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Phase development in normal and ultra high performance cementitious systems by quantitative X-ray analysis and thermoanalytical methods

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ABSTRACT

Quantitative X-ray diffraction (QXRD) and thermogravimetry (TG) methods are used to determine the phase development up to 28 days of hydration in normal and ultra high performance cementitious systems (UHPC) that do not contain aggregate. The phase development in ultra high performance cementitious formulation is quantitatively and kinetically different from that in normal concrete formulation. This is related to the different components employed and their associated reactions. For both formulations the most remarkable changes of the phase contents are recorded between the first and second hydration day and up to the seventh day. After the seventh day less phase content changes are measured. Because of the non sufficient water amount for hydration, considerable amount of cement remains non hydrated in the UHPC formulation. The portlandite content, which is present in the UHPC specimen, gives evidence for non complete pozzolanic reactions even after 28 days of hydration, whereas the absence of calcite in the UHPC specimen indicates an insignificant carbonation in this specimen.

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1. Introduction

Cements and their corresponding hydration products are multiphase systems. Phase quantifications in cementitious systems are therefore needed for their characterisation. For this purpose phase analyses are carried out as well on cements as on their hydration products.

The increasing need to perform quality control on raw materials (cement and other supplementary cementitious materials) and the development of new cementitious products, along with their continuous and reproducible manufacturing requires reliable and reproducible quantitative phase analysis. Also, the accurate knowledge about phase composition of a hydrating cementitious system, at a given time of hydration, is needed for the elucidation of complex hydration processes and their associated mechanisms. During the past few years several authors have described the possibility for quantitative analysis of cements, clinkers, supplementary cementitious materials and hydrated cementitious systems using the X-ray diffraction (XRD) and Rietveld method [1–6]. XRD is a powerful tool for the characterisation of cementitious materials, but, in order to be exploited correctly, measurement conditions should be carefully chosen. Investigations and quantifications of chemical reactions in synthesis and hydration of cements and their corresponding phases are typically carried out *ex-situ* on reaction products after the reaction has been stopped in some way [1,2,4]. However, with short measurement times these quantifications can also be done nearly online so as to follow the reactions progress *in-situ* without the need for stopping the reactions [2,7]. Using high performance X-ray equipment with highly efficient X-ray detectors and advanced software packages it is possible to analyse complex phase mixtures and obtain reliable results of phase composition [2,7]. Quantitative X-ray diffraction (QXRD) by applying the Rietveld method gives phase fractions normalised to 100% crystalline phases, while the amorphous, non-diffracting content is not accounted for [8]. Amorphous phases can be quantified only indirectly by QXRD, since they do not give reflection peaks in the diffraction pattern. For this purpose a defined quantity of crystalline inert material (internal standard) is added to the sample and is used to calculate the amount of amorphous content [1,6,9]. In the last few years an increasing number of papers have been dealing with phase quantification of hydrated products obtained in normal cementitious systems that are characterised by high water contents [2,6,7]. However, as far as we are concerned, there has been no reported work in the literature that is dealing with the phase development in high and ultra high performance cementitious systems that contain supplementary cementitious additives and very low water to binder ratios. There exists also a lack of knowledge whether there is a substantial difference between the phase composition and time dependent phase development of normal and ultra high performance concrete (UHPC) formulations. Based on the observed hydration behaviour and the results of other investigations, the phase development in the high and ultra high performance concretes is expected to be kinetically and quantitatively different from that in normal concrete systems [10]. Therefore, we are dealing here with the phase development in ultra high performance concrete

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Table 1
Mix proportioning of both formulations

System A, normal concrete (mortar) without aggregate		System B, UHPC without aggregate	
Portland cement I 52.5R HS/NA	1	Portland cement I 52.5R HS/NA	1
		Silica fume (SF)	0.25
		Fly ash (SWF)	0.17
		SP (polycarboxylate - ether)	<0.025
Water (extra)	0.45	Water	<0.3

Table 2
Phase composition of PC I 52.5R HS/NA by QXRD

Phase	Phase quantity in wt.%
Ca_3SiO_5 (C_3 S, Alite)	54.7(4)
Ca_2SiO_4 (C_2 S, Belite)	11.7(3)
$Ca_3Al_2O_6$ (C_3A, Aluminate, cubic)	0.9(1)
$Ca_3Al_2O_6$ (C_3A, Aluminate, orthorhombic)	1.0(2)
$Ca_2(A,F)O_5$ ($C_2(A,F)$, Brownmillerite)	10.2(2)
$CaSO_4 \cdot 2H_2O$ (Gypsum)	0.8(1)
$CaSO_4 \cdot 0{,}5H_2O$ (Bassanite)	0.7(1)
$CaSO_4$ (Anhydrite)	0.1(1)
SiO_2 (Quartz)	0.1(1)
$CaCO_3$ (Calcite)	0.4(1)
$Ca(OH)_2$ (Portlandite)	0.3(0)
Amorphous content	19.2(6)

systems and comparing it with the phase development in normal concrete by using thermogravimetry (TG) and QXRD for phase quantification. For quantification ease the cementitious systems of this work do not contain any aggregate, even though we preserve the labelling "concrete" to these systems, which contain all other components required for producing normal or ultra high performance concrete, expect aggregates. In this paper we are going to present only the *ex-situ* obtained results on hydration reaction products, after the reaction has been stopped. The *in-situ* following of phase development in normal and ultra high performance concrete systems will be the matter of a subsequent issue.

