Effect of Curing Temperature at an Early Age on the Long-Term Strength Development of UHPC

Summary

In order to achieve compressive strengths above 200 MPa, UHPC is normally heat treated at an early age (2 days) for 24 to 48 hours at 90℃. Essentially, this accelerates the pozzolanic reaction of silica fume with $Ca(OH)_2$. Contrary to expectation, this long-term study shows that the strength development of UHPC after heat treatment has not ceased. The compressive strength of a heat treated UHPC was observed to increase from 220 to 280 MPa over 8 years' storage in water. ^{29}Si MAS NMR spectroscopy revealed that the chain length of the C-S-H phases increased from values between 5 and 6 to 9 during this period. A distinct increase in compressive strength of UHPC not subjected to heat treatment (20℃) was also observed at high ages. The compressive strength was 250 MPa at an age of six years which was 58% more than the 28 day strength of 160 MPa. This is due to the slow, but continuous, pozzolanic reaction of the silica fume and the increase in C-S-H phase chain length.

Keywords: *UHPC, silica fume, heat treatment, ^{29}Si MAS NMR, C-S-H chain length*

1 Introduction

Between 1990 and 1995 in France and Canada progress was made in the development of a type of concrete called Poudres Réactives (BPR) or Reactive Powder Concrete (RPC). In the mean time the term ultra high performance concrete (UHPC) has become established as the international designation for this type of concrete. Since the end of the 1990s several UHPC demonstration structures have been built such as filigree footbridges with wide spans in Sherbrooke (Canada, 1997), Seoul (South Korea, 2002) and Kassel (Germany, 2007). In Cattenom (France, 1997), a UHPC substructure of a cooling tower may be found which is very durable despite exposure to an aggressive environment. Other examples of UHPC realization include several aesthetically ambitious demonstration objects like the toll station in Millau (France, 2004). These structures are all less than ten years old and therefore the concrete still relatively young. The design of the structures was usually based on test results for concrete specimens with an age of at most 28 days. The experience gained during the design and realization of some of these structures influenced the French guidelines for UHPC [i] which appeared in 2002. The results of this study on the long-term development of compressive strength at high ages of up to eight years should increase the level of trust and acceptance for the novel cementitious material UHPC. Since it is not possible to extract cores from the highly stressed UHPC structural components, the development of compressive strength at high ages is of particular interest with regard to the assessment of safety margins.

In the present investigations, not only specimens stored under normal conditions (20℃, enclosed in polyester foil or submerged in water) were considered, but also specimens subjected to heat treatment for 24 hours at 50, 65 or 90℃ at an early age. Besides measurements of compressive strength, ^{29}Si MAS NMR spectroscopy was used to determine the degree of hydration of cement and silica fume as well as the chain length of the C-S-H phases.

2 Experimental

2.1 Materials and Compositions

The present investigations were performed using four different UHPC compositions and a model binder paste mix which were produced between 1999 and 2001. The same cement and silica fume were used for three of the UHPC mixes stored at 20℃ and the model mix (made in 2001). The heat treated UHPC1 (produced in 1999) contained different binder materials. The 28 day compressive strengths after storage at 20℃ were between 155 and 171 MPa, see Table 1. The composition of the UHPC and the curing method are in Table 1.

Table 1: Composition and curing of the UHPC mixes

Mix	**UHPC1 (1999)**		**UHPC2 (2001)**		**UHPC3 (2001)**		**UHPC4 (2001)**	
28 d compressive strength* **	160 MPa		171 MPa		165 MPa		155 MPa	
Temperature, storage and heat treatment	20℃ 50, 65 and 90℃		20℃		20℃		20℃	
Cement	CEM I 42.5 R		CEM I 42.5 R-HS		CEM I 42.5 R-HS		CEM I 42.5 R-HS	
w/c	0.23		0.27		0.33		0.27	
Silica fume content [wt.%] w.r.t . cement	28		30		30		18	
	Quantity		**Quantity**		**Quantity**		**Quantity**	
Material	**kg/m³**	**l/m³**	**kg/m³**	**kg/m³**	**kg/m³**	**l/m³**	**kg/m³**	**l/m³**
Quartz sand (< 0.5 mm)	872	329	943	356	943	356	943	356
Stone flour (< 0.063 mm)	153*	56	458**	149	458**	149	458**	149
Cement	889	287	683	212	636	198	736	229
Silica fume	248	105	205	87	189	80	132	56
Superplasicizer	57	52	44	41	28	25	43	39
Water	171	171	155	155	192	192	171	171
Total	2390	1000	2488	1000	2446	1000	2483	1000

