

# Quantitative Microstructural Study Of The Effect Of Temperature On The Properties Of Concrete

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## Abstract

High temperature curing is well known to greatly influence the properties of concrete. So far, numerous studies have investigated the modifications induced by temperature but very few quantitative results are reported to support the observed effects, and to try to link them with microstructural modifications. This paper reports a systematic quantitative study on the relation between microstructural properties (degree of hydration, C-S-H composition and density, porosity) and mechanical and transport properties. By means of SEM, XRD, solid state NMR, TGA, isothermal calorimetry, the microstructure of concrete at high temperature was characterized. It was shown that temperature modifies the intrinsic structure of C-S-H which density increases, due to less bound water and higher degrees of polymerization of the silicate chains. As a consequence, the microstructure is unevenly filled with hydrates and shows a coarser porosity which in turn lowers the mechanical properties. Materials exposed to high temperatures for only short periods of time, such as what might be experienced in the fields of pre-cast concrete and curing of large concrete masses, showed a recovery of their properties from the detrimental effects of high temperature.

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## 1. Introduction

Proper curing has long been identified as one of the most essential parameter for obtaining desired performance of concrete. Under elevated temperature exposure, Portland cement based materials experience physical and chemical changes, which contribute to influence their structural properties and durability.

Extensive research has been carried out on the complex processes involved in the hydration of Portland cement and concrete at different temperatures [1-7]. High curing temperature accelerates the gain of early strength but has a deleterious effect on the long term properties [1,8-10]. It increases the hydration of concrete components but leads to a coarser pore structure. The rims of inner C-S-H formed around unreacted cement grains were reported to be denser with temperature [1,4,5]. Higher sulfate concentrations have been widely reported in C-S-H formed at temperatures above 60 °C [6,11-13]. The width of the inner C-S-H shell around hydrating cement grains was observed to increase. A greater proportion of portlandite was found to form dense clusters as opposed to the more usual lamellar-type morphology observed under ambient conditions [6]. The effects on mechanical properties may be related to the increase of the degree of polymerization of the silicate chains in C-S-H [14-16], which densifies and stiffens the C-S-H [4,17,18].

Despite all these data, most efforts have been generally focused on the qualitative description of the microstructural or mechanical changes induced by temperature, and virtually few quantitative results are reported to support these observations. Especially, the links between early microstructural development and long term mechanical properties are not clearly established nor understood.

This paper reports a systematic and quantitative study of the effect of temperature on both the macro and micro properties of concrete in order to try to connect the observed behaviours.

## 2. Experimental

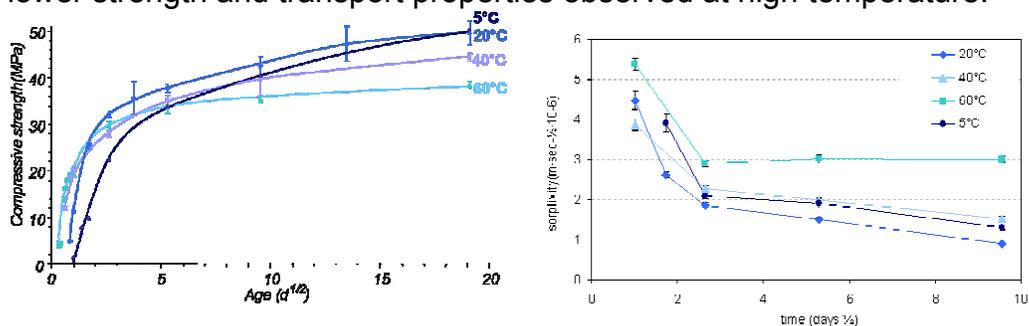
The concrete used in this study was made from a CEM I 42.5 cement (350 kg.m<sup>-3</sup>) with a continuous grade of standard swiss aggregates ranging up to 32mm. Only one mix was prepared at a water-to-cement ratio of 0.5 and then separated in four identical batches, cast in cylinders (11 cm diameter / 22 cm height) and stored throughout their maturation in isothermal rooms or baths at 5, 20, 40 and 60°C/100 RH. Mechanical and flexural strengths, Young modulus and transport properties were measured up to 1 year of curing. Small cuts of the tested concretes were systematically taken for microstructural characterisation by SEM. Cement pastes with equivalent W/C were produced for the characterisation by XRD-Rietveld, thermogravimetry solid state NMR.

