effect being more flagrant in the water-entrained system. According to Powers model, 0.23 grams of water are required for the complete hydration of one gram of cement, and a maximum degree of hydration of 0.72 is to be found in a cement system with w/c ratio equal to 0.30. In pioneer work by Jensen [7] on this matter, a value of 0.82 for a water-entrained plain cement system may be obtained. The measured hydration degree for the plain cement system is inconsistent with Powers model (0.60), being consistent with the results in Ref.[2].

5.2 Microcracking in restrained systems

As registered in section 4., the compressive strength of the mortar systems is substantially lower than the strength level registered in the paste systems. The introduction of 35 vol.-% of aggregate leads to a strength decrease of 28% at the age of 28 days, in respect to the reference system (P1_SF15%). Thus, the beneficial volumetric instability of SF-modified high strength composites in non-restrained systems, via autogenous deformation, is not all exploitable in restrained systems. The existence of aggregate particles results in build-up stress at early age, as soon as the paste matrix starts to shrink. This occurs when the strength properties of the matrix are not appropriate to support such deformation. As a result, microcracking develops, explaining the strength reduction of the SF-modified mortar system. On the other hand, the strength of the water-entrained mortar system is slightly higher. In this case, and despite the

existence of a weak part in the system (SAP-pores), the internal curing by susperabsorbent polymers is beneficial in maintaining the strength level of the mortar system.

Hasholt et al.[8], have proposed that the strength of a water-entrained concrete system could be modelled by a conjunction of the well-known concept of the gel/space ratio and a corrected compressive strength, the microcracking only slightly affecting the compressive strength of the composite. However, this idea is only valid in open systems and with relatively high w/c ratios. In addition, no silica fume was added in their experiments, and therefore, the self-desiccation phenomena could not be operating at all. Here relies the weakness of the classical approach by Powers to model new composite materials. Further research is required to understand better the relation between the pozolanic activity and the strength development of the material.

Another indirect evidence of that microcracking may be propagating in the system is the instability of the systems (dispersion of the measurement of compressive strength). It is noted that the SF-modified cement paste is stable at 28 days (COV=2%). However, the water-entrained cement-based materials may require more time to achieve mechanical stability. Long-term tests are required to verify this.

5.3   Relative humidity versus strength development

The absolute strength of the water-entrained system is lower than may be related with the existent level of moisture in the system and the additional porosity inherent to the system-physics of this mixture. It is well know the effect of drying on the mechanical properties of cement-based materials [9]. Therefore, it is debatable the direct comparison between the water-entrained paste and the standard paste system. The RH-profiles of the systems show substantial differences in the RH at the age of 28 days. While the plain cement paste desiccate till 92%, the addition of SF results in a RH as low as 75% at 28 days. The internal pressure is therefore, significantly different between the systems. Lura et al.[2] have shown that by conditioning a similar plain system to 75% after 28 days, the strength of the system slightly increases. It is expected that a longer period is required for a water-entrained system to achieve stability in respect to the internal pressure (RH). In any case, it is possible to conclude that the strength properties of water-entrained systems may be potentially higher as function of the decrease of the internal relative humidity.

6.   CONCLUSIONS

  − The compressive strength of water-entrained cement-based composites is not linear-correlated with the hydration degree, taken from TG/DTA hydration profiles in SF-modified cement-based systems.
  − The applicability of classic models is not satisfactory to describe the strength development in water-entrained SF-modified mortar and concrete systems. The simple approach of the gel-space ratio does not take into account both the effect of microcracking within the autogenous phenomena, or the internal relative humidity. Therefore, further work on the degree of microcracking of these systems is required to assess the strength properties of the material.

ACKNOWLEDGEMENTS

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