Microstructural investigation of innovative UHPC

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Abstract

The production of ultra high performance concrete (UHPC) with target strengths greater than 200 MPa has recently been considered for specific structural applications that need this enhanced mechanical performance. The main purpose of developing these innovative UHPC mixtures is to produce high-strength precast concrete elements with excellent durability to serve as both the inner wedges and the outer barrel of a new nonmetallic anchorage system. The anchorage is for post-tensioning applications using carbon fibre-reinforced polymer tendons. The UHPC mixtures examined show very dense microstructures with some unique characteristics. The bond between the micro carbon fibres and the cement paste seems to be very good and the cement paste observed in the vicinity of the fibres was shown to be very dense and homogeneous. The micro carbon fibres seem to govern the strength and postcracking behaviour of these materials. © 1999 Elsevier Science Ltd. All rights reserved.

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Ultra high performance concrete (UHPC) with target strength greater than 200 MPa was desired for a specific structural application. The main purpose in developing innovative UHPC mixtures was to produce precast concrete elements that show excellent mechanical and durability performance to serve as both the inner wedges and the outer barrel of a new nonmetallic anchorage system. The nonmetallic anchorage would be used as part of a corrosion free post-tensioning system [1]. Some of the UHPC mixtures examined incorporated micro carbon fibres. Microstructural investigation of hardened mixes is intended to help understand how to enhance further the performance of this type of concrete.

1. Experimental program

The microstructure of UHPC mixtures was investigated. The following are the key points of the experimental programme.

1.1. Materials and mixture proportions

The cementitious materials used in the mixtures investigated were Type 10 portland cement and silica fume. Silica fume is believed to act as both a filler and a pozzolanic material, and has the ability to enhance concrete performance.

Four different combinations of limestone, calcined bauxite, and silica sand were used as aggregate. The limestone and calcined bauxite aggregates used were of nominal maximum size of 4–6 mm. Two types of siliceous aggregate were incorporated: Ottawa sand of uniform size >150 μm and silica flour, which is a pulverized quartz, of a uniform size <75 μm. The rationale behind the mixture proportions selected has been discussed elsewhere [2]. Table 1 shows the composition of the mixtures examined.

The silica flour was reported to work as an inert material in concrete mixtures cured at ambient temperature and to be pozzolanic when the concrete is cured at temperatures $>150°C$ [3]. A powder superplasticizer was also used to provide good workability performance.

Panex® (Zoltek Corp., St. Louis, MO) PAN based micro carbon fibres 3–6 mm long were incorporated to improve the fracture toughness and other mechanical properties of the mixtures cured at temperatures $>200°C$. Although micro carbon fibres may be the most expensive fibres, they have higher tensile strength, strength/weight ratio, and modulus of elasticity than other commercially available fibres and are corrosion free at ambient temperatures. On the other hand, the low-failure strain values observed for most types of micro carbon fibres and the obvious lack of yield plateaus constitute the main structural disadvantages for this

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Table 1
Mixture proportions of the UHPC mixtures

	Mixture						
	A	B	C	D	E	F	G
Cement (kg/m^3)	1040	1040	1040	1040	510	510	450
Silica fume (kg/m^3)	310	310	310	310	65	65	50
Aggregate (kg/m^3)	800	800	800	800	1700	1700	1720
Water (L/m^3)	240	240	240	240	140	140	180
Fibers (vol. %)	0	2	0	2	0	0.5	0.5
Superplasticizer %	2	2	2	2	2	2	2
Cement type	10	10	10	10	10	10	10
Coarse aggregate type	Crushed limestone	Crushed limestone	Calcined bauxite	Calcined bauxite	Calcined bauxite	Calcined bauxite	Calcined bauxite
Fine aggregate type	Ottawa sand + silica flour	Ottawa sand + silica flour	Calcined bauxite	Calcined bauxite	Ottawa sand + silica flour	Ottawa sand + silica flour	Ottawa sand + silica flour
Nominal maximum size (mm)	4.0–6.0	4.0–6.0	4.0–6.0	4.0–6.0	4.0–6.0	4.0–6.0	4.0–6.0
Water/binder ratio	0.18	0.18	0.18	0.18	0.24	0.24	0.36

material. The different mechanical properties and environmental performance of carbon fibres have demonstrated that these fibres are a reliable and suitable alternative to steel fibres. The different physical and mechanical properties of these fibres compared to conventional steel fibres used in cement composites are shown in Table 2.

