POSSIBILITIES FOR IMPROVING THE PROPERTIES OF UHPC BY MEANS OF THERMAL TREATMENT

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Abstract

A further improvement of the excellent properties of UHPC can be realized with thermal treatment. Like for normal concrete, it accelerates the hardening and prevents shrinkage after the treatment. Additionally, an increase in strength can be achieved. Aim of this study was the optimisation of the thermal treatment conditions of UHPC for very different treatment methods; heat treatment at 90 °C for unprotected and sealed samples, hot water bath at 90 °C and hydrothermal treatment at 185 °C/1.1 MPa. The pre-storage time and the dwell time were systematically varied for each method to gain a higher strength. The compressive strength depends on the manner of treatment at which higher water accessibility leads to higher strengths. The phase composition changes considerably with different treatment temperatures. Finally, it can activate unhydrated binder components forming additional C-S-H, leading to higher strength.

Résumé

Des améliorations supplémentaires des excellentes propriétés des BFUP peuvent être réalisées avec un traitement thermique. Comme pour les bétons courants, cela accélère le durcissement et élimine le retrait postérieur au traitement. De plus, une augmentation de la résistance peut être atteinte. Cette étude était destinée à l'optimisation des conditions de traitement thermique des BFUP pour des méthodes de traitement très différentes : traitement thermique à 90 °C pour des échantillons scellés ou sans protection ; immersion en eau chaude à 90 °C et traitement d'autoclavage à 185 °C/1.1 MPa. Le temps de pré-conditionnement et le temps de séjour ont systématiquement varié pour chaque méthode afin d'obtenir une résistance plus élevée. La résistance à la compression dépend des modalités des traitements pour lesquels une plus grande accessibilité à l'eau conduit à des résistances plus élevées. La composition des phases hydratées change considérablement selon les différentes températures de traitement. Finalement, le traitement peut activer les composés anhydres du liant qui formeront des C-S-H supplémentaires, conduisant à une plus grande résistance.

1. INTRODUCTION

Extensive research of UHPC in the last decades prepared the path for its wide and substantial application. Besides the optimization of the mixture and the mixing process, the thermal treatment is a central technique for a robust and reliable production of UHPC, like for the UHPC components of the Pont du Diable (France, 2005) or the Gärtnerplatzbrücke (Germany, 2007) [1].

The thermal treatment of UHPC accelerates, similar to normal concrete, the hardening. Because of the special conditions of UHPC (high cement content, high tightness, low water/cement ratio and thus low degree of hydration), additional capabilities can be exploited. Especially in comparison to untreated concrete the following advantages are important:

1. After finishing the treatment, no further hydration occurs and the strength development is completed. In certain cases, the strength is increased. [2-4]
2. The microstructure of the cement paste matrix becomes denser and more homogeneous, effecting positively the durability. [2-4]
3. After thermal treatment, the shrinkage and the creep are reduced, so that the components have an improved dimensional stability. [2, 4]
4. The large amounts of unhydrated cementitious components that are commonly remnant in hardened UHPC can be activated more extensively. [4, 5]

A thermal treatment applied during the first hours with moderate temperatures with the aim of accelarated initial hardening, like it is described in [2] or in EN 1992-1-1, is not subject of this paper. It is focused to a treatment after the setting with the aim to improve the properties of hardened UHPC.

'Thermal treatment' can be differentiated between heat treatment (temperatures beneath 100°C at ambient pressure) and hydrothermal treatment (temperatures above 100°C at saturation water pressure), technically referred to as 'autoclaving'. The term 'curing' means originally the protection of the young concrete from damaging. Therefore, potentially confusing terms like 'heat curing' or 'steam curing' are not used in this paper.

The thermal treatment of UHPC is commonly performed as follows: a pre-storage time of minimum 1 day followed by a dwell for 24 to 48 hours at a temperature between 60 and 90 °C [4, 6]. Generally, the higher temperatures and pressures of a hydrothermal treatment offer the potential for effective property improvement and higher strengths [7-9], to the account of higher energy and cost intensity.

The protection of UHPC against drying during thermal treatment is mandatory, but mostly not precisely described. Options for protection are for example airtight wrapping with a foil, wrapping in humid fabric or storage in a humid climate. This protection seems to be more important for UHPC in comparison to normal concrete, because higher treatment temperatures are typically used, the water cement ratio is lower and the water content is exactly adjusted. Therefore, small changes in the water balance through drying or moistening can strongly influence the final properties of UHPC.