* Quartz flour

** Basalt flour

*** Stored at 20 ℃

2.2 NMR Spectroscopy

Solid state NMR experiments were performed with a Bruker Avance 300 spectrometer (magnetic field strength 7.0455 T, resonance frequency of ^{29}Si is 59.63 MHz). To measure the ^{29}Si MAS NMR spectra, the samples were packed in 7 mm zirconia rotors and spun at 5 kHz at an angle of 54°44' (MAS). The chemical shifts were recorded relative to external tetramethylsilane (TMS). The single pulse technique was applied with a pulse width of 6 µs. Owing to the slow relaxation of the silica fume, a repetition time of 45 s was chosen [ii] and a typical number of scans was 2000. Thirty Hertz line broadening was applied to all spectra prior to deconvolution. The signal patterns of the spectra were deconvoluted with the Bruker WINNMR software using a Lorentz curve which led to the best result. The interpretation of the ^{29}Si NMR spectra was performed according to the Q^n-Quotation, Figure 1.

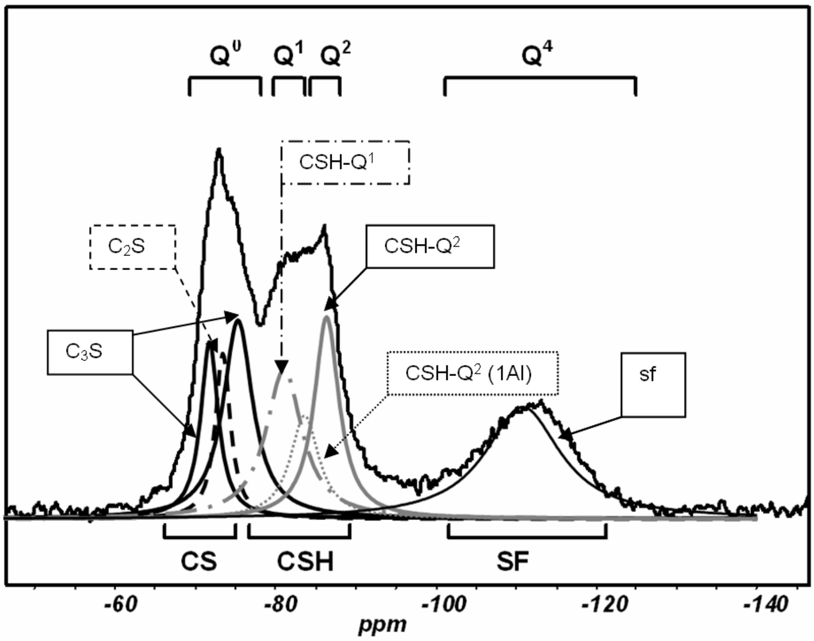

Figure 1: ^{29}Si MAS NMR spectrum for the model binder mix Portland cement and 20 wt.% silica fume (w/c = 0.27) at an age of 28 days [iii]

By combining the integrated intensity of the different NMR signals, it is possible to calculate the degree of hydration of cement *Z* and silica fume *sf* with respect to Si as well as the mean chain length of the C-S-H phases, equations 1 to 3 [4].

$$H_{Si,Z}, = \frac{I(Q^1)+I(Q^2)+I(Q^4)-{}^{sf}\!/_{Z}\cdot I(Q^0)}{I(Q^0)+I(Q^1)+I(Q^2)+I(Q^4)} \quad \textbf{Eq. 1}$$

$$H_{Si,sf} = \frac{I(Q^1)+I(Q^2)+I(Q^0)-{}^{sf}\!/_{Z}\cdot I(Q^4)}{I(Q^0)+I(Q^1)+I(Q^2)+I(Q^4)} \quad \textbf{Eq. 2}$$

$$\overline{C} = \frac{2\left(I(Q^1)+I(Q^2)\right)}{I(Q^1)} \quad \textbf{Eq. 3}$$

