# Hydration of cement with superabsorbent polymers

Luis Pedro Esteves · Irena Lukošiūtė ·
Jūratė Česnienė

**Abstract** Hydration of cement is a complex thermodynamic system where a number of heterogeneous compounds interact with each other to form cement hydrates. Superabsorbent polymers (SAP) can be added to cement systems with many different reasons, so it is relevant that the basic knowledge of this new compound on the development of hydration is well understood. This paper reports basic research on thermal analysis of cement pastes with SAP—a suspension-polymerized poly acrylic acid–acrylamide copolymer. Several parameters were analysed: the concentration of SAP, the effect of particle size distribution and their influence on the hydration process with focus on ordinary Portland cement. The methodology included thermogravimetric analysis and differential scanning calorimetry. Combined water method was employed at different thermodynamic conditions, so the energy of activation in the different systems can be accessed. The introduction of SAP in cement-based materials significantly affects the chemical balance of ordinary Portland cement. The effect is not only in terms of the amount of hydrates, but also the type of hydrates being generated, thermodynamically favourable to precipitation of calcium hydroxide. This paper provides information relevant to hydration modelling and comprehension of cementitious materials when internal curing is active.

## Introduction

The use of superabsorbent polymers (SAP) in cement-based materials is very promising in concrete technology. Beside the internal curing ability and their contribution to reduce autogenous shrinkage and control microcracking, there are unexplored fields that are now in perspective, such as the use of SAP for frost protection, as rheology modifiers in shotcrete or other special applications [1–4]. In cementitious materials, we are slowly realising how the chemical nature and the physical properties of SAP affects the hardened properties of cement-based materials, and still, there is no systematic ground on the influence of this component on both hydration products and kinetics in a more fundamental way [5]. SAP can be added to cement systems for many different reasons, so it is relevant that the basic knowledge of this new compound on the development of hydration is well understood.

Thermal analysis of cement systems is very helpful for understanding of many different properties of cementitious compounds, both with regards to the original reacting compounds, and also for the hydration products. For example, the phase transition occurring at 1,300 °C will lead to the sintering of certain types of calcium silicates with a specific mineral composition [6]. At lower temperatures, cement compounds also show singular thermal properties, such as the dehydration of $Ca(OH)_2$ at about 400 °C.

This paper reports research on thermal analysis of cement pastes with SAP. Several parameters were in focus: the effect of concentration of SAP in the system, the effect of particle size distribution and their influence on the

L. P. Esteves (✉)
Technical University of Denmark, Brovej, Bygning 118,
2800 Kgs., Lyngby, Denmark
e-mail: luies@byg.dtu.dk

I. Lukošiūtė · J. Česnienė
Lithuanian Energy Institute, Breslaujos 3, 44403 Kaunas,
Lithuania
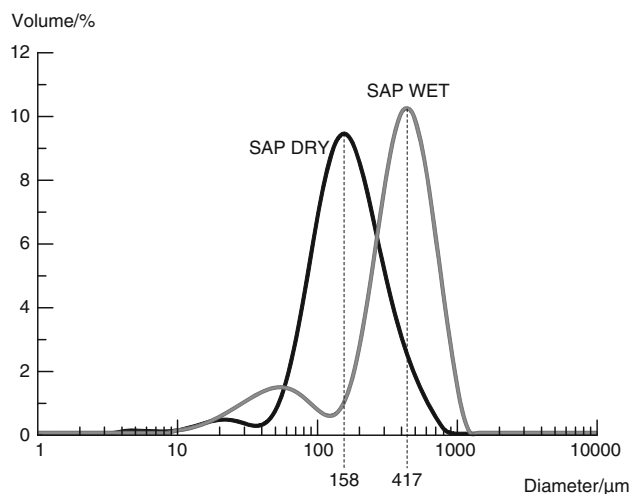
**Fig. 1** Measurement of absorption capacity of superabsorbent polymers by laser diffraction particle size analysis (see reference for details on the measurement technique [7])

hydration of cement. This is done at different temperature conditions, so that the energy of activation in the different systems can be derived. This paper provides information relevant to hydration modelling and understanding of cementitious materials when internal curing is active.

## Materials and methods

The materials used in this work included a suspension-polymerized poly acrylic acid–acrylamide copolymer and Aalborg rapid hardening Portland cement type I 52.5 N.

The chemical composition according to Bogue calculation is $C_3S = 62$, $C_2S = 13$, $C_3A = 8$, $C_4AF = 12$. The sulphate content $SO_3$ is 3.2 % and $Na_2O$ (eq.) = 0.6. Free CaO is 1.4 %.

The SAP consists in spherical particles of a suspension-polymerized poly acrylic acid–acrylamide copolymer. Several particles sizes were sieved into specific size fractions, from a sample with an average size of about 150 μm. Both dry and swollen sizes of the polymer are shown in Fig. 1. The measurement in a synthetic pore fluid leads to an absorption capacity of 20 mL $g^{-1}$ of dry polymer.

Samples of the different cement paste systems were produced in a standard mortar mixer, poured into small polyethylene cylindrical vials, and placed in a thermostatically controlled bath at a temperature of 20, 30 and 40 °C. A superplasticizer was used to maintain workability of the low-water systems. The composition of the cement systems is shown in Table 1, along with the research methodology. At each curing age, samples were evacuated under vacuum as a procedure to stop further hydration. This was operated overnight from where the samples were conditioned to a temperature of 105 °C for the next 24 h. Either TG/DSC profiles or chemical-bound water (HD) were then obtained by subjecting each sample to 1,050 °C.