2. Experimental

2.1. Materials

For the purposes of this work two cementitious formulations were employed; a normal concrete and an ultra high performance concrete. The ultra high performance concrete formulation that contains silica fume and fly ash has been developed and extensively characterised in our laboratory. Its strength, performance and additional properties that belong well to the ultra high performance concrete class are shown elsewhere [10,11]. Here we are interested mainly about its phase composition and time dependent phase development and are comparing these with the respective properties of the normal concrete formulation. The mixture formulation of the (UHPC) specimen together with that of the normal concrete, both employed for the phase calculations using QXRD and TG, are shown in Table 1. For quantification ease these formulations did not contain aggregate. The predominantly peak intensity obtained by quartz aggregates would otherwise further complicate the phase calculations. The oxide and phase composition of the raw materials (Portland cement type PC I 52.5R HS/NA, silica fume (SF) type G983, fly ash (SWF) employed for both formulations as well as other properties are shown in Tables 2–4. These parameters were assessed by means of quantitative X-ray diffraction (QXRD), gas adsorption (BET), X-ray fluorescence analysis (RFA) and thermogravimetry methods. For both formulations the same Portland cement type PC I 52.5R HS/NA, silica fume and fly ash products of our previous works were employed [10,11]. The HS/NA cement that is characterised by low tricalcium aluminate content was chosen for the ultra high performance concrete formulation, because of its lower water demand and moderate heat of hydration development. The median phase composition value of three refinements (QXRD), for this cement, is shown in Table 2. The error values are deduced from the standard deviation of the three results. The seemingly high content of the amorphous phase (19.2 wt.%) might be plausible for a material like cement that is obtained by a quenching process. Investigations of different clinkers, cements and pure clinker phases by QXRD have shown that they can contain significant amounts of amorphous material [12]. In order to control the quantification results for the dry mixture of system B (UHPC), as well as for the cement and fly ash, the expected composition of the UHPC was calculated for this purpose. This was done by means of its mixture proportioning and the respective QXRD phase composition results for cement and fly ash. The calculated values are compared with the results from the QXRD for the system B and are presented in Table 5. As it can be seen there is a good agreement between the calculated and the measured phase composition of system

Table 3
Oxide composition, particle size, specific surface area

Phase content	PC I 52.5 R HS/NA	Silica fume SF1 (G983)	FA (SWF)
SiO_2	19.60 wt.%	98.70 wt.%	54.10 wt.%
Al_2O_3	3.22 wt.%	0.28 wt.%	22.10 wt.%
Fe_2O_3	4.90 wt.%	0.10 wt.%	7.71 wt.%
CaO	66.90 wt.%	0.23 wt.%	5.11 wt.%
MgO	0.87 wt.%	0.11 wt.%	2.98 wt.%
Na_2O eq.	0.73 wt.%	0.30 wt.%	4.22 wt.%
SO_3	3.12 wt.%	0.19 wt.%	2.28 wt.%
P_2O_5	0.20 wt.%	0.02 wt.%	0.18 wt.%
Others + LOI	0.46 wt.%	0.07 wt.%	1.32 wt.%
d_{50}	6.70 µm	0.35 µm	6.50 µm
Spec.surf.area (BET)	0.5 m^2/g	17 m^2/g	0.65 m^2/g
Disponibility form	Powder	Powder	Powder

Table 4
Chemical composition of fly ash (QXRD)

Phase	Phase quantity in wt.%
SiO_2 (Quartz)	15.3(3)
$CaSO_4 \cdot 2H_2O$ (Gypsum)	0.2(2)
$CaSO_4$ (Anhydrite)	0.7(7)
$Al_8[(O,OH,F)|(Si,Al)O_4]_4$ (Mullite)	14.2(2)
Fe_2O_3 (Hematite)	0.6(6)
Fe_3O_4 (Magnetite)	0.6(6)
$CaCO_3$ (Calcite)	0.6(6)
MgO (Periclase)	1.2(2)
Amorphous content	66.6(10)

Table 5
Phase composition of System B (UHPC)

Phase	Phase quantity in wt.% calculated by raw materials	Phase quantity in wt.% results from QXRD
Ca_3SiO_5 (C_3 S, Alite)	37.4	37.9
Ca_2SiO_4 (C_2 S, Belite)	8.0	8.1
$Ca_3Al_2O_6$ (C_3A, Aluminate, cubic)	0.6	0.7
$Ca_3Al_2O_6$ (C_3A, Aluminate, orth.)	0.7	0.5
$Ca_2(A,F)O_5$ ($C_2(A,F)$, Brownmillerite)	7.0	7.1
$CaSO_4 \cdot 2H_2O$ (Gypsum)	0.6	1.1
$CaSO_4 \cdot 0{,}5H_2O$ (Bassanite)	0.5	0.2
$CaSO_4$ (Anhydrite)	0.2	0.7
SiO_2 (Quartz)	2.4	2.5
$CaCO_3$ (Calcite)	0.3	0.3
$Ca(OH)_2$ (Portlandite)	0.2	0.3
$Al_8[(O,OH,F)|(Si,Al)O_4]_4$ (Mullite)	2.1	1.3
Fe_2O_3 (Hematite)	0.1	
Fe_3O_4 (Magnetite)	0.1	
$CaCO_3$ (Calcite)	0.1	
MgO (Periclase)	0.2	
Amorphous content	39.7	39.2

Table 6
Measurement conditions XRD

Diffractometer type	Bragg–Brentano, theta–theta-goniometer
Generator settings	45 kV, 40 mA
Anode material	Cu
Primary and secondary soller	0.02 rad
Detector type	RTMS-Detector, X'Celerator, PANalytical
Scanning length of the detector in 2 theta	2.122
Sample rotation	1 r/s
2 Theta scanning range	7–70°
Step size	0.017°
Step time	29.8 s
Programmable divergence slit	12 mm
Programmable snti scatter slit	12 mm
K_{β}-filter	Ni

B, giving in this way additional evidence for the appropriate results of the measured phase composition. The employed silica fume, as expected, did not show any crystalline phase.