3 Experimental Results

3.1 Investigation of Hydration Using ^{29}Si NMR Spectroscopy

The slow pozzolanic reaction of silica fume at 20℃ which led to a change in the structure of the C-S-H phases (see Figure 2) was responsible for the increase in compressive strength at high ages. Parallel strength and ^{29}Si MAS NMR measurements performed with hardened binder specimens at an age of 28 days (w/c = 0.27, 20 wt.% silica fume) and UHPC at an age of one year (w/c = 0.27, 18 wt.% silica fume) and eight years (w/c = 0.23, 28 wt.% silica fume) confirm this relationship, cf. Table 2.

Using ^{29}Si MAS NMR Zanni et al. [5] proved that at 20℃ quartz flour in concrete is absolutely inert - even after long storage times. Moreover, silica fume has a larger specific surface than quartz flour. Thus the model mix, which is almost identical in composition to the binder paste matrix of one of the UHPC mixes, is comparable to UHPC.

Table 2: Degree of hydration of cement and silica fume it dependence of age, heat treatment and composition

Specimen	**Age**	**Degree of hydration**		**Mean chain length**	**Compressive strength**
		CEM	**SF**		
Specimens stored at 20℃	[days]	[%]	[%]	[-]	[MPa]
Model mix (0.27 – 20)	1	30.6	10.2	3.5	92
Model mix (0.27 – 20)	7	38.5	26.2	4.4	135
Model mix (0.27 – 20)	28	37.8	47.1	5.7	156
	[years]	[%]	[%]	[-]	[MPa]
UHPC2 (0.27 – 30)	1.123	39.1	51.3	7.6	199
UHPC3 (0.33 – 30)	1.123	47.2	66.3	6.0	175
UHPC4 (0.27 – 18)	1.123	35.2	72.8	5.8	172
UHPC1 (0.23 – 28)	8.370	30.7	76.4	8.4	252
Heat treated specimens **UHPC1 (0.23 – 28)** **Temperature / Prestorage time**	[years]	[%]	[%]	[-]	[MPa]
50℃ / 1 d	8.438	25.2	85.0	7.7	263
90℃ / 1 d	8.553	30.9	90.4	9.1	247
50℃ / 5 d	8.427	35.4	78.8	8.3	* ≥ 256
65℃ / 5 d	8.427	34.6	81.3	7.6	* ≥ 272
90℃ / 5 d	8.543	35.6	83.3	8.1	249