The experimental methods included the combination of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) techniques to study the thermal decomposition of the pastes. TG/DSC curves were obtained in a Linseis STA PT1600 DTA–TG/DSC. A total quantity of 17–19 mg of sample was heated at 10 °C $min^{-1}$ up to 1,050 °C. The measurements were performed in dry nitrogen

**Table 1** Material composition and methodology for the study of hydration of cement pastes with superabsorbent polymers

| Code | System[a] | Water ratios | | Components/kg $m^{-3}$ | | | | | Methods | Temperature/°C | Curing age/days | | | | |
|------|-----------|------|-------|--------|-------|-----|-----|-------|---------|----------------|---|---|---|----|----|
| | | w/c | (w/c)$_e$[b] | Cement | Water | SAP | SP | Total | | | 1 | 3 | 7 | 28 | 56 |
| T1 | REF.0.25/SAP.0.00 % | 0.25 | 0.00 | 1,747 | 437 | 0 | 9 | 2,192 | TG/DSC/HD | 20, 30, 40 | x | x | x | x | x |
| T2 | SAP.0.25/SAP.0.25 %/ #75–125 | 0.25 | 0.05 | 1,584 | 475 | 4 | 19 | 2,083 | TG/DSC/HD | 40 | | x | | x | |
| T3 | SAP.0.25/SAP.0.5 %/ #75–125 | 0.25 | 0.10 | 1,465 | 513 | 7 | 18 | 2,002 | TG/DSC/HD | 40 | | x | | x | |
| T4 | SAP.0.25/SAP.1.0 %/ #75–125 | 0.25 | 0.20 | 1,272 | 572 | 13 | 15 | 1,872 | TG/DSC/HD | 20, 30, 40 | x | x | x | x | x |
| T5 | SAP.0.25/SAP.2.0 %/ #75–125 | 0.25 | 0.40 | 1,007 | 655 | 20 | 12 | 1,694 | TG/DSC/HD | 40 | | x | | x | |
| T6 | SAP.0.25/SAP.1.0 %/ #50–75 | 0.25 | 0.20 | 1,272 | 572 | 13 | 15 | 1,872 | TG/DSC/HD | 40 | | x | | x | |
| T7 | SAP.0.25/SAP.1.0 %/ #125–150 | 0.25 | 0.20 | 1,272 | 572 | 13 | 15 | 1,872 | TG/DSC/HD | 40 | | x | | x | |
| T8 | SAP.0.25/SAP.1.0 %/ #150–180 | 0.25 | 0.20 | 1,272 | 572 | 13 | 15 | 1,872 | TG/DSC/HD | 40 | | x | | x | |

[a] Designation code of cementitious systems is built on—[system name· ]. [w/c]/[SAP dosage by cement mass]/[SAP particle size]

[b] (w/c)$_e$ corresponds to the additional water amount that is absorbed by SAP during mixing. This is obtained by multiplying the SAP dosage (expressed by cement mass) by its absorption capacity

atmosphere at 2 mL s$^{-1}$ gas flow. Platinum crucibles were used in experiments. The heat transfer was measured by thermocouple type S (one wire Pt/Rh with 10 % of rhodium and second—100 % of Pt). The amount of calcium hydroxide in the system (by TG) was calculated according to Esteves [8]. The calculation of CH by DSC technique was done through a calibration constant determined in a system comprehending pure substances—$Ca(OH)_2 + Al_2O_3$. The amount of $Ca(OH)_2$ can be then derived from Eq. (1), where $A_{Ca(OH)2}$ is the peak area taken from DSC profile in J g$^{-1}$.

$$Ca(OH)_2/mass\% = 0.064 \cdot A_{Ca(OH)2}. \tag{1}$$

For the analysis of the effect of SAP on the energy of activation and reaction kinetics, a third technique was selected—combined water method, a well-known technique to estimate the hydration degree (HD) of cement. This method is useful for cement pastes, under the assumption that water has different volatilities to support the description of evaporable and non-evaporable (or chemically bound) water, and it was thoroughly used as a measurement of cement hydration after Powers [9]. Chemically bound water—$w_{chem}$ (g g$^{-1}$ cement)—is obtained according to Eq. (2), where $m_{105}$ is the mass of the dried sample and $m_{1050}$ is the mass of the ignited sample. The term LOI refers to the loss of ignition of cement powder when it is fired up to 1,050 °C. The measured LOI for this cement was less than 2 %.

$$w_{chem} = \frac{m_{105}}{m_{1050}}(1 - LOI) - 1. \tag{2}$$

However, the introduction of new component such as SAP introduces an uncertainty in the mass balance obtained when the samples are ignited up to 1050 °C. In fact, Eq. (2) should be corrected for the loss of SAP mass during ignition. The amount of SAP used in the experiment is equal to 0.7 % of the total mass of the system, from where Eq. (2) can overestimate the value of chemically combined water ($w_{chem}$) in maximum of 5 %. Within the framework of this work, it seems straightforward to consider the calculation of the chemically bound water per gram of cement without any correction for the mass loss of SAP.