2.2. Specimen preparation

After the specified mixing time (the mixing time for the UHPC formulation, about 8 min, was remarkably longer than that for normal concrete) the fresh concrete (cementitious binder without aggregate) was filled into three moulds (1.5×1.5×6 cm) in two layers (according to the norm DIN EN 196-1) and vibrated for 2 min. The prism-shaped specimens were demoulded after 24 h of hydration time and then stored in a climate chamber (20±1 C and 95±5% rh) for the rest of the specified curing time. Measurements were carried out for respectively 1, 2, 7 and 28 day old specimens. For this, 10 g of hardened specimen were carefully fine milled. The portion that is characterised by a suitable fineness for XRD was taken and subsequently vacuum dried for 24 h, employing a vacuum pump that could maintain a vacuum level of 10 mbar. The mass loss due to this drying process is referred to as the free water content here. For the calculation of the amorphous content 7 g of the vacuum dried powdered specimen were mixed with 0.7 g ZnO (10%) as internal standard. A Brindley correction is only possible if each phase is characterised by a narrow and well defined particle size distribution [13]. Multi-component powders like these employed in this study do not meet this condition. To minimize the effect of the micro-absorption, ZnO was chosen as internal standard because its linear absorption coefficient, being 279 cm^{-1} for CuKα radiation, is close to those of the main cement phases $\mu(C_3\ S)=323\ cm^{-1}$, $\mu(C_2\ S)=311\ cm^{-1}$, $\mu(C_3A)=274\ cm^{-1}$ and $\mu(C_2(A,F))=509\ cm^{-1}$. The powdered specimen-standard mixture was homogenised for 15 min. From this homogeneous mixture three equal amounts were prepared for the XRD measurements. The mean particle size (d_{50}) of the powdered material employed for the XRD measurements was 20 µm (assessed by laser granulometry). The calculated values of phase content presented here below represent the mean value of the three measurements. The calculated phase content represents the normalised value after the inclusion of the “free water” and subtraction of the ZnO contribution. The 0 day values include the phase composition for the dry powder (non hydrated system) by QXRD and the mixing water content. Simultaneous thermogravimetry analysis were carried out on powdered specimens (fineness <50 µm) using a heating rate of 10 °C min^{-1} from 20 to 1000 °C under air atmosphere. Sample amounts of 50±2 mg were packed into a Pt-Rh crucible. The value obtained by the thermogravimetry analysis (TG) is the representative mean value of two measurements.

2.3. Methods and equipments

An X'Pert Pro (Panalytical) diffractometer, Cu $K_{\alpha 1,2}$ radiation (154,178 Å), 45 kV and 40 mA was employed for the X-ray diffraction