### 3. Results and discussion

#### 3.1. Influence of temperature on bulk and macroscopic properties of concrete

##### 3.1.1. Compressive strength and water sorptivity

As previously reported in the literature, a high temperature cure induces a faster early development of compressive strength (figure 1). After three days of hydration, the strength of the concrete cured at 20°C catches up with the concretes cured at 40 and 60°C. After 28 days, it exceeds them, whereas the development of the 60°C concrete seems to stop. After one year, the strength of the 5°C concrete catches up with the 20°C one, while the 60°C shows a strength 25% lower. These results are in agreement with those observed in former studies [1,9] and show well that the development of optimal resistances passes through a singular and optimised microstructural arrangement. Capillary sorptivity measurements also illustrate clearly the influence of the microstructure on the macro properties of concrete since higher water fluxes are observed in the case of high temperature curing. From previous studies, it is anticipated that a lower hydration degree and a higher porosity may be at the origin of the lower strength and transport properties observed at high temperature.

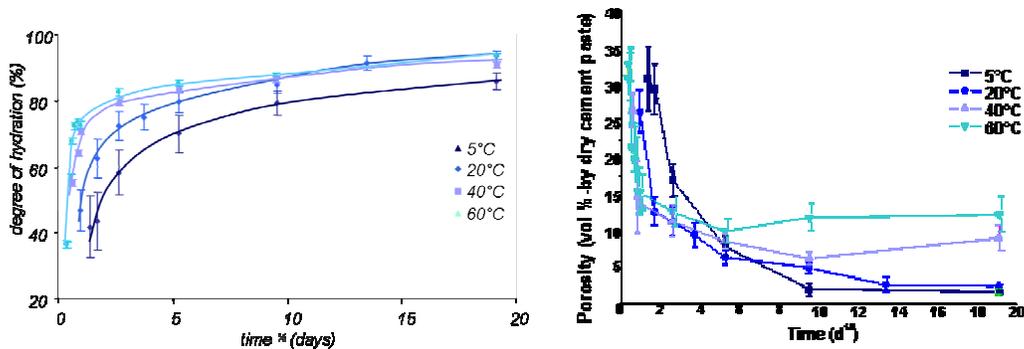


**Figure 1.** Compressive strength and capillary porosity of studied concrete / Trends remains the same after 90 days (not reproduced here to enlarge early age data)

##### 3.1.2. Degree of hydration

The degree of hydration of concretes was measured by image analysis of SEM-BSE images [19]. From Figure 2, very marked differences are observed at early age according to the temperature and are to be related to the strength development. After 90 days of hydration, the degrees of reaction reach similar levels (except for the concretes cured at 5°C which catch up the other temperatures at 1 year). At advanced stages of maturation, the measured degrees of hydration are not any longer directly related to compressive strength: after 1 year, the lower the temperature, the higher the resistance for similar degrees of hydration which seem to

have reached their maxima. Therefore, temperature affects the strength development without limiting the hydration of the concrete. These results disagree with the assumption of Verbeck and Helmuth [1] who suggested that temperature induces dense layers of hydrates with low porosity around the unreacted grains, limiting their further hydration. The results obtained here clearly show that whatever the temperature, the ultimate degree of hydration is not affected.



**Figure 2.** Degree of hydration and capillary porosity as measured by image analysis (data after 90 days not reproduced here to enlarge early age area)

### 3.1.3. Capillary porosity

Similarly to the degree of hydration, capillary porosity was measured by image analysis. As previously reported in the literature, high temperature curing generates a broader porous network over the long term, as observed above. Two main periods can be distinguished (Figure 2): at very early age (< 7days), lower temperatures lead to higher porosity and this is to be related to the weak measured degrees of hydration.