## Results

### Thermogravimetry and differential scanning calorimetry

The results from TG/DSC measurements performed to the system T1–T8 after 3 and 28 days in sealed conditions are shown in Fig. 2.

It is not straightforward to perform a precise calculation of C–S–H phase due to overlapping peaks in the temperature range of 100–200 °C. This range of water volatilities includes the decomposition of ettringite, dehydration of monocarbonate and other minor Aft hydrates along with C–S–H [6]. An attempt to deconvolute these peaks would require another experimental framework. In any case, it is possible to conclude that the addition of increasing amounts of SAP leads systematically to higher mass loss during the TG test. Full hydration of cement (chemically bound water in the range of 0.23) is achieved with the additions of 1 % by cement mass or higher. The size distribution of SAP does not seem to affect the amount of chemically bound water and the hydration degree of system T4, which was used as a reference point for this parameter. A value between 20 and 25 % is found for all systems T6–T8. The substance $CaCO_3$ decomposes at 700 °C, with the release of $CO_2$ [10]. The peak under this temperature is not significantly influenced by changes in the concentration or distribution of SAP. The average amount of $CO_2$ released by the systems at 28 days is 2.61 ± 0.59 % (the $CO_2$ release of the anhydrous cement is 1.56 %).

It seems relevant to find which phases are being generated in excess. Dehydration of $Ca(OH)_2$ occurs at the temperature of 450 °C, so this substance can be straightforwardly described individually. The calculated values taken by TG measurements are shown in Fig. 3, along with the water bound to C–S–H and other hydrates deducted of the mass loss due to $CO_2$ release. It is observed that CH phase increases substantially with higher amounts of SAP and with the hydration duration. The effect is