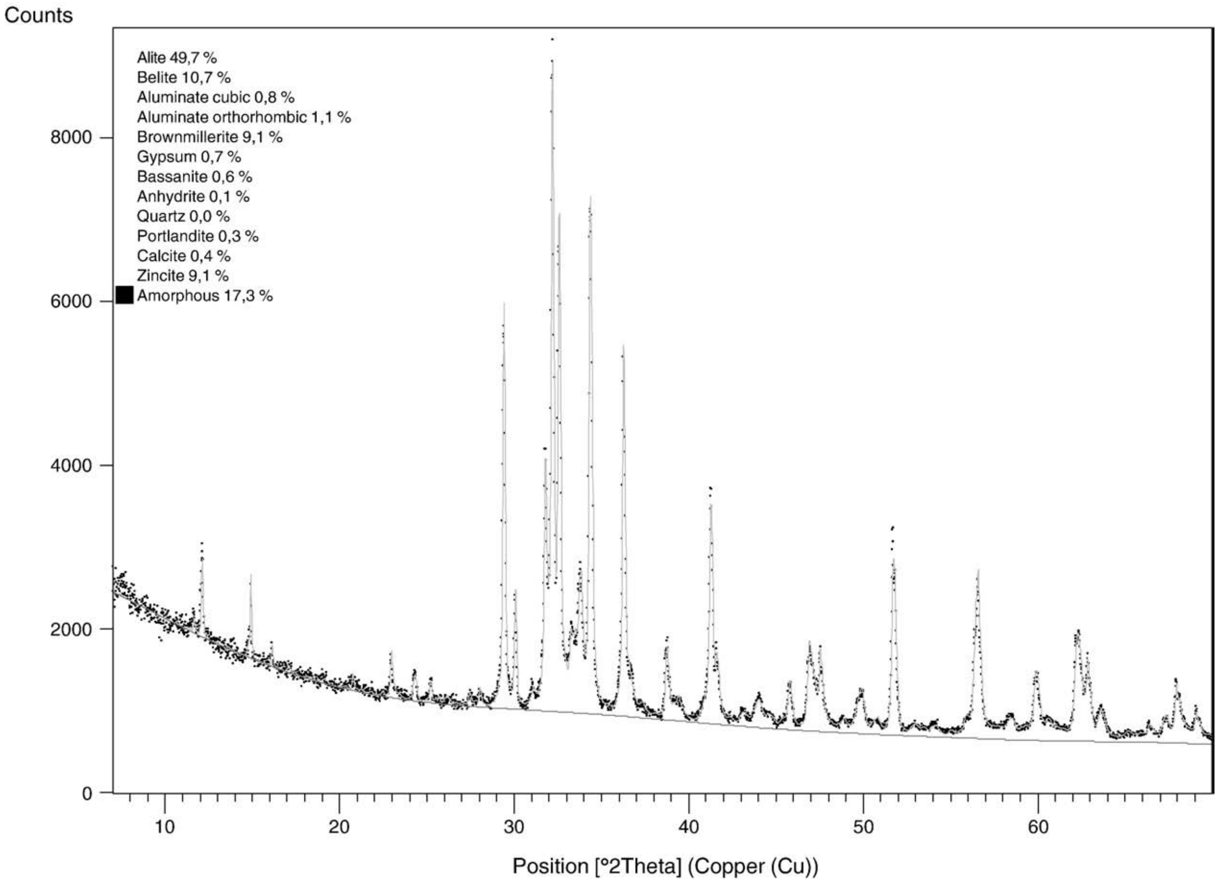

Fig. 1. Rietveld refinement plot for normal “concrete” dry mix (system A); the results are not corrected for ZnO content.

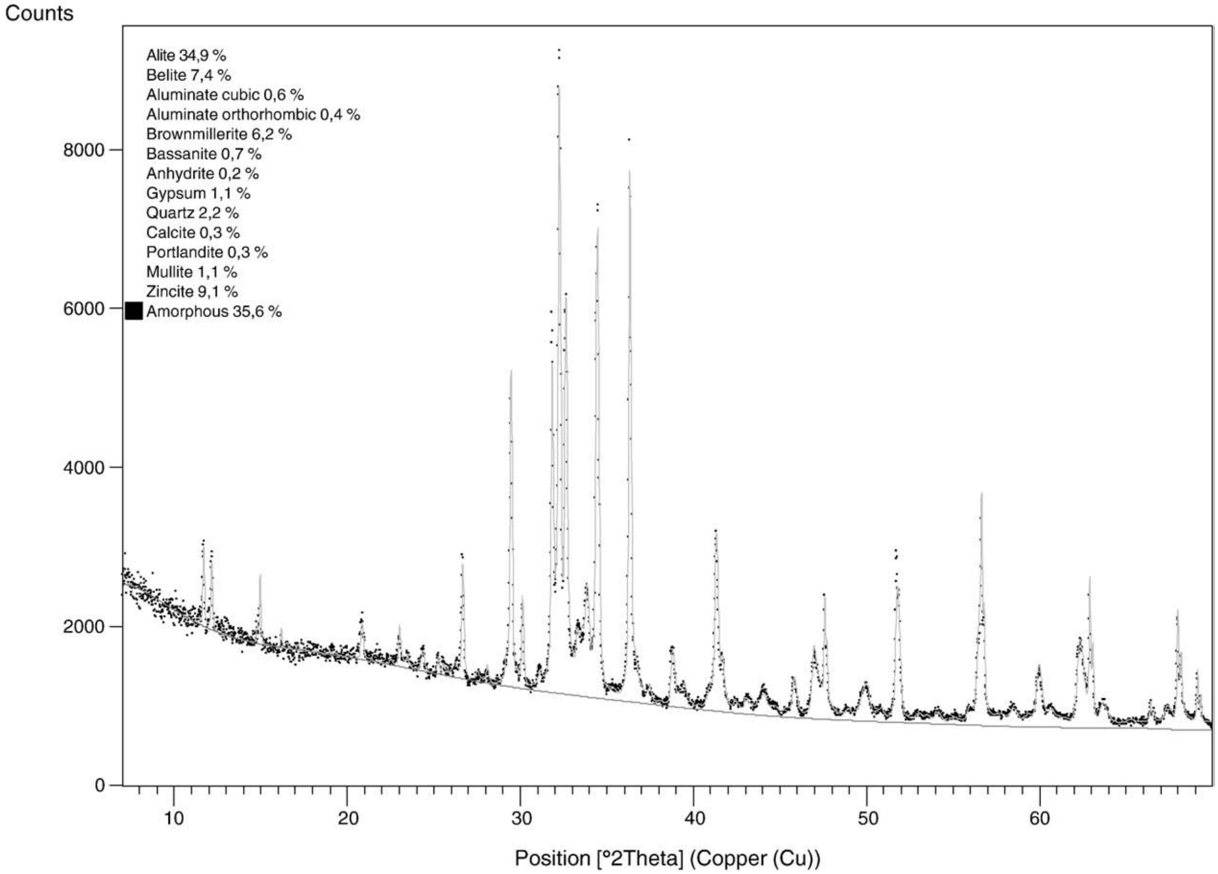

Fig. 2. Rietveld refinement plot for the ultra high performance "concrete" dry mix (system B); the results are not corrected for ZnO content.

experiments. The parameter configuration of the employed XRD equipment is depicted in Table 6. The measurements were performed with standard Bragg–Brentano optics. All Rietveld refinements were done using the X'Pert HighScore Plus program from Panalytical. In the Rietveld method for the analysis of powder diffraction data the entire pattern is calculated using a model for the positions of the peaks (the unit cell parameters), their intensities (dependent on atomic positional and thermal parameters, preferred orientation, etc.) and their widths and shapes, together with a description of the background [14]. The calculated pattern is then compared with the observed step profile, point by point, and the model parameters are adjusted by least-squares method [8]. The typical sources of error in conventional X-ray diffraction analysis, such as preferred orientation, solid solutions or peak overlapping, can be minimised or taken into account by making corrections with rigorous physical meaning. Thus some restrictions during the refinement had to be done. For the portlandite phase it was considered the preferred orientation factor, whereas the site occupancy for brownmillerite and the profile functions for minor phases (<2 wt.%) has not been refined. For the QXRD calculations of the non hydrated systems were considered the structures depicted in Tables 2 and 4. For the hydrating systems additionally portlandite ($Ca(OH)_2$) and ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$) were accounted for. All samples were scanned within 7–70 2θ using CuK_α radiation. For the calculation and refinement of the background a "Shebyshev II" polynomial approach was employed. The cell and profile parameters were refined only for the phases with a content of more than 2 wt.%. For each cell parameter, the upper and the lower limits were set. During