* these compressive strengths were already determined at an age of 6.041 years

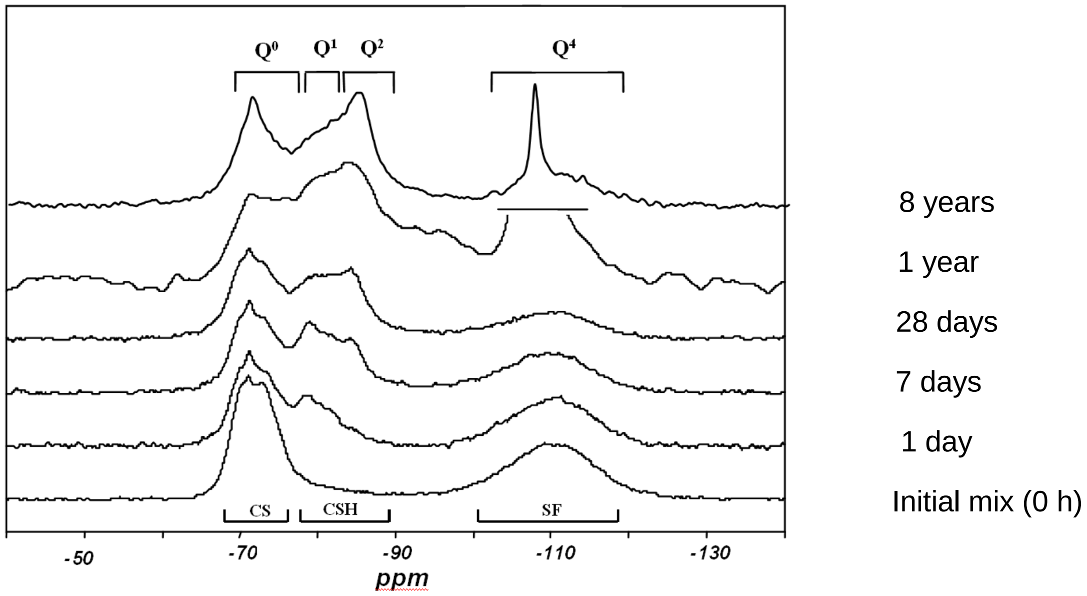

Figure 2: [29]Si MAS NMR spectra for the model mix (0.27-20) up to 28 days (bottom) and UHPC mixes after 1 year (0.27-18) and 8 years (0.23-28)

At an age of 28 days, the proportion of hydrated silica phases of the cement in the model mix was approximately 38%. The hydration reaction of the cement was completed after, at latest, seven days, see Figure 3. The proportion of reacted silica fume increased during normal storage from 47%, at an age of 28 days, to 76% after eight years. During this period the amount of C-S-H formed clearly increased and the Q^2 signal for bridging silicate tetrahedra at -85 ppm increased indicating a growth in mean chain length of the C-S-H phases from 5.7 to 8.4. In the case of the heat treated specimens, the proportion of reacted silica fume (80 to 90%) was much larger. The degrees of hydration of cement and silica fume determined by ^{29}Si NMR spectroscopy and the chain lengths of the C-S-H phases are shown in Table 2.

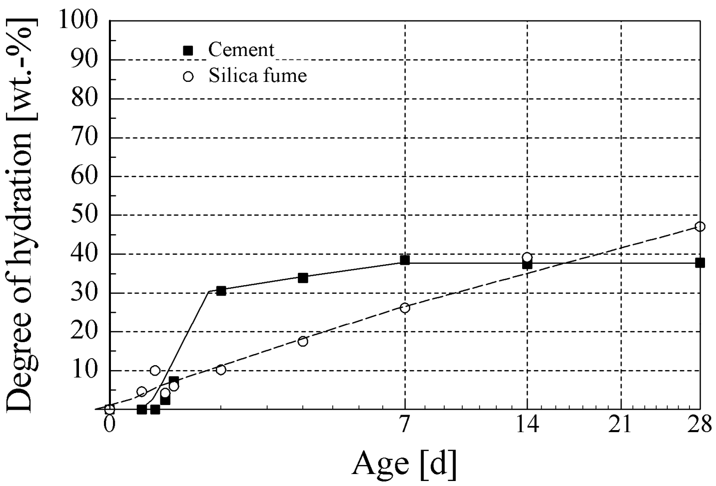

Figure 3: Hydration of the silicate phases of cement and silica fume measured with [29]Si MAS NMR for the model mix (w/c= 0.27, CEMI, 20% sf)

3.2 Long-Term Development of Compressive Strength at 20°C

The results for the compressive strength measurements for very different UHPC compositions at the high ages of 1, 3.5, 6 and 8 years are shown in Figure 4. At an age of 3.5 years the strength is 40% above the 28 day value indicating a considerable increase in hardening at high ages. Since all the UHPC mixes were produced without fibres, the specimens were extremely brittle - especially at high ages. Because of this, specimen preparation and mounting in the testing machine led to a large scatter of the measured values: It was up to 50 MPa within a test series. This explains the lower compressive strength of the eight year old compared with the six year old specimens in Figure 4; 225 as opposed to 250 MPa, respectively.