also visible when the surface area is increased (T6). There are clear differences in the absolute values of water bound to CH registered by TG and DSC. The TG measurement leads systematically to a higher value (average of 1.25 ± 0.2 %) with regards to the DSC measurement. The determined excess can be due to the overlap with the water bound to C–S–H captured in the TG measurement. The continuous release of water in this phase is not present in the peak measured by DSC. All systems that include SAP show higher values of water bound to CH. The reasons for this are discussed further in the following sections. The amount of water bound to C–S–H and other hydrates—Aft/Afm—increases consistently with SAP addition, with maximum values observed in the paste T4. Higher amounts of SAP in the system (paste T5) do not necessarily lead to a higher amount of these hydrates. This means that SAP potential for promoting the hydration of C–S–H may be limited to about 1 %, valid for this type of polymer with the used particle size distribution. Pastes T6 and T7 show higher values of combined water to C–S–H with relation to T4, despite being constituted by bigger particles, thus with longer distances to hydration sites. The effect of the particle size is not conclusive.
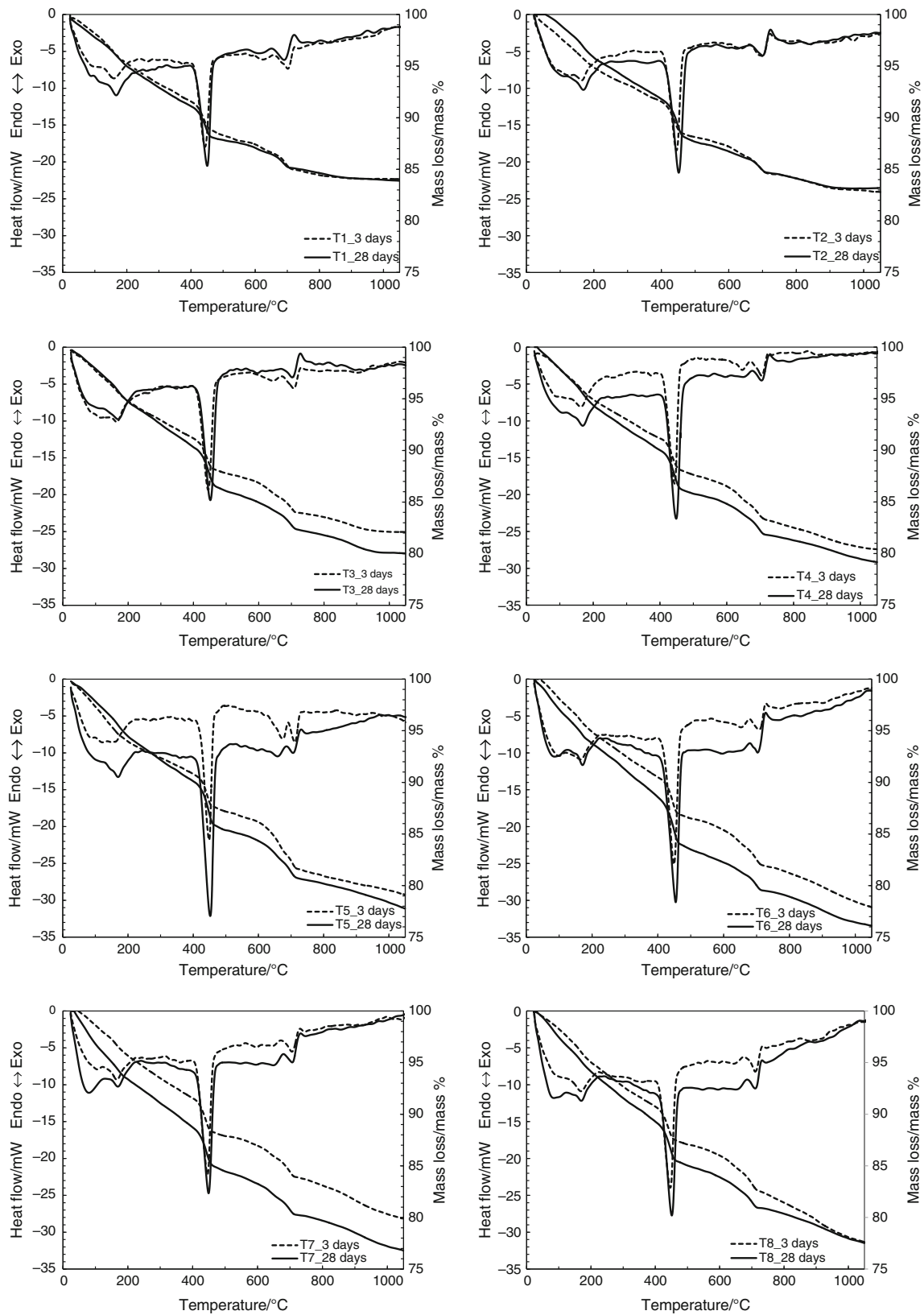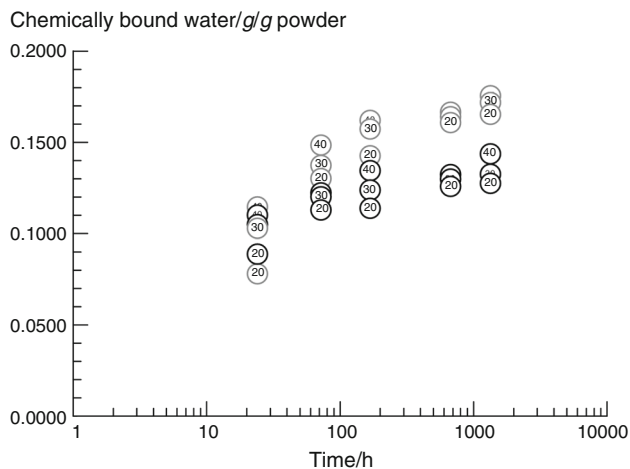
**Fig. 2** TG/DSC profiles of cement samples (systems T1–T8) after 3 and 28 days in sealed conditions. The TG measurement is scaled in the *right* y-axis and DSC in the *left* y-axis
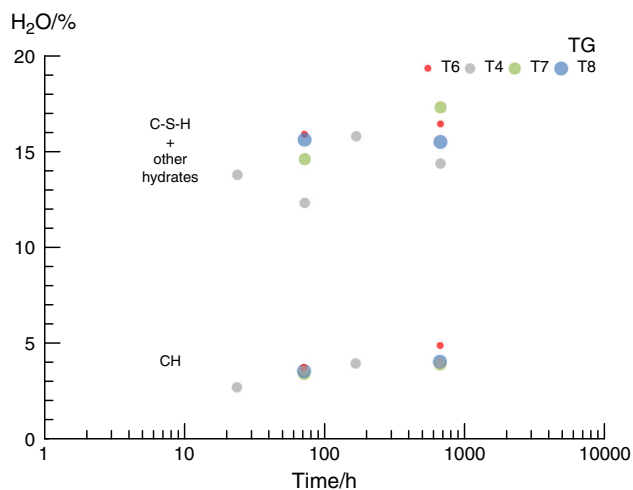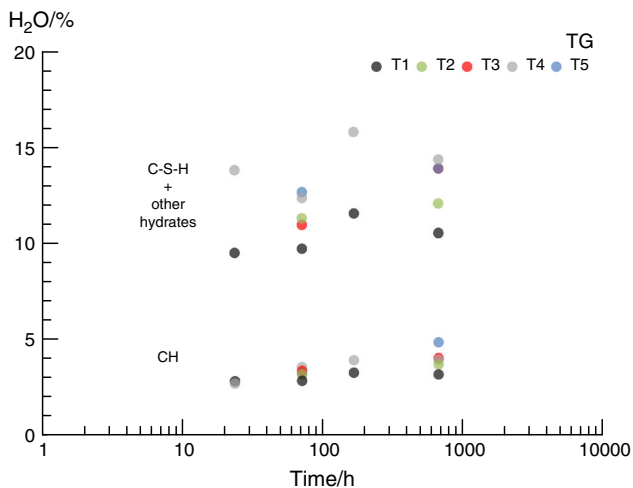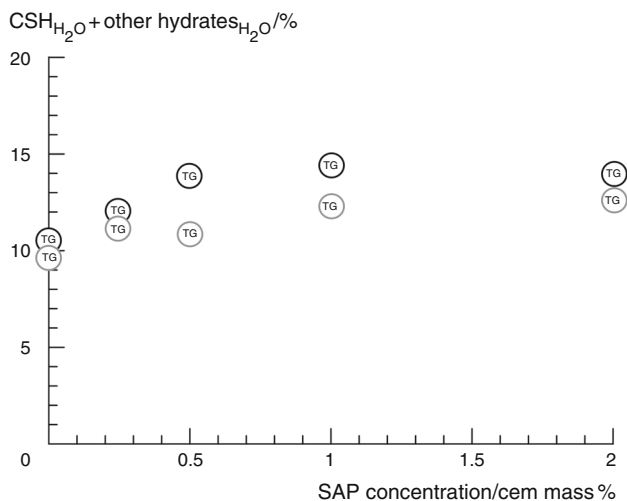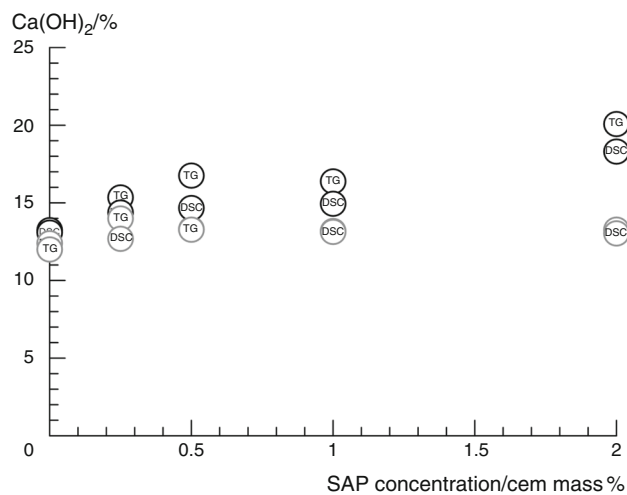
**Fig. 3** Water bound to the different hydrates in the cement pastes T1–T8, as measured by TG. Water bound to C–S–H and other hydrates—Aft/Afm was calculated with the deduction of the mass loss due to the release of $CO_2$ and $H_2O$ bound to CH