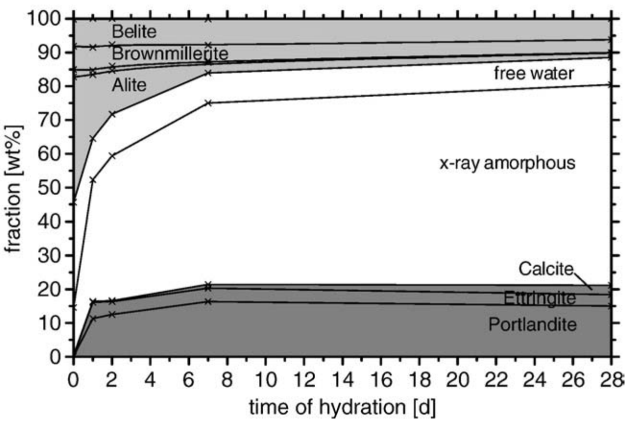

Fig. 3. Time dependent phase development for normal "concrete" (system A).

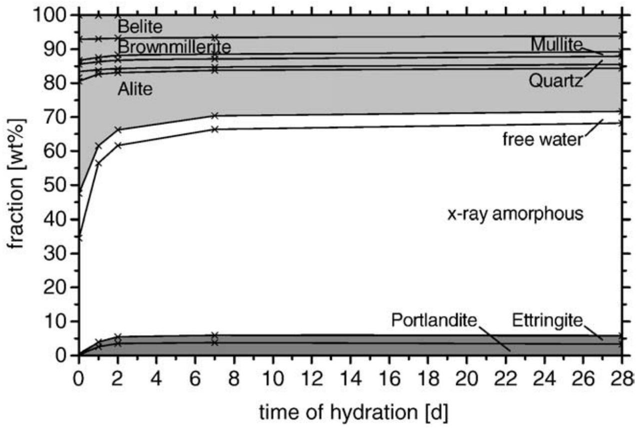

Fig. 4. Time dependent phase development for the ultra high performance "concrete", (system B).

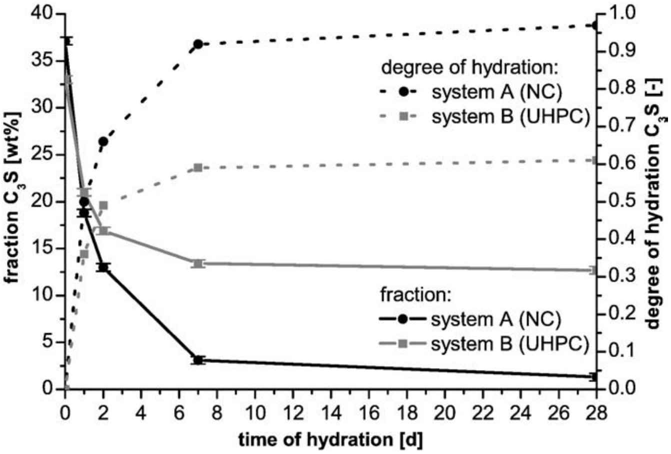

Fig. 5. Time dependent phase development and degree of hydration for alite.

the refinement these values were checked if they were run against the set limits. The site occupancies and thermal parameters of the structural information were not refined. The preferred orientation of alite, portlandite and calcite were refined by using the "March–Dollase" model, when required. One example of the three refinements for the dry mixtures of both systems A and B is shown in Figs. 1 and 2.

Thermogravimetry analysis (TGA) were additionally conducted to quantitatively estimate the $Ca(OH)_2$ using a "STA 2000, BÄHR" equipment. The results of $Ca(OH)_2$ content obtained by TGA were compared with those calculated using the Rietveld method.

3. Results and discussion

3.1. Phase development comparison in normal and ultra high performance concrete

We will label concrete both cementitious formulations of this work, as it was already mentioned in both introduction and experimental parts, even though they are not concrete systems, since they do not contain coarse aggregate. Therefore with concrete here should be understood the basic cementitious formulation for producing concrete, which has been removed the aggregates. In the following the results of phase development in both concrete systems are going to be presented and compared between them. In the following the normal "concrete" formulation is going to be labelled system A, and the UHPC formulation system B. In Fig. 3 and 4 are respectively presented the time dependent phase development for all the main phases (amorphous phase C-S-H, ettringite, CH, C_3S, C_2S, C_3A, C_4AF, etc) of hydrating normal and ultra high performance "concrete" (UHPC) formulations. In these figures the crystalline phases of cementitious powder mixture (raw materials) are presented in light grey, the crystalline hydration reaction products in dark grey and the X-ray amorphous phases in white colour. By referring to both figures a remarkable difference of phase development between both concrete types can be observed. As it is expected, due to the much higher water content employed in the normal concrete formulation, the amount of non hydrated cement in the UHPC formulation is remarkably higher than that in the normal concrete [15]. The values of the degree of hydration and the remaining amount, during 28 days of hydration, of the most abundant phase of the cement employed (tricalcium silicate, C_3S) for both concrete formulations are presented in Fig. 5. They were calculated based on the QXRD-results. The knowledge about the remaining amount of C_3S is of great interest in the cases when dealing with self healing effect in UHPC systems. The hydration degree of the C_3S phase in the normal concrete formulation is higher than for the UHPC formulation during all the investigated hydration time. It reaches about 95% after 28 days, whereas for the UHPC it reaches only about 65%. The non hydrated amount of C_3 S in the normal concrete remains lower and its total consumed value is higher than in UHPC formulation during all the hydration period of 28 days. The C_3S phase is especially faster consumed during the first 7 days for both formulations and more slowly during the rest of the hydration period up to 28 days. For the normal concrete formulation only a small amount of C_3S remains (2.5 wt.% referring to the formulation weight)