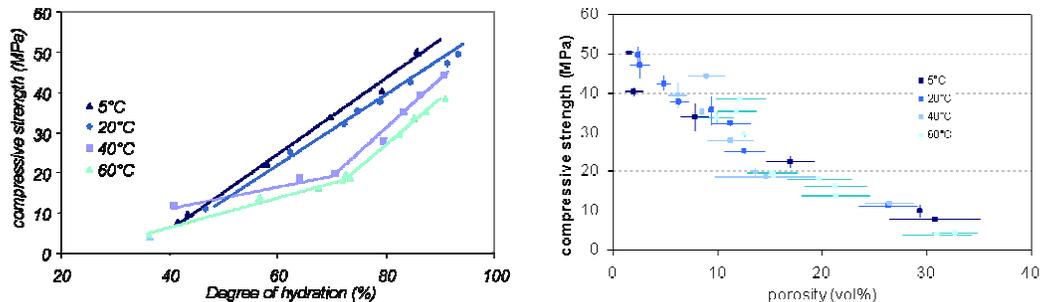
Rapidly, this trend is inverted with stronger porosities at high temperature. The evolution is thus similar with that of compressive strength and these two parameters are thus connected. This also explains the higher water sorptivity measured at high temperature and therefore the expected lower durability properties (increase of transport phenomena).

### 3.1.4. Correlation of results

The results obtained so far tend to show that temperature effectively improves the early age properties of concrete thanks to a faster reaction which fills the microstructure more rapidly with hydrated phases and thus leads to higher strengths. On the other hand, over the long term, this rapid early development induces higher porosities and lower strengths.

Since the ultimate degree of hydration is not affected by temperature, a direct link should exist between the capillary porosity and the compressive strength. Figure 3 effectively shows a linear relation between these two parameters with a decrease of the strength when the porosity increases.

Linear relations can also be established between the degree of hydration and the strength. However, contrarily to capillary porosity which shows a unique master trend for all temperatures, there exists one trend per curing temperature. The fact that these relationships be dependant on temperature while the final degree of hydration is unchanged shows that the microstructural development (i.e. the nature of the hydrated phases) is responsible for these properties but not the degree of hydration itself as claimed for several decades[1].



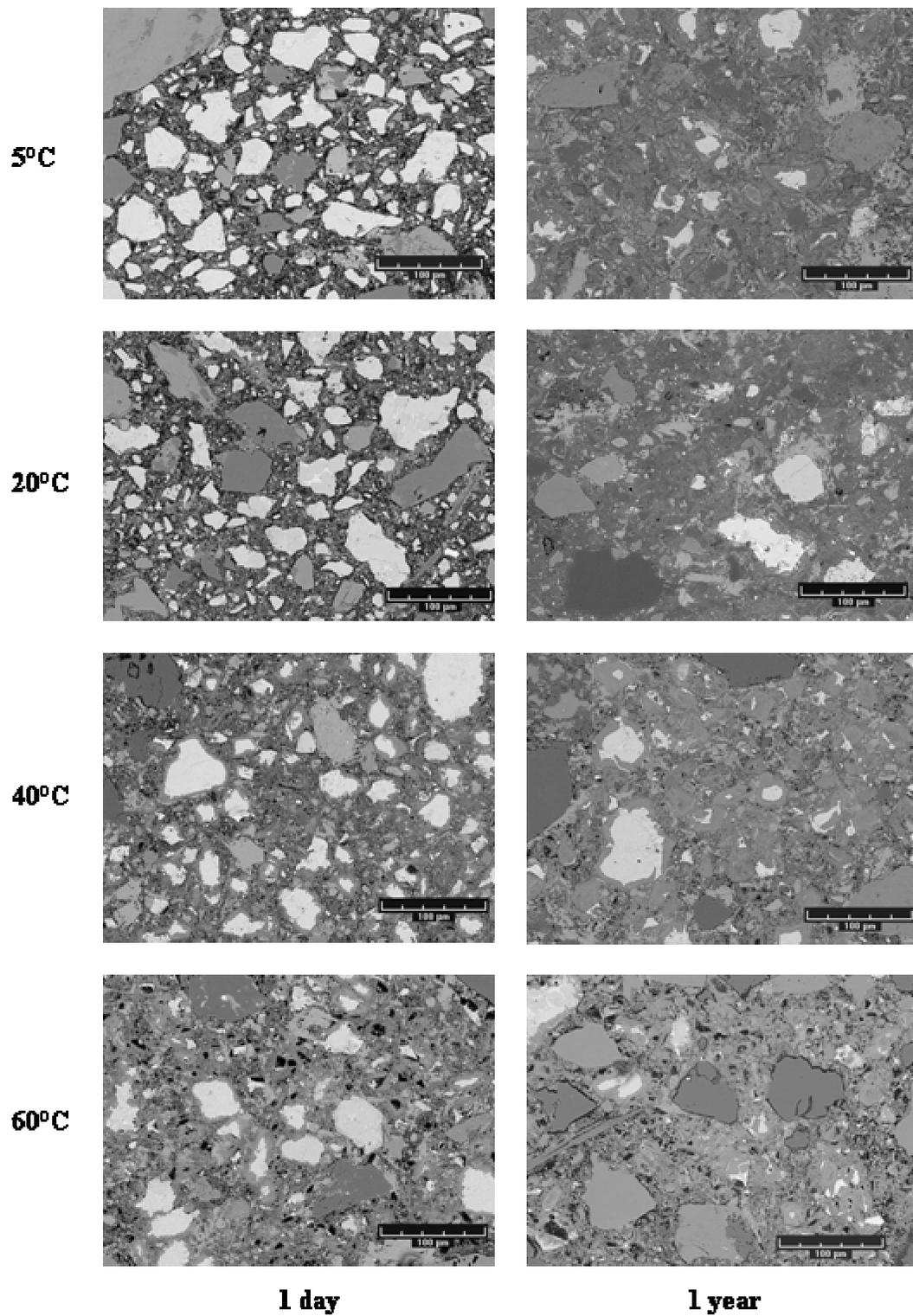
**Figure 3.** Correlation plots between compressive strength and degree of hydration (left) and capillary porosity (right)