**Fig. 4** Non-evaporable water of cement pastes T1 and T4 measured at 20, 30 and 40 °C. *Black* and *light grey* refers to systems T1 and T4, respectively





**Fig. 5** Effect of SAP concentration on the quantities of hydrated products—CH, and water in C–S–H and other hydrates, as measured by TG and DSC techniques. Light grey and black refers to data points at 3 and 28 days, respectively
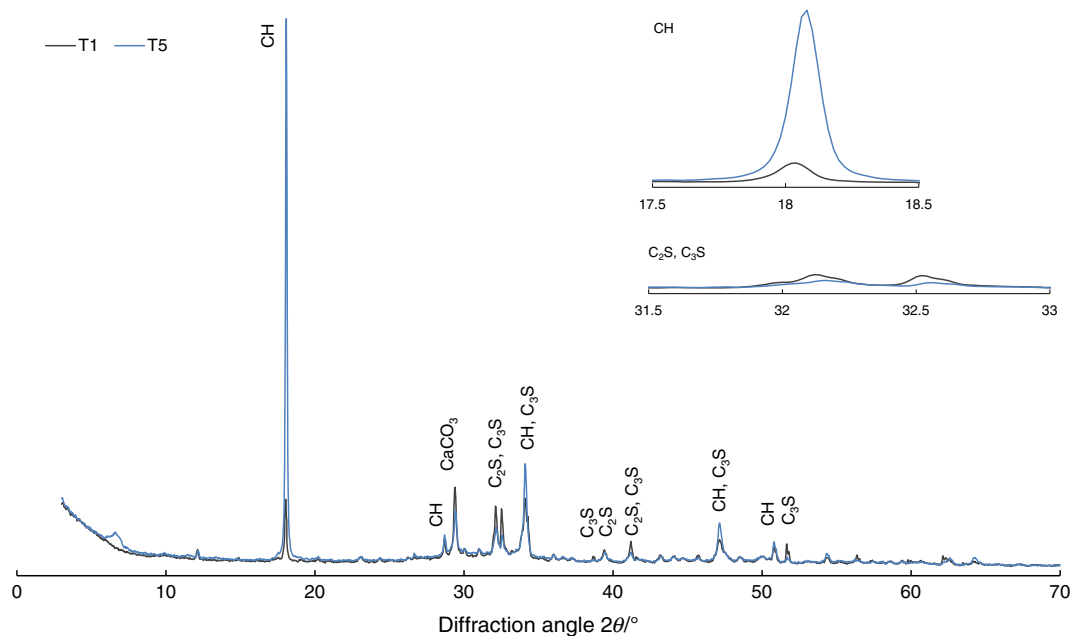
## Chemically combined water

The results of combined water are shown in Fig. 4. There are notable differences in the evolution of chemically bound water per gram of powder. In both systems, a faster reaction is obtained with the increase of the curing temperature. At 28 days, chemically bound water is approximately the same in all temperatures, but the maximum values are obtained for higher curing temperature. According to the classical theories of cement hydration, a system cured at a lower temperature should be able to prolong hydration up to higher values, due to a more ordered arrangement of the hydration products during the chemical reaction [6]. It can also be seen the effect of adding SAP in the hydration kinetics. The chemically bound water is practically the same at 24 h for systems T1 and T4. However, substantial new hydration products are

**Fig. 6** Measured intensity/a.u by XRD of cement pastes at 28 days in sealed conditions. The *insets* show the relevant peaks for the main hydration products. XRD was obtained in a D8 Advance Powder Diffractometer—Bruker AXS, operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with a Ni 0.02-mm filter to select the CuKα wavelength. Diffraction patterns were recorded in a Bragg–Brentano geometry using a fast counting detector Bruker LynxEye based on silicon strip technology. The specimens were scanned over the range of 1–70 $2\theta°$ at a scanning speed of 6 $2\theta°$ min$^{-1}$, using a coupled $2\theta/\theta$ scan type

developed afterwards and the value of combined water rises significantly for the systems with SAP. The activity of the internal water sources is limited to about 7 days, from where a less significant development of hydration is observed. The introduction of this amount of SAP corresponds to an increase of 25 % in new hydrated products, as measured by this method. This is consistent with the measurements taken with the TG/DSC.