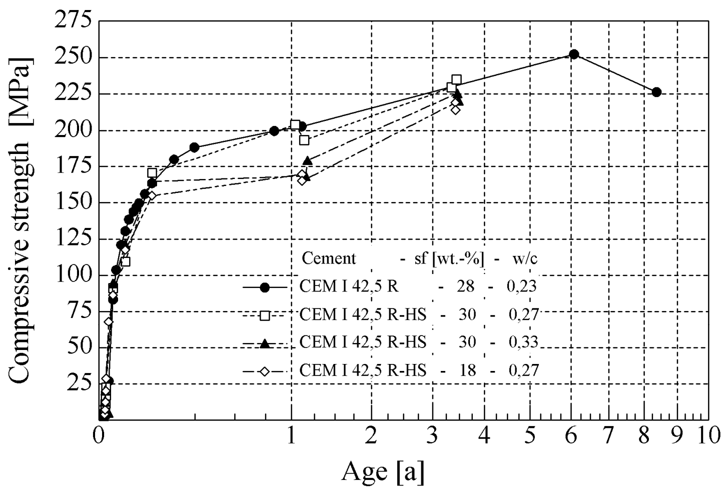

Figure 4: Long-term compressive strength of different UHPC compositions stored at 20°C (enclosed in a polyester sheet or submerged in water). Values are plotted versus time on a square root scale.

The results of the ^{29}SI MAS NMR investigations showed a distinct increase in mean chain length of the C-S-H phases at high ages. Obviously, strength increases with the mean chain length of the C-S-H phases. This relationship confirms the results of Zanni et al. [iv].

4 Effect of Age at Heat Treatment and Temperature on Compressive Strength at Ages up to 28 Days

Beginning the 24 hour heat treatment at an age of five days was found to be most favourable for the achievement of high strengths at ages up to 28 days, Figure 5. This was valid for heat treatments at 50, 65 and 90°C, Figure 5. After five days, the maximum possible hydration of the Portland cement is reached which is below 100% owing to the low w/c ratio. The effect of the storage time before heat treatment is confirmed by the results of Ma [v] who recommended commencing heat treatment on reaching a UHPC compressive strength of 90 MPa. The present UHPC compositions reached this strength in just under three days. Depending on the type and dosage of superplasticizer, strength development can be delayed by up to two days under certain conditions.

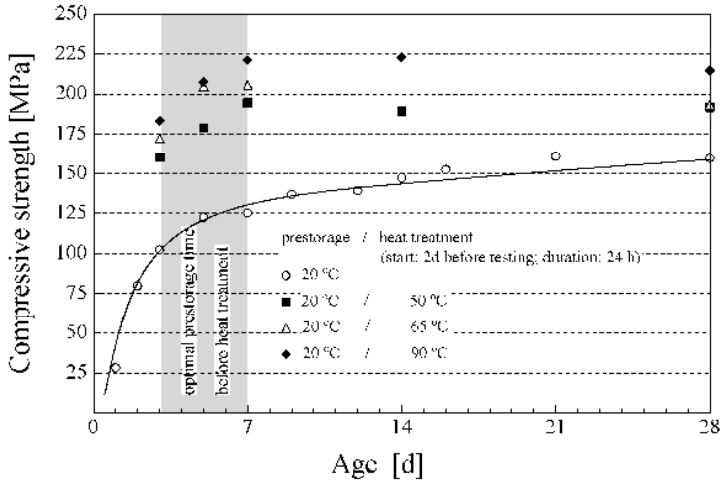

Figure 5: Effect of age at the beginning of heat treatment and heat treatment temperature on the compressive strength of UHPC 1 at ages up to 28 days.

A high compressive strength of 225 MPa, obtained by optimal heat treatment (beginning at an age of five days, 90℃) and reached after only s even days, was equalled only after a very long storage period (roughly 3.5 years) at 20℃, cf . Figure 4.

5 Long-Term Development of Compressive Strength after Heat Treatment at an Early Age

The results of these investigations contradict statements in the literature where the development of shrinkage and strength as well as the chemical reactions causing them are terminated by heat treatment at an early age. All the heat treated specimens with ages up to eight years exhibited a further gain in strength of as much as 30%, see Figure 6.