### 3.2. Influence of temperature on the microstructural development

#### 3.2.1. Microstructural design of concretes

Figure 4 shows characteristic SEM-BSE images of cross sections of the concretes studied under the several temperature conditions at 1 day and 1 year. After one day of hydration, with increasing temperature, the hydration is much more advanced since the 60°C concrete shows a more homogeneous microstructure with well developed rims of inner C-S-H and many Hadley grains (small completely hydrated grains) while the 5°C concrete still exhibits the characteristic 'gap' between the anhydrous cement grain and the first hydrated shell. The 20 and 40°C microstructures evolve logically from the 5 to the 60°C ones.

After 1 year of hydration, whatever the temperature, the microstructure of the concretes is denser. The hydration is very advanced in all cases (few anhydrous grain remain and are surrounded by thick crowns of inner C-S-H).



**Figure 4.** Microstructural development of the same concrete cured under different temperature

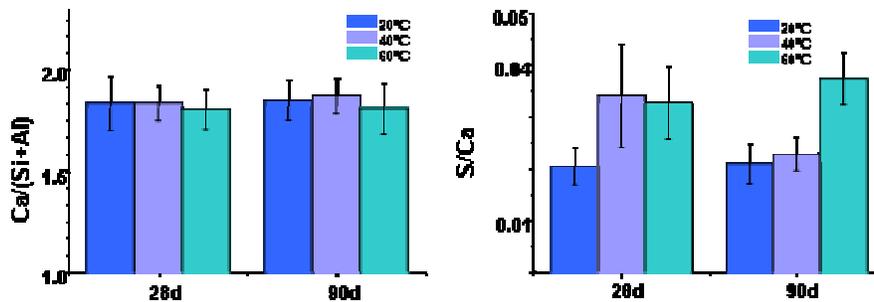
The homogeneity of the matrices is on the other hand significantly affected since with temperature the various phases are distributed less evenly. At 60°C, the microstructure has not much evolved since 1 day, particularly with regard to capillary porosity. At low temperature, the matrix is filled in a more homogeneous way with hydrated products whereas with increasing temperature, they tend to concentrate around the original cement grains, inducing a network of broader capillary pores.

### 3.2. Characterization of hydrated phases.

Since C-S-H is the most abundant phase generated through the hydration of cement and since it is the only one which is known to have a variable composition and structure, most of the investigations reported here concern its modification by temperature. The other main phases such as portlandite, Aft and Afm phases are hardly affected by temperature; only their relative content varies in small amounts.