## Discussion

### The effect of SAP concentration

Figure 5 shows the effect of the SAP concentration on the development of hydration. Higher amounts of CH are measured in cement pastes with increasing amounts of SAP. Tests performed to the pure compounds do not indicate any peaks overlapping. It may be then concluded that the addition of SAP influences the development of hydrates in their chemical nature. Enhanced nucleation of CH phases in the cement system seems to be thermodynamically favourable and they are stable on the "matured" system (28 days). At high concentrations of SAP, there is an increase in 50 % the amount of substance with regards to the reference system. However, this is not markedly observed for the C–S–H and other hydrates. The hydration

of these compounds is not extended beyond a polymer concentration of 1–2 % by mass of cement. The increase of the crystalline phase CH and the decrease of the crystalline cement compound $C_3S$ were confirmed by X-ray diffraction (XRD) analysis of the relevant peaks in cement pastes T1 and T5. This is shown in Fig. 6.

### The effect of particle size distribution

Figure 7 shows the effect of the SAP particle size on the development of hydration. A higher amount of CH was determined when 50–75 μm grain-size SAP were used. The effect is more marked on the "matured" system (28 days), although the value at the third day is also higher when compared with the other size distributions. According to Nestle et al. [11], this is explained by a rapid desorption kinetics of SAP with smaller grain size. However, the value of the total chemically bound water does not change substantially in the systems at the same instant of time (see Fig. 2 systems T4, T6–T8). Therefore, it is rather a mechanism related to the surface area and locking of $Ca^{2+}$ ions in the SAP structure than an effect related to water release and desorption kinetics that is enhancing the hydration of this substance. The underlying mechanism can be either attributed to an exchange of ions bonded in the polymer network with calcium ions dissolved in the cementitious solution, or simply to a re-arrangement of the

Ca(OH)$_2$/%



CSH$_{H_2O}$ + other hydrates$_{H_2O}$/%
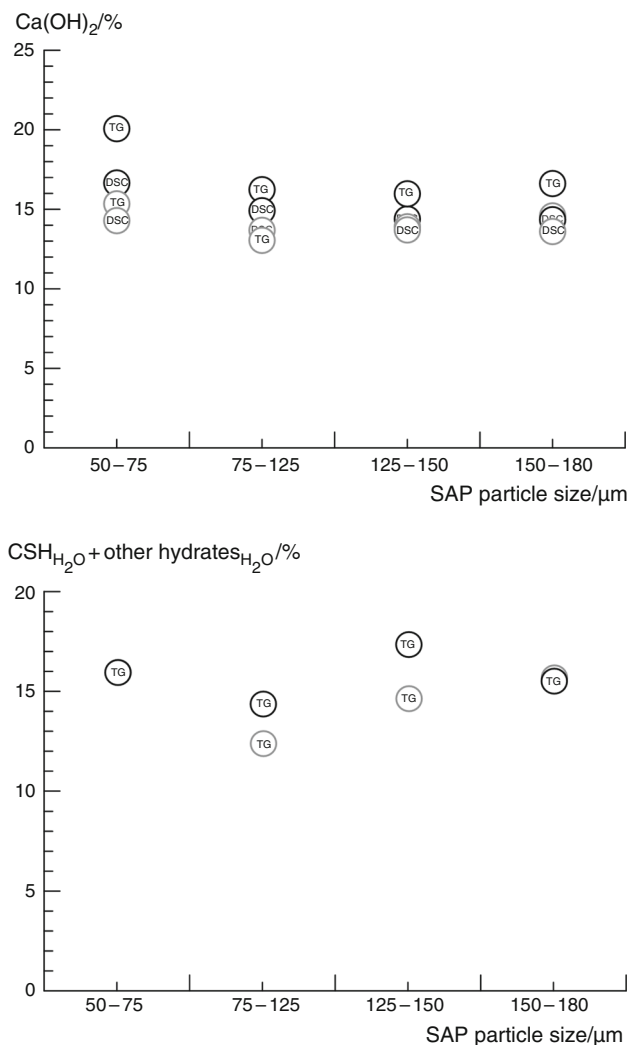


**Fig. 7** Effect of SAP particle size on the quantities of hydrated products—CH, and water in C–S–H and other hydrates, as measured by TG and DSC techniques. *Light grey* and *black* refers to data points at 3 and 28 days, respectively

polymer network with the calcium ions interlocking the polymer chains. This effect is not found in the amount of water in C–S–H and other hydrates. It would be expected that the distribution of the particles has a significant effect over the hydration of the cement compounds. This raises an interesting discussion over the applicability of the concept of paste-protected volumes to internal curing and subsequent hydration of cement-based materials. According to this concept, the distance between the particles has a marked influence on the availability of internal curing water to the surrounding paste [12]. The size distribution of SAP does not substantially affect the amount of chemically bound water, so the hydration degree is not significantly affected. This confirms that the differences in the absorption by different particle size distributions of SAP particles do not result in substantial differences in the amount of

hydrates. The effect can however be operational at lower concentrations of the polymer particles.