1.2. Production of UHPC

A conventional three-speed mortar mixer was used to blend these mixtures by vibrating for 15 min. Pressure was applied to fresh concrete in the range of 10–80 MPa. The pressure was increased gradually to its maximum value at a slow rate of loading (2 kN/s) and kept constant for 4 hours. The maximum value of applied pressure for each concrete mixture was governed by the compaction attained and varied with the workability of the concrete. The specimens were demoulded after 24 h and one of two curing regimes was used for each group tested [2].

1.3. Curing regimes

Specimens were immersed until testing in a hot water bath at 50°C to minimize the shrinkage and thermal cracking expected from the hydration of these high cement content mixtures. Specimens were denoted as having been hot water (HW) cured. Specimens cured in a hot water bath at 50°C until 2 days prior to testing when they were oven-dried at 200°C, were denoted as having been oven-cured (OV).

Table 2
Physical and mechanical properties of micro carbon fibres and steel fibres [2]

Property	Micro carbon fibre	Steel fibre
Diameter (microns)	7.4	25
Length (mm)	3–6	12–25
Unit weight (kg/m^3)	1780	7850
Tensile strength (MPa)	3600	1900
Strength/weight ratio (MPa · m^3/kg)	2.0	0.24
Modulus of elasticity (GPa)	228	200

Table 3 shows the different production parameters of the prepared UHPC groups including the mixture number, the pressure applied to the fresh concrete, and the curing regime used.

1.4. Compressive strength test

Compressive strengths were determined at 7 and 28 days on 5×5 cm cubes tested in triplicate; average results are shown in Table 4.

Four innovative UHPC groups (4, 7, 9, and 10) have been developed with 7 and 28 days compressive strengths up to 240 MPa. All these groups incorporated micro carbon fibres. Various well-graded aggregates were involved, and three of the four mixtures were pressurized after casting (groups 4, 9, and 10). The pressure squeezes water out, dropping the water/cement ratio and increasing the packing density of the cement matrix. Therefore, the improvement achieved appears to be mainly a result of the reduced porosity of concrete.

The superior performance of the UHPC trial mixtures containing crushed limestone, calcined bauxite, and/or silica sand may be due in part to the epitactic growth of cement hydration products on these aggregates [4,5]. Establishment of this hypothesis was beyond the scope of this work and was difficult due to the involvement of many variables in this investigation. Further work should be able to shed light on the influence of epitaxy on bond strength. The high compressive strength of the mixed limestone/silica sand mixtures (A and B) is consistent with HPC results reported by Luciano et al. [6], explained by a balance between water demand and bond strength when a combination of these types of aggregate is used. In this work, strengths up to 200 MPa were achieved in a mixture containing only about 35% cement paste by volume (group 10). This is thought to be due to the combined effect of the bauxite aggregate at elevated temperatures (see below) and the application of pressure during fabrication. On the other hand,

Table 3
Production parameters of the groups examined

	Group											
	1	2	3	4	5	6	7	8	9	10	11	12
Mixture no.	A	A	B	B	C	D	D	E	F	F	G	G
Pressure on fresh concrete (MPa)	0	40	40	40	0	0	0	80	80	80	0	12
Curing regime	HW	HW	HW	OV	HW	HW	OV	HW	HW	OV	OV	OV

concrete made with limestone aggregate (groups 3 and 4) required 60–70% cement paste by volume to attain the same strength level.

Due to the mineralogical nature of the calcined bauxite aggregate [7], a reaction between the aggregate surface and the cement paste may be expected to occur when elevated temperatures are applied. In comparison to group 1 (limestone aggregate), group 5 (bauxite aggregate; hot water cured) shows a slight increase in compressive strength at 7 days but no effect at 28. When elevated temperature curing is applied, compressive strengths >200 MPa were attained when the fresh limestone concrete (group 4) was also pressured up to 40 MPa. The same level of strength was obtained under the same curing conditions but with no pressure applied to the fresh concrete, by group 7 incorporating bauxite aggregate. Improved bonding of the cement paste to the aggregate at elevated temperatures may well be partly responsible for these high compressive strengths.

1.5. Fracture toughness measurement

The fracture toughness of UHPC group 11 was compared to a 100 MPa HPC mixture to detect the effect of micro carbon fibres on the fracture toughness of UHPC using the modulus of rupture test in accordance with ASTM C78-84. Simply supported beams were loaded in third-point loading. The specimens were $100 \times 100 \times 400$ mm bars tested over a span of 350 mm. The test was controlled by crosshead stroke.