The phase development in UHPC, i.e. the formation of hydration products, is similar to that of normal concrete. The same phases occur in the same sequence, but the fractions of the phases and the kinetics are strongly different [6, 10]. Especially the amount of non-reacted clinker is higher caused by the low w/c ratio. During the thermal treatment of UHPC the phase composition is changing. Besides further hydration reactions, connected to a decrease of clinker and an increase of C-S-H, the formation of crystalline C-S-H is expected. The nature of the

formed phases is depending on material composition (mainly Ca/Si ratio) and temperature. In particular, the formation of 1.1 nm-tobermorite after hydrothermal treatment is assumed and desired, because it is associated with high strength [11, 12].

While the efficacy of thermal treatment is generally undoubted, systematic insights for a purposeful control and optimisation of thermal treatment of UHPC are still missing since the impact of the thermal treatment is a result of the interaction of all process conditions.

In the presented study the influences of two single parameters, i.e. duration of pre-storage time and dwell time, was investigated considering the influence of different manners of thermal treatment on the compressive strength.

2. MATERIALS AND METHODS

The composition of the UHPC used in this study is given in Table 1. This mixture without any supplementary cementitious materials (SCM), lime stone powder or composite cement was selected to keep the system simple and clear, allowing a more fundamental understanding of the phase changes. Fibre reinforcement was not used to exclude additional influencing factors, e.g. distribution and orientation of fibres, that might impede the analysis of the correlation between phase assemblage and strength development. Anyway, the influence of fibres on the compressive strength is considered small [13].

After mixing in a high-energy mixer the UHPC was cast in silicone moulds to produce small cylinders: diameter = 22.6 mm, height = 22.6 mm (see Figure 1). This small size allows for the preparation of homogeneous specimens without inducing major internal temperature gradients even with fast heating and cooling. For comparison, standard UHPC prisms (40 x 40 x 160 mm³) were thermally treated and tested as well.

After 1 day the samples were demoulded and stored under water at 23 °C until heat or hydrothermal treatment. The thermal treatment was performed in four different manners listed in Table 2. In the test series the storage time (1 day to 27 days) and the dwell time (up 8 days) were varied. Subsequently the samples were stored under water again until strength testing after 28 days. Reference samples were continuously stored under water at 23 °C.

Table 1: Mix composition of UHPC based on [14]

Material	**Content in kg/m³**
CEM I 52.5 R	832
Silica fume (uncompacted)	135
Quartz powder (0 – 0.125 mm)	207
Quartz sand (0 – 0.5 mm)	975
PCE superplasticizer	40
Water	209

The compressive strength was tested following EN 12390-3 [15] with an adjusted load of 960 N/s considering the small sample size of the cylinders. A direct comparison with other commonly used specimen sizes is not possible, because the conversion factors depend both on specimen size and on strength [16].

The qualitative phase analysis was done with a Rigaku Ultima IV in Bragg-Brentano-Geometry with a DTex-detector and Cu-$K\alpha$ radiation on solid samples. The samples were ground to obtain a smooth and homogeneous surface. Measurements on solid specimens are

advantageous, because of the smaller efforts for preparation and the possibility to use the same specimen again for further treatments or testing.

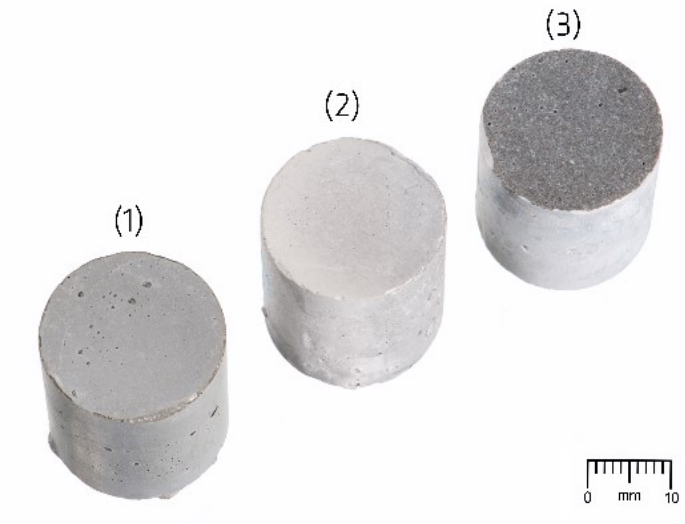

Figure 1: UHPC cylinders in three different states: after demoulding (1), after heat treatment in hot water bath (2) and after grinding (3).