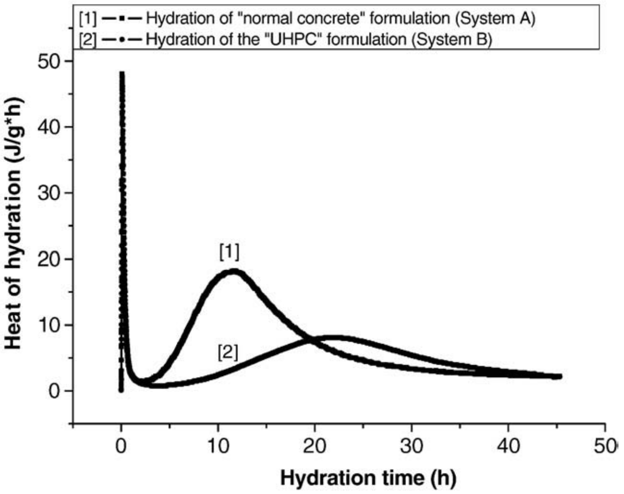

Fig. 7. Hydration behaviour of both systems (heat conduction calorimetry).

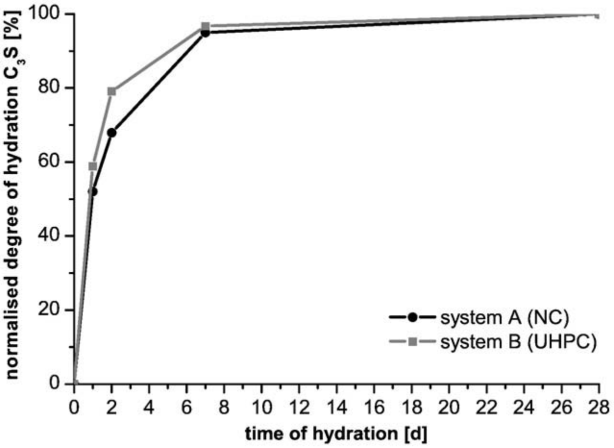

Fig. 6. Time dependent normalised values of the degree of hydration for alite.

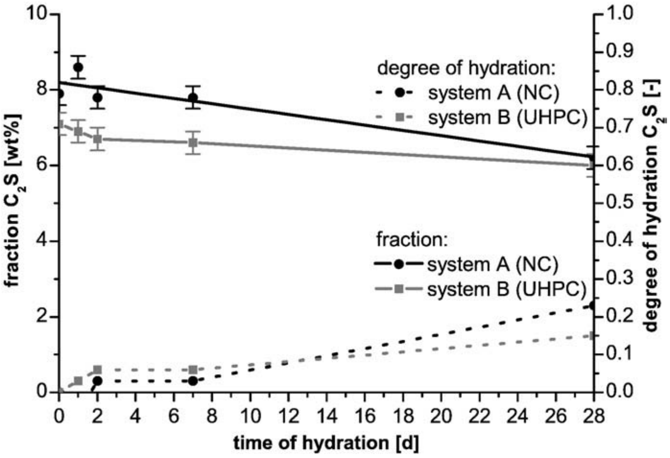

Fig. 8. Time dependent phase development and degree of hydration for belite.

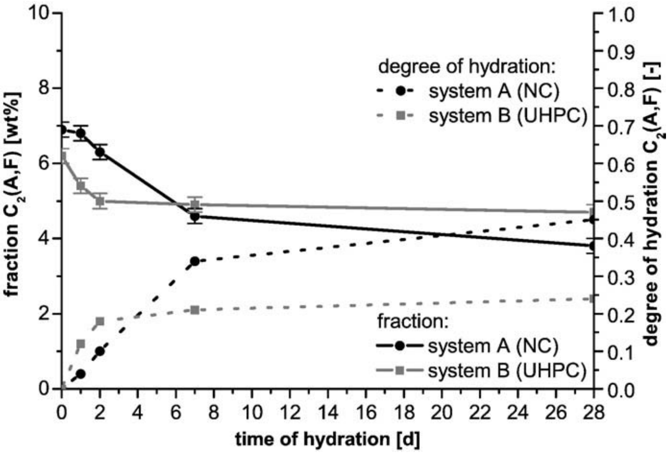

Fig. 9. Time dependent phase development and degree of hydration for brownmillerite.