**Thermodynamics of internal curing**

The description of a physical property such as hydration degree or combined water can be described by means of the dispersion model [13], which may be defined by Eq. (3). P expresses the hydration degree (−) or combined water (g g$^{-1}$ powder) at time $t$ (h), with characteristic times at the end of the dormant period—$t_0$ and at time $t_{50}$, where the property achieves 50 % of its infinite value $P_\infty$.

$$P = P_\infty \cdot \left[ 1 + \left( \frac{t_{50} - t_0}{t - t_0} \right)^i \right]^{-1}. \qquad (3)$$

The fitting of (3) to the experimental values was performed for the cement paste considering both linear and parabolic kinetics by the variation of relevant parameter—$i$ (see Fig. 7). It is seen that both values can be used to describe the hydration kinetics of the cement system. However, previous studies on this type of cement at 20 °C show that the term $t_0$ falls in the first hours after water addition, leading to the conclusion that the dispersion model based on linear kinetics would better describe the physical property [14]. The infinite value of combined water is situated around the range of 0.13–0.14 for all systems, although the value is endemically higher at higher curing temperatures.

The same procedure was applied to the cement paste with internal curing by means of SAP. This is shown in Fig. 8, hydration of cementitious systems with SAP being described by linear kinetics ($i = 1$). This is still the value leading to higher correlation coefficient. However, the fitting parameters differ substantially with relation to those obtained in a cement paste. The parameter $t_0$ is displaced to a later time, and at a curing temperature of 20 °C, the reaction is only initiated at about 6 h. There is no reference of a relevant effect of SAP on delaying setting or reaction times in cement systems. However, system T4 is composed by a higher amount of SAP with regards to the normal amount used for internal curing of cement systems. This is an indication that the hydration temperature has a relevant effect on the property development of cement pastes with SAP (Fig. 9).

Even though there is a large amount of water for the hydration of all the cement in the system, the value of non-evaporable water does not reach the maximum value of combined water (full hydration)—typically 0.23.

The energy of activation was calculated by Arrhenius equation—(4).

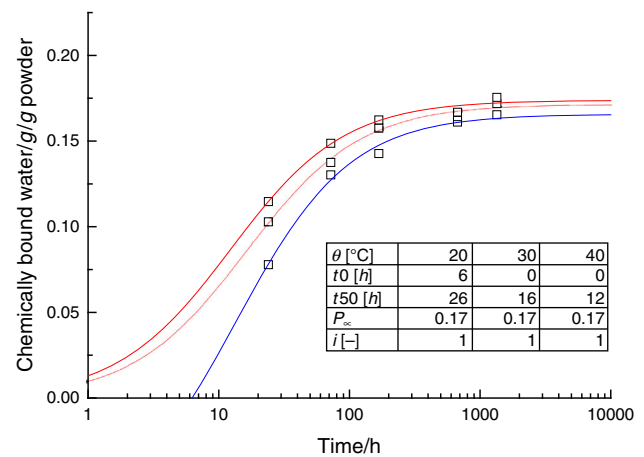$$k(T) = k \cdot \exp^{\left( -\frac{E_a}{RT} \right)}. \qquad (4)$$
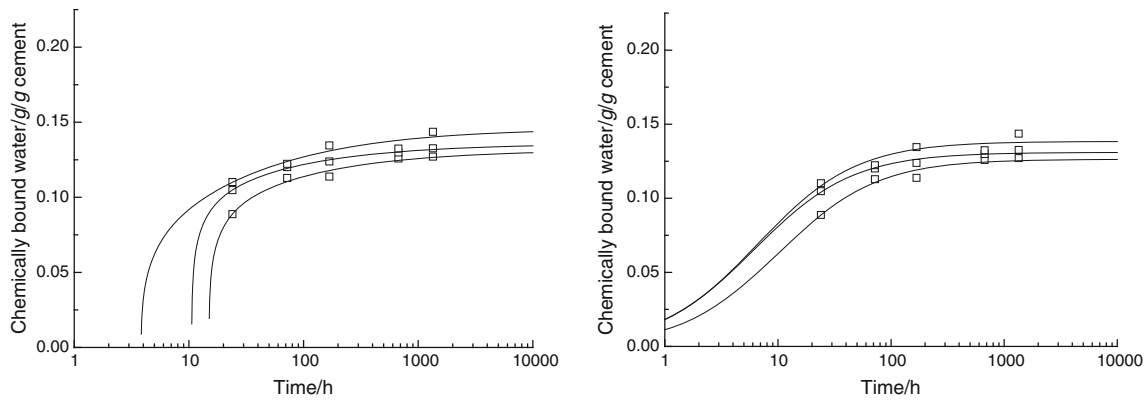
**Fig. 8** Simulation of the dispersion model on the measured values of non-evaporable water in system T0. Parabolic kinetics is shown at the *right* and linear kinetics is shown in the *left*