Table 2: Variations of thermal treatment.

No.	Type of treatment	Manner of treatment	Temperature	Pressure
1	Heat treatment	Without protection in heat cabinet	90 °C	Normal = 1 bar
2	Heat treatment	Wrapped in foil in heat cabinet	90 °C	Normal = 1 bar
3	Heat treatment	Water bath	90 °C	Normal = 1 bar
4	Hydrothermal treatment	Autoclave	185 °C	1.1 MPa = 11 bar

3. RESULTS AND DISCUSSION

3.1 Compressive strength

The strength development of the water-stored UHPC cylinders can be described using a Weibull distribution function [17, 18]. The compressive strength $f'_{c,t}$ for a certain concrete age (in days) amounts:

$$f'_{c,t} = f'_c \left[1 - \exp\left(-\left(\frac{t}{T}\right)^k\right)\right] \quad (1)$$

The factor f'_c (strength after infinite time; final strength) as well as k and T (scale and shape parameters) need to be fitted. For the cylindrical samples stored under water (reference) the

parameters yielded to: f_c' = 203 MPa; k = 0.39; T = 4.9. Using these parameters, the reference graph in Figure 2 is used to estimate the impact of the thermal treatments.

The samples treated without any protection showed the lowest strength values followed by the samples wrapped in foil and the samples treated in a hot water bath. The highest strength values were observed with hydrothermal treatment. This general trend is complicated through the dependence on the pre-storage time and the dwell time. Heat treated and hydrothermally treated samples behave very different in this aspect, what is described hereafter using the example of hot water bath and hydrothermal treatment.

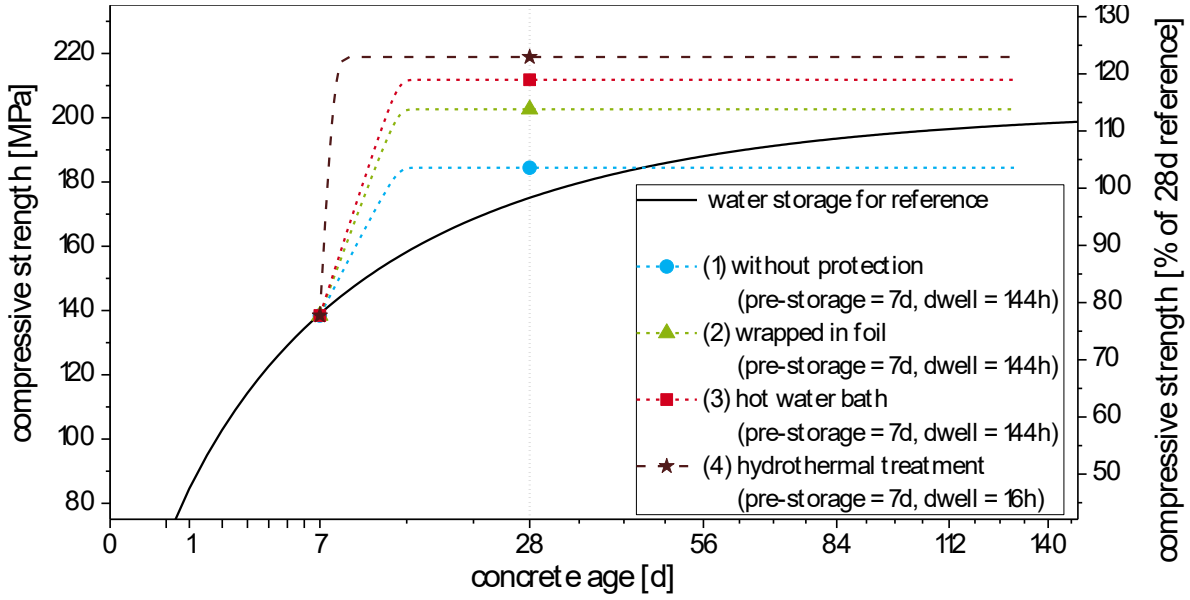

Figure 2: Impact of thermal treatment in comparison to water storage. The continuous bold line represents the strength development of reference samples sored in water according to equation (1). Measured values are marked with a symbol, assumed trends of strength development are indicated with dashed lines.