2. Microstructural investigation

Two main techniques were used to examine the microstructure of the mixes. The first was direct observation with scanning electron microscope (SEM) and the second was qualitative mineralogical analysis by X-ray diffraction (XRD). Combined use of the two techniques facilitates an understanding of the link between engineering behaviour and composition and microstructure.

2.1. SEM

Eight UHPC groups (3, 4, 6, 7, 9, 10, 11, and 12) were examined on the SEM at 14 days. Specimens were taken from the inner part of the test sample to avoid possible artifacts caused by thermal effects at the surface. Specimens were fractured and coated with gold prior to examination.

2.2. XRD

Eight UHPC groups (3, 4, 6, 7, 9, 10, 11, and 12) were examined by XRD at 14 days. X-ray diffractograms were recorded from samples of powdered concrete compacted in Al holders, over a 2θ angular range from 2° to 140°, using Fe filtered Co Kα radiation. Specimens were taken from similar parts of the 14-day-old concrete as for observation on the SEM. Phases were identified by the use of the Joint Committee on Powder Diffraction Standards powder data file.

3. Microstructural features of UHPC

3.1. SEM micrograph interpretation

3.1.1. Dense and homogeneous microstructure

All the UHPC mixtures examined showed a very dense microstructure compared to the known microstructure of conventional concrete and even high performance concrete (HPC). The calcined bauxite (groups 7, 9, 10, 11, and 12) showed a more homogeneous and denser microstructure than the limestone ones (groups 3 and 4). The dense microstructure of the cement phase in these groups extended to the aggregate boundary and as a result the well-known microstructure gradient of the cement paste toward the transition zone was absent. This was observed even when no pressure was applied to fresh concrete of such mixtures

Table 4
7 and 28 days compressive strength of the UHPC mixtures examined

	Group											
Compressive Strength (MPa)	1	2	3	4	5	6	7	8	9	10	11	12
7 days	120	160	180	220	130	150	200	160	190	240	130	170
28 days	140	165	195	230	140	165	210	175	195	240	145	175

(groups 6 and 7). It is worth mentioning that mixtures containing both silica fume and silica flour generally showed a very dense and homogeneous microstructure.

The micro carbon fibres are randomly distributed within the hydration products. Fig. 1 shows the distribution of some micro carbon fibres within the homogeneous microstructure of the UHPC mixtures.

3.1.2. Absence of CH crystals

The UHPC mixtures differed from conventional concrete in that large crystals of CH were generally absent. However, CH crystals were found in mixtures made with limestone aggregate and cured in the hot water bath only (Fig. 2) and in the calcined bauxite mixture made with a relatively high water/binder ratio (group 11). It is believed that the very low water/binder ratio and the pressure applied to the fresh concrete results in a very low porosity that restricts the space available for the growth of CH crystals. The relatively high content of silica fume, especially in groups 1–7, together with the inclusion of silica flour and the elevated temperature curing regime, created an effective pozzolanic environment which consumed most of the weak CH crystals produced during hydration. These crystals were converted to strong C-S-H. The combined effect provided excellent mechanical properties. However, the effect of dry curing seems very pronounced, especially at 28 days. Comparing groups 3, 6, and 9 (where hot water curing is used) to groups 4, 7, and 10 (where oven-curing is used), a significant enhancement in strength can be observed for the oven-cured groups. The effect of oven-curing was confirmed when CH crystals were observed in group 3 where only hot water curing regime was applied.

3.1.3. Characteristics of UHPC transition zone

The transition zone observed in the UHPC mixtures examined was of very small thickness with respect to that of HPC and conventional concrete. Microcracks in the vicinity of the aggregate particles were very small and no CH crys-
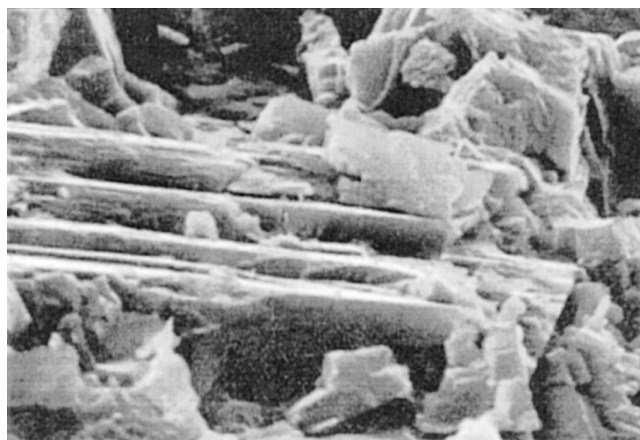

Fig. 2. SEM micrograph showing densely packed CH crystals in the limestone mixture (group 3; ×2480).

tals were deposited in this vicinity. These fracture cracks are well known in SEM specimens and have been attributed to the preparation process. The reduction in the width of the transition zone may indicate a well-developed bond between the cement paste and the aggregate surface. Fig. 3 shows the vicinity of an aggregate particle with a very small microcrack in a UHPC mixture.