The reaction rate constants—$k$—were derived for each temperature assuming the rate constants obtained at the first measurement. By plotting ln $(k)$ versus the inverse of the absolute temperature $T$ (K), a value of 82.8 kJ mol$^{-1}$ is obtained for T1 and a slightly higher value for system T4. This is higher than the reference values reported for the energy of activation of Portland cement—57–61 kJ mol$^{-1}$ [14]. The value for the activation energy was derived by considering that the reaction rate constants are equivalent to the difference between $t_{50}$ and $t_0$. It is debatable that the reaction rate constant may be obtained from a value where the reaction reached half of its maturity. The translation of the reaction rate constants at an earlier age by another experimental technique would be appropriate. In the present work, it seems sufficient to conclude that the internal curing by SAP may have a significant influence on the chemical activity of cement compounds, especially at lower curing temperatures. This result is particularly relevant for the production of new cements with both inorganic and organic compounds.

## Conclusions

With this work, a more fundamental knowledge about the effect of SAP on the hydration of cement compounds was reached. We can draw some relevant conclusions:

1. The introduction of SAP into a cementitious system results in substantial "new" hydration products. The effect is not only in terms of the amount of hydrates, but also the type of hydrates being generated. According to the results obtained with TG/DSC (also confirmed by XRD), it is seen that a slight increase of the SAP concentration is favourable for the precipitation of calcium hydroxide. We do not know whether



**Fig. 9** Simulation of the dispersion model on the measured values of non-evaporable water in system T4

this is happening inside the pores or in the paste fraction.

2. The size distribution of SAP does not substantially affect the amount of chemically bound water, so the hydration degree is not significantly affected. This confirms that the differences in the absorption by different particle size distributions of SAP particles do not result in substantial differences in the amount of hydrates. In the same line of thinking, it can be concluded that the concept of *paste-protected volumes* does not apply to the hydration of porous cement systems. The effect can be operational at lower concentrations of the polymer.

3. However, the size fraction of 50–75 μm results in a higher amount of calcium hydroxide, so the chemistry of cement hydration can be affected by the same mechanism described in 1—exchange of cation ions with the cementitious solution and interlocking of

$Ca^{2+}$ ions within the polymer structure, enhanced via surface area.

4. A mathematical description of the thermodynamics of cement pastes when internal curing is active was proposed. The classical models apply naturally to these systems, and can be used to describe the kinetics and activation energy involved in the reactions of cement. In the analyse case, the dispersion model with linear kinetics showed better approximation to the measurements. It is suggested that the curing temperature has a relevant influence in the development of the hydration reactions of systems with SAP.

# References

1. Esteves LP. Internal curing in cement-based materials. PhD thesis. Portugal: Aveiro University; 2009.
2. Cusson D, Mechtcherine V, Lura P. Practical applications of superabsorbent polymers in concrete and other building materials. In: Mechtcherine V, Reinhardt H-W, editors. Application of super absorbent polymers (SAP) in concrete construction. RILEM state of the art reports. Dordrecht: Springer; 2012. p. 137–48.
3. Snoeck D, Van Tittelboom K, Steuperaert S, Dubruel P, De Belie N. Self-healing cementitious materials by the combination of microfibres and superabsorbent polymers. J Intell Mater Syst Struct. 2014;25(1):13–24.
4. Esteves LP. Water-entrained SHOTCRETE. Internal communication. Technical Univerisity of Denmark; 2006 (unpublished work).
5. Ye G, Breugel K, Lura P, Mechtcherine V. Hardening process of binder paste and microstructure development. In: Mechtcherine V, Reinhardt H-W, editors. Application of super absorbent polymers (SAP) in concrete construction. RILEM state of the art reports. Dordrecht: Springer; 2012. p. 51–62.
6. Taylor HFW. Cement chemistry. London: Telford; 1997.
7. Esteves LP. Recommended method for measurement of absorbency of superabsorbent polymers in cement-based materials. Mater Struct. 2014;2014:1–5.
8. Esteves LP. On the hydration of water-entrained cement–silica systems: combined SEM, XRD and thermal analysis in cement pastes. Thermochim Acta. 2011;518(2–2):27.
9. Powers TC. The nonevaporable water content of hardened Portland cement paste: its significance for concrete research and its method of determination, vol. 29. Philadelphia: ASTM—American Society for Testing Materials; 1949. p. 68–76.
10. Hewlett PC. Lea's chemistry of cement and concrete. London: Arnold; 2004.
11. Nestle N, Kühn A, Friedemann K, Horch C, Stallmach F, Herth G. Water balance and pore structure development in cementitious materials in internal curing with modified superabsorbent polymer studied by NMR. Micropor Mesopor Mater. 2009;125(1–2):51–7.
12. Zhutovsky S, Kovler K, Bentur A. Revisiting the protected paste volume concept for internal curing of high-strength concretes. Cem Concr Res. 2011;41(9):981–6.
13. Knudsen T. The dispersion model for hydration of Portland cement.1. General concepts. Cem Concr Res. 1984;14(5):622–30.
14. Geiker M. Studies of Portland cement hydration by measurements of chemical shrinkage and a systematic evaluation of hydration curves by means of the dispersion model: Lyngby DTH Licentiatafhandling, PhD Thesis. Technical University of Denmark; 1983.