For 90 °C heat treatment in hot water bath longer dwell times yielded higher strength (Figure 3 left). This result does not agree with literature, in which no further strength increase after 48 hours is assumed, as reported in [4]. No clear dependence on the pre-storage time was observed (Figure 3 right). It is important to note that the optimum of pre-storage time depends on the dwell time. A pre-storage time of 4 days and treatment of 144 hours yielded the highest value: 20 % higher than the reference samples. The results for a heat treatment are described in detail in [18].

For hydrothermal treatment longer dwell times up to 20 hours resulted in 25 % higher strength at maximum compared to the reference samples. Further extension of dwell times did not yield further increase of compressive strength. On the other hand, no significant decrease of strength was observed, as described in [19]. While in those previous studies the dwell time was 48 hours at longest, the dwell times in this study were extended to more than one week. As result the compressive strengths were similar or only slightly lower compared to shorter dwell

times, but always significant higher (> 20 %) than the strength of the reference samples. The pre-storage time in the range between 1 day and 27 days does not influence significantly the compressive strength. A detailed description of the impact of hydrothermal treatment can be found in [20].

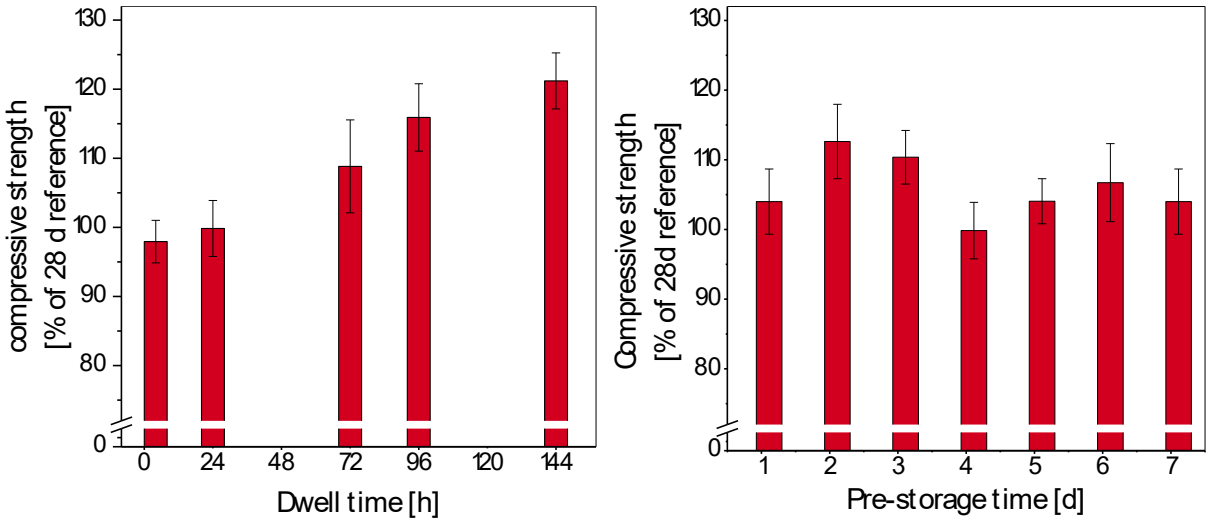

Figure 3: Compressive strength of UHPC samples treated at 90 °C in hot water bath. Left: as a function of dwell time (pre-storage time = 4 days); Right: as a function of pre-storage time (dwell time = 24 hours).

3.2 Phase composition

Thermal treatment has a significant effect on the phase composition. In Figure 4, X-ray diffractograms of differently treated samples are compared. In the reference samples, typical phases for hardened concrete were present: portlandite, ettringite, and clinker phases. Ettringite is reduced in all samples treated at 90 °C, because it decomposes when the temperature is exceeding 70 °C [21]. In hydrothermally treated samples, ettringite is completely disintegrated. In contrast to normal concrete, UHPC is not susceptible to the risk of delayed ettringite formation (DEF) [9]. The insufficient water supply, which is due to the low permeability of UHPC, is suspected to prevent a harmful formation of secondary ettringite.