#### 3.2.1 C-S-H composition

The composition of the rims of inner HSC was measured by EDS microanalysis. The results presented Figure 5 are means of more than 100 independent elementary analyses. The Figure 5-left gives the average C/S ratio (Ca/Si). Whatever the temperature, this ratio is constant and does not change with time. As observed in other studies, the C-S-H formed at high temperature shows higher sulphur contents than at low temperature (Figure 5-right). However, this must be moderated by the very low detected sulphur levels and the composition of the C-S-H must be considered as independent from the temperature.

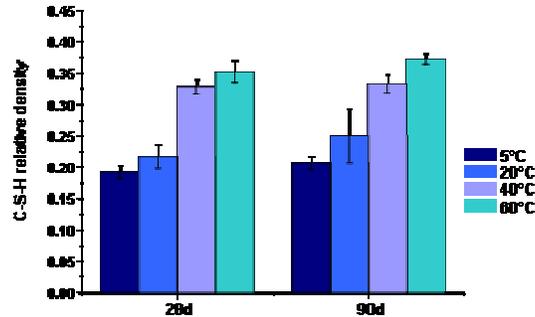


**Figure 5.** Mineral composition of C-S-H measured by EDS microanalysis

#### 3.2.2. C-S-H density

The C-S-H density was estimated image analysis. The phase contrast generated by backscattered electrons in an SEM is a function of the composition and the density of the observed phases. Since it was measured by EDS analysis that the composition of C-S-H is independent

from the temperature, any variation of its grey level is then due to a variation of its density. Results in Figure 6 show that the higher the temperature, the higher the grey level of C-S-H and therefore the higher its density

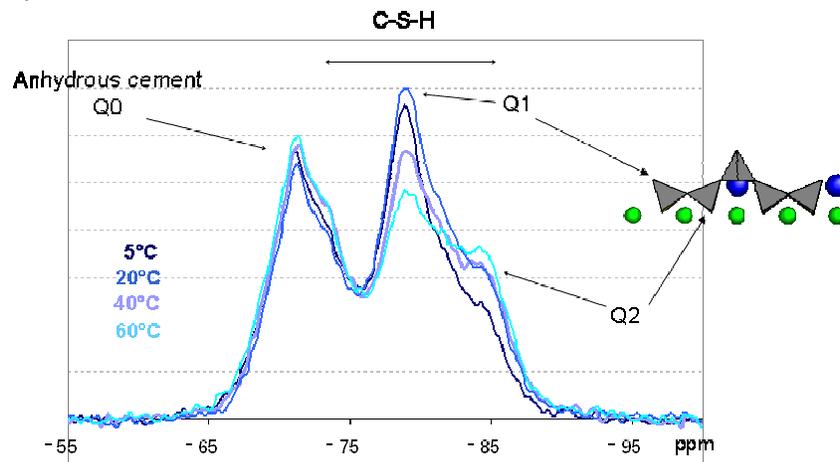


**Figure 6.** C-S-H relative densities estimated by SEM image analysis (arbitrary units)

This confirms the assumption formulated by Verbeck and Helmuth [1], that high temperatures support a fast deposition of the hydrated products in the close environment of the unreacted cement grains.

### 3.2.3. C-S-H structure

The C-S-H structure has been investigated by Silicon NMR (solid state NMR) and confirms previously reported results [21] with an increase of the degree of polymerization of Si chains in C-S-H with the increase of the Q2 peak (inside chain Si atoms) and a decrease of the Q1 peak (end of chain Si atoms).



**Figure 7.** Evolution of Si-NMR spectrum with temperature.

## 4. Conclusions

The careful collection of numerous data on C-S-H brings a detailed overview on how temperature influences its properties during hydration. It was observed that although its mineral composition is hardly influenced by temperature (Ca/Si constant / only a small uptake of sulfur), the increase of the polymerization of the silicate chains” seems to induce a densification of the C-S-H.

The results obtained so far are in good agreement, showing that temperature affects the intrinsic structure of C-S-H which stiffens. As a consequence, the influence of such a local effect is huge at a larger scale, on the whole microstructure: it leads to a less evenly filling of the cementitious matrix with a coarser porosity and therefore to poor mechanical and durability properties.

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