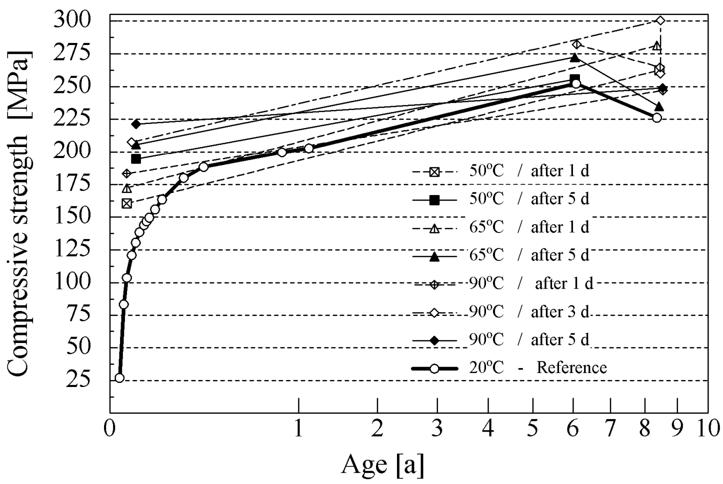

Figure 6: Long-term evolution of compressive strength of UHPC 1 during storage under normal conditions and after heat treatment at early ages

Irrespective of treatment history, the specimens between six and eight years old all had high compressive strengths of 250 to 300 MPa which corresponds to values measured for natural stone, e.g. granite.

If UHPC is not heat treated at an early age or only at temperatures up to 90℃ then it may be assumed that a final strength of 250 to 300 MPa will be reached after six years. Significantly higher strengths are only possible through the more complicated process of heat treating at temperatures around 250℃. By adding steel fibres t o the mix, typically 3 vol.%, ductility increases and the statistical scatter of strength values is reduced. It must therefore not be expected that fibres increase strength.

6 Conclusions

- To obtain high compressive strengths at early ages it is expedient to heat treat UHPC for at least 24 hours following storage for five days at 20℃. After five days, the hydration of the cement, which is 35 to 40% due to the low w/c ratio, is essentially complete.
- Heat treatment at 50 to 65℃ at an early age resul ts in high compressive strengths of 200 MPa. At 90℃ the pozzolanic reaction of silica fume is greatly accelerated so that compressive strengths of 225 MPa are reached at an age of only seven days.
- Irrespective of previous treatment, all specimens exhibited very high compressive strengths ranging from 250 to 300 MPa at high ages of six to eight years. This corresponds to values measured for natural stone, e.g. granite. The ongoing increase in strength at high ages is due to the pozzolanic reaction of silica fume and growth of C-S-H phase chains to lengths between eight and nine SiO_4 tetrahedra.
- Since the design of structural components made of UHPC is based on compressive strength measured at an age of 28 days or following heat treatment, a safety margin of 20 to 50% is valid for concrete strength at an age of 6 years.

7 References

[1] Interim Recommendations for Ultra High Performance Fibre-Reinforced Concretes. Association Francaise de Genie Civil (AFGC) / Service d´ètudes techniques des routes et autoroutes (SETRA), working group on Ultra-High Performance Fibre-Reinforced Concrete, Januar 2002.

[2] H. Hilbig, F.H. Köhler, P. Schießl: Quantitative 29Si MAS NMR spectroscopy of cement and silica fume containing paramagnetic impurities, Cem. Concr. Res. 36 (2006) 326-329

[3] H. Hilbig, F.H. Köhler, P. Schießl: Hydratation von Hochleistungs-Feinkorn-Betonen, NMR-spektroskopische Untersuchungen, 15. Internationale Baustofftagung, Tagungsband, 2003, Weimar, 1-0489 – 1-0496.

[4] Zanni, Hélène; Cheyrezy, Marcel; Maret, Vincent; Philippot, Samuel; Nieto, Pedro: Investigation of Hydration and Pozzolanic Reaction in Reactive Powder Concrete (RPC) Using 29Si NMR. Cement and Concrete Research, (1996) Vol. 26, No. 1, S. 93-100.

[5] Ma, Jianxin: Experimental Investigations for the Production of Ultra-High Strength Concrete. Lacer No. 6, 2001, S. 215-228.