Portlandite diminishes like ettringite. In the samples treated at 90 °C portlandite was reduced, while after hydrothermal treatment, portlandite was consumed completely in the pozzolanic reaction with the available SiO_2 (originating from silica fume and quartz) to C-S-H, which contributes to the strength development. This reaction is very pronounced and is presumably the main factor for the increase of strength [20].

No reduction of clinker phases (alite) was observed in the case of the treatment at 90 °C. For hydrothermal treatment, the amount of alite decreased slowly with longer dwell time and was abundantly present even after 120 hours of dwell time.

Thermodynamic experiments predict the occurrence of tobermorite between 100 and 200 °C in the saturated C-S-H system [11, 22]. Yazıcı et al. [19] supposed, that the formation of tobermorite is causing the high strength of autoclaved Reactive Powder Concrete (RPC). However, in this study tobermorite was not detected in the samples, but two other phases were

identified: hydroxylellstadite and hydrogarnet. Therefore, tobermorite cannot be generally considered as responsible for the increased strength of hydrothermally treated UHPC.

From the experimental results, it is obvious that the reason for the higher strength of thermally treated UHPC samples is simply an intensified pozzolanic reaction. In the case of hydrothermal treatment, the strength development is additionally supported by an intensified hydraulic reaction. Hence, more C-S-H is formed that may fill voids, leading to a denser structure and finally to higher strength. At 90 °C these reactions are much less pronounced than at 185 °C and corresponding water vapour saturation pressure, of course, resulting in lower strength of the former.

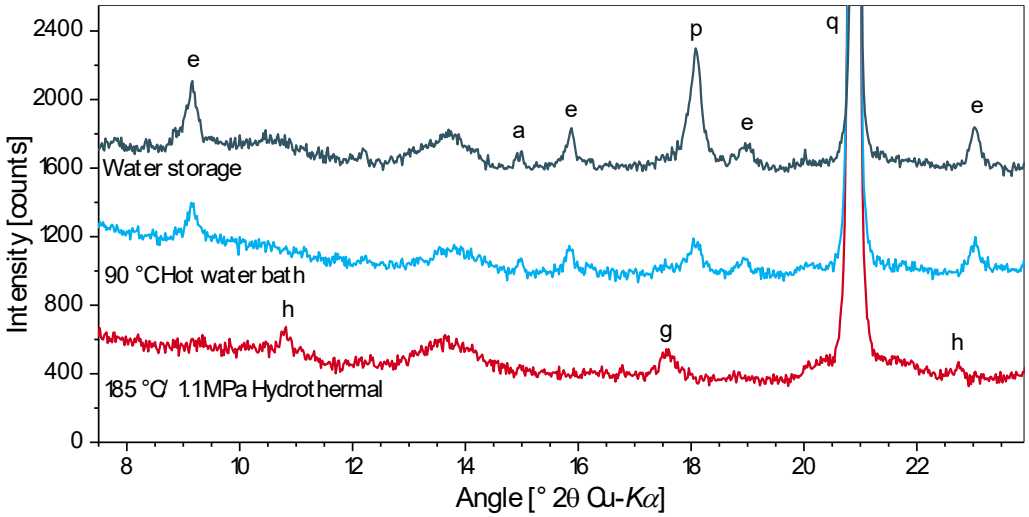

Figure 4: X-ray diffractograms of reference sample (water storage), sample heat treated at 90 °C in water and sample hydrothermally treated: e – ettringite; a – alite; p – portlandite; h – hydroxylellestadite; g – hydrogarnet.

3.3 Zonation

After the 90 °C heat treatment without protection or wrapped in foil, a zonation occurred on the fracture surfaces of the prisms. Three zones are formed in dependence from pre-storage time, dwell time and curing conditions: 1) an inner dark core, 2) an inner lighter zone and 3) an outer very dark zone (Figure 5). This very dark outer zone occurs only when the sample is stored under water after the heat treatment. When the sample is stored in air (< 65 % RH) this zone is missing. The zones are broader after unprotected treatment than after treatment of wrapped samples.