3.1.4. Unidentified microstructure region

An unidentified microstructure region of fibre/cement paste was found (groups 3, 4, 6, and 7). The materials in these regions were gel-like and of amorphous appearance. Fig. 4 shows a typical unidentified region.

It was initially suspected that an epoxy coating material on the fibres may have had a secondary material attached that melted at the high curing temperature, but similar features were found in specimens cured in hot water at only 50°C. However, when the micro carbon fibres were examined separately before and after exposure to 200°C for 2
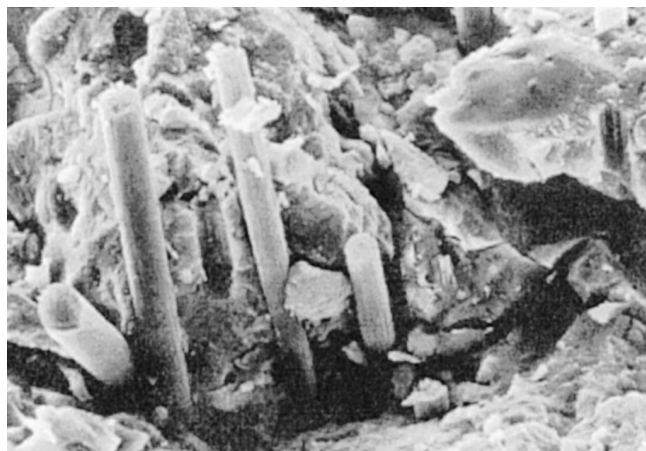

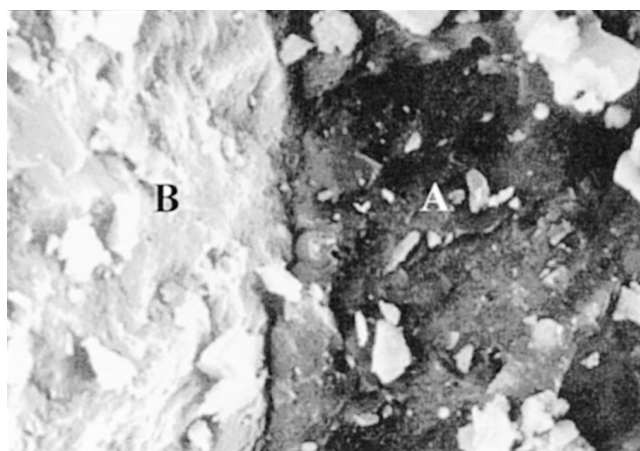Fig. 1. SEM micrograph showing the micro carbon fibres distributed within the microstructure (group 4; ×616).

Fig. 3. SEM micrograph showing the transition zone characteristics in a UHPC mixture (group 7); (A) aggregate, (B) cement paste. ×1210.
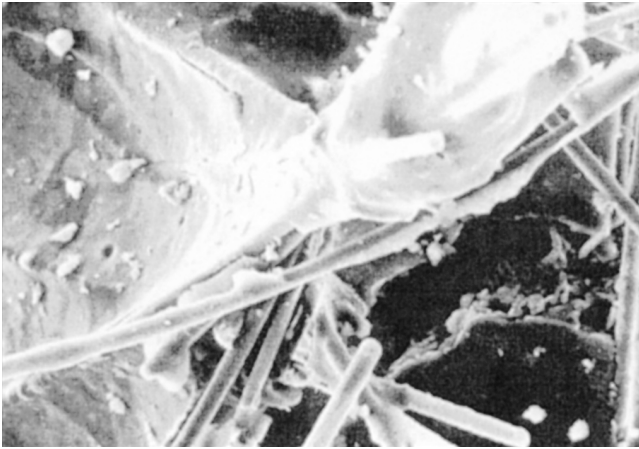
Fig. 4. SEM micrograph showing the interactive fibre/cement paste unidentified region (group 4