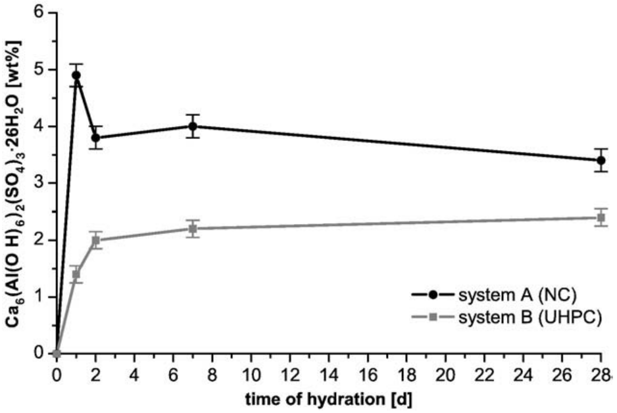

Fig. 11. Time dependent phase development for ettringite.

after 28 days of hydration, whereas the remaining amount of C_3S in the UHPC formulation is considerably higher (13 wt.%). The calculated value for the remaining C_3S content after 28 days is slightly lower than that found in the literature from previous work on similar subject [16], which can be attributed to the various cements and experimenting conditions employed in both works (the C_3 S phase content of the cement employed, shown in Table 2, was about 54.7%). The plots of Fig. 6 depict the time dependent, normalised degree of hydration where the 28 day value of the remaining C_3 S content (1.3 wt.% C_3S for system A and 12.7 wt.% C_3 S for system B) is taken as the maximal value that can be consumed by the hydration reaction within the observed period of time. These plots takes already into account the higher amount of non hydrated (remaining) C_3S in the UHPC formulation due to the lower water content (different water amounts available to hydration). Fig. 6 shows the well known acceleration effect of silica fume on the C_3S hydration [15,17,18], which is especially pronounced during the post-acceleration period up to 7 days of hydration. To study the hydration behaviour of both systems at early age the heat conduction calorimetry method was additionally employed. The comparison of the hydration behaviour, at early age, of both systems, indicates however a retardation of the hydration and a shift of the acceleration period towards higher hydration times in system B (curve 2), within the first hours (Fig. 7). The accelerating effect caused by silica fume is totally overcome by the presence of superplasticizer (SP) [10,19]. The total effect is therefore a resulting delay on the hydration of the UHPC specimen up to 40 h (Fig. 7). For summarising the phenomena two main differences could be observed: a retardation of the hydration process for the UHPC during the early stages of hydration, which is mainly caused by the superplasticizer (SP) and the lower w/c ratio, but an earlier reaching of the maximum degree of hydration during the post-acceleration period that is already earlier reached because of the pozzolanic reactions. During all the 28 days period of hydration, higher amounts of portlandite and ettringite crystalline hydration products are measured for the normal concrete formulation (Figs. 3 and 4). The calculated total content of amorphous phases (which include C-S-H) is however higher for the UHPC specimen. This is of course, mainly, due to the extra amount of the amorphous C-S-H produced by the pozzolanic reactions of employed silica fume (SF) and fly ash (FA) [11,15,17,18]. The content of the calculated amorphous phases in the normal concrete specimen is in good agreement with the values found in the literature [20]. The calculated hydration degree for the normal concrete referring to the C_3S phase is also in very good agreement with the amount of amorphous phase content. The evolution of the C_3A phase is not shown, since its content in the employed cement is low (C_3A orthorhombic and cubic 1.9 wt.%, Table 2) and the errors related to its quantification are relatively high (up to 20% in the hydrated systems). The cement phases belite and brownmillerite (Figs. 8 and 9) are characterised, as expected in the conditions of simultaneous phase hydration [21], by lower hydration degrees than alite phase and are also showing acceleration up to 7 days. (The apparent increase of the C_2S at 1 day is very probably a calculation error; rather the trend of the curve should be considered). Figs. 10 and 11 depict the time dependent development of portlandite and ettringite crystalline phases in both concrete types. There is a much more pronounced difference of the portlandite content than of ettringite content between both concrete types (Figs. 10 and 11). The decreasing of the ettringite amount for the "normal concrete" formulation at hydration times beyond 1 day may

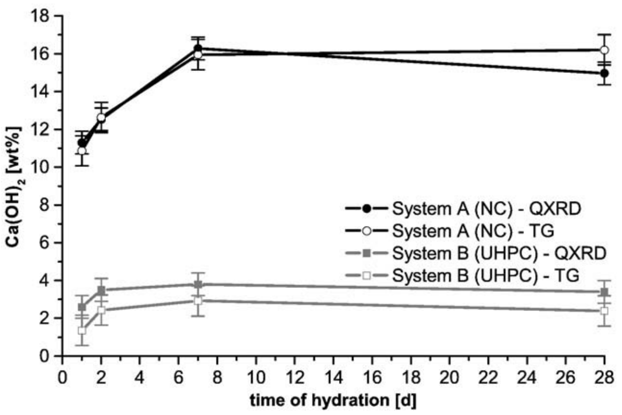

Fig. 10. Time dependent phase development for portlandite.

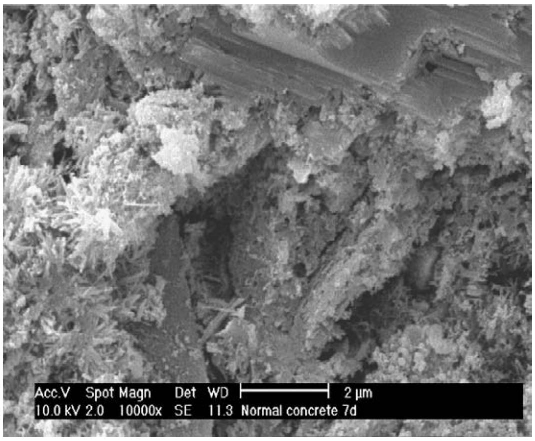

Fig. 12. SEM image of the normal concrete specimen.