The zonation is stable even after several months under ambient conditions. It is thus not a temporary difference in humidity of the zones. The reason for these differences in lightness might be a permanent change in texture and/or phase content. Probably, the zones represent drying during heat treatment (inner light zone) and re-moistening (outer very dark zone).

To date a similar zonation was only described for hydrothermal treatment of UHPC [8]. Any kind of change in the colour may be of concern related to strength or durability. A local loss in strength or a local increase in permeability could induce deterioration. Therefore, a further explanation of this zonation is of interest for future research. Currently it can only be established that there are no noticeable changes at fracture pattern or at the macroscopic visible pore

distribution and no signs for microcracking. But it is obvious, that samples treated in this way are not homogenous.

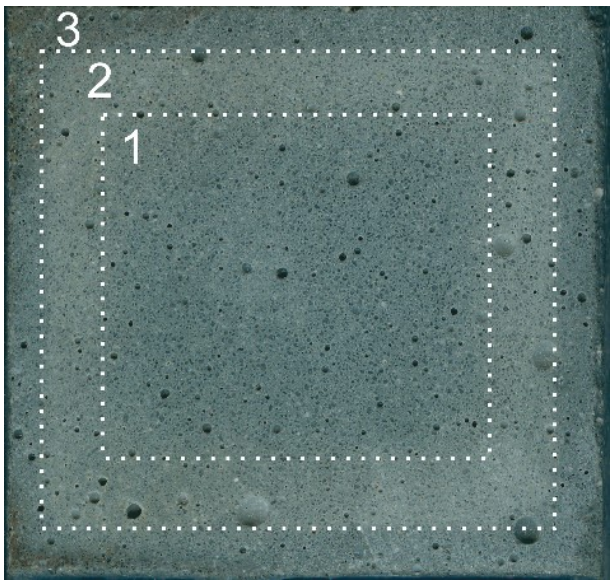

Figure 5: Cross section of an unprotected sample, heat treated in a heat cabinet at 90 °C. The three zones are described in chapter 3.3. Image width is 40 mm.

3.4 Environmental impact

At first glance it seems obvious that heat or hydrothermal treatment should result in more overall energy consumption of an entire prefabricated concrete building element. However, the energy consumption of the autoclaving process can be compensated when Portland cement is replaced by industrial by-products, such as fly ash and slag. In the case of autoclaved fibre-reinforced UHPC, the embodied energy per m³ might be in the range of standard reinforced concrete [23]. Considering that autoclaving is improving considerably the structural performance of the UHPC, the reduced thickness of the building elements, and thus the total reduction of material, is assumed to overcompensate the additional energy consumption and the costs of the autoclaving process. Moreover, reduction of thickness and weight of such UHPC elements will result in reduction of transport costs and construction time. Thermal and hydrothermal treatment of concrete building elements is feasible with the use of facilities available in Aerated autoclaved concrete (AAC) or sand-lime brick industry.

4. CONCLUSIONS

Thermal and hydrothermal treatment can significantly increase the compressive strength of UHPC depending on manner of treatment with fundamental variations in strength and phase composition. A strength increase of about 20 % and 25 % in comparison to 28 d water storage is possible for 90 °C heat treatment and hydrothermal treatment, respectively.

The manner of protection against drying is a major factor for heat treatment at 90 °C. While for hot water bath, the strength depended in a complex way on pre-storage time and dwell time, it seems to be independent from pre-storage time for hydrothermal treatment reaching a maximum with a dwell time of about 20 h.

During the thermal treatment at 90 °C ettringite and portlandite diminished, but they were still present after the treatment. After the hydrothermal treatment both were absent and hydroxylellestadite and hydrogarnet were formed.

Unexpectedly, tobermorite was not detected in the hydrothermally treated UHPC. Therefore, in contrast to AAC, the formation of tobermorite is not considered as mainly responsible for the increase of strength, but the intensified pozzolanic and hydraulic reactions.

It is clear, that the presented results are valid only for the chosen, simple UHPC composition. The obtainable strength depends from the combination between composition and treatment parameters, of course.

The environmental impact and the costs of thermal and hydrothermal treatment of the UHPC can be compensated or even overcompensated through the replacement of Portland cement by secondary cementitious materials and the light-weight design of UHPC building elements.

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