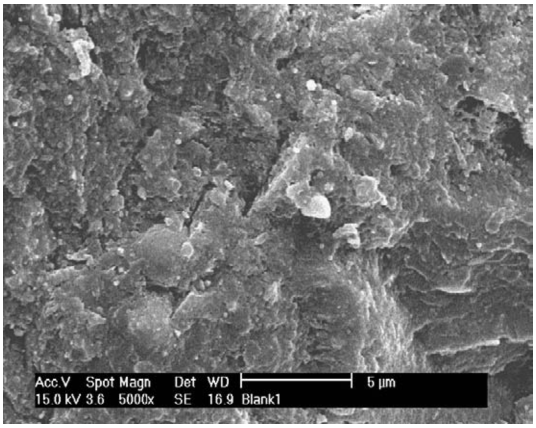

Fig. 13. SEM image of the UHPC specimen.

be attributed to a conversion to monosulphate phase, since no crystalline monosulphate could be detected by qualitative X-ray analysis. Further more the formation of X-ray amorphous monosulphate due to this conversion might be possible. The remarkably lower content of the portlandite in the UHPC formulation is again a reflection of the pozzolanic reactions [22,23] and the lower water to binder ratio. In Fig. 10 are additionally plotted the contents of portlandite obtained by both TG and QXRD. Inside the error margin there is a good correlation of the values assessed by both methods employed. The difference of the 28 days portlandite content between two methods for the normal concrete arises very probably because of the specimen carbonation [24,25]. The lower 28 days amount of portlandite in normal concrete, which is measured by the Rietveld method, may also be related to this carbonation effect, in addition to the imperfection of its crystalline lattice [21]. The calcite content of normal concrete that is due to the carbonation is calculated to be around 1.1 wt.% after 7 days and reaches already 2.8 wt.% after 28 days of hydration. Whereas, the missing of calcite at the UHPC specimen may be attributed to the much denser structure of its hydration phases (SEM images in Figs. 12 and 13). The low amount of portlandite at the UHPC specimen on the one hand and the denser structure of this specimen on the other, hinder the penetration of the CO_2 and humidity required for the carbonation reactions. Hence no apparent calcite crystals are detected. The amount of portlandite in normal concrete increases continuously and fast between the first and the seventh day of hydration and increases only slightly during the rest of the hydration time up to 28 days. The faster portlandite formation is recorded between the first and the second hydration day. A similar trend of portlandite content evolution in normal "concrete" system is also reported by others [16]. For the UHPC formulation not only a much more lower total content of portlandite is measured as compared to the normal concrete formulation, but also a very small uptake of its amount during the second and the seventh hydration day. Between the seventh and the twenty-eighth day of hydration a kind of decrease of portlandite content is again observed. Also for this specimen the faster portlandite formation is measured between the first and the second hydration day. This kind of behaviour for the evolution of portlandite content in the UHPC formulation is of course directly related to the pozzolanic reactions of silica fume and fly ash, which seem to be clearly remarkable after the second day of hydration and proceed simultaneously with the hydration reactions. In good agreement with the conclusions of others, the amount of measured portlandite gives evidence for non complete pozzolanic reaction in the UHPC specimen even after 28 days of hydration [23,26]. However, the content of portlandite present in the normal concrete after 28 days is found to be much higher (ca. 16.5 wt.%) in comparison to its content in the UHPC specimen (ca. 2.5 wt.%). The evolution of ettringite contents in both formulations is depicted in Fig. 11. For the UHPC specimen a continuous increase of the ettringite content, which is much faster during the first 2 days, is recorded. Whereas for the normal concrete, after a very strong increase of the ettringite content during the first day of hydration, a decrease of its content until the second hydration day is recorded, which with some slight variation continue to further decrease for the next hydration period up to 28 days. The most probable assumption for explaining the variations of ettringite content development would be the conversion of ettringite to monosulphate phase, and it is also probable that significant amount of aluminate may have entered the X-ray amorphous C-S-H phases [16]. As aforementioned no crystalline monosulphate phase could be identified by qualitative X-ray analysis. However additional experiments are required to explain this trend of ettringite content evolution. The mullite and quartz phases detected in the UHPC specimen come from the fly ash product employed for producing this specimen.

4. Conclusions

In this paper dealing with the phase development in a UHPC, which is the first of its sort, a quantitative comparison between the phase development in normal and ultra high performance cementitious systems during 28 days of hydration is presented. It is shown that qualitatively, there is no great difference between the main phases obtained in both systems. However, the phase development in ultra high performance cementitious formulation is quantitatively and kinetically different from that in normal concrete formulation. This is related to the different components employed and their associated reactions. For both formulations the most remarkable changes concerning the phase contents are recorded between the first and second hydration day and up to the seventh day. After the seventh day less phase content changes are measured. Because of the non sufficient water amount for hydration, nearly 13 wt.% (referring to system weight) of the main cement phase C_3S remain non hydrated in the UHPC system. The corresponding value is much lower in the normal concrete formulation. The content of crystalline phases is considerably higher in the normal concrete, whereas less amorphous phases than in the UHPC formulation are measured. The difference arises from the pozzolanic reactions associated with the relatively high amounts of the employed silica fume and fly ash. The pozzolanic consumption of portlandite becomes remarkable after the second hydration day. The portlandite content present in the UHPC specimen after 28 days, even though much lower than in the normal concrete give evidence for non complete pozzolanic reactions. The fact that no calcite is detected by X-rays in the UHPC specimen even after 28 days may be interpreted as indication of non considerable phase carbonation in this specimen. The variations of ettringite content development between the first and second hydration day indicate that some conversion of ettringite to monosulphate phase is possible, and that significant amount of aluminate may enter the X-ray amorphous C-S-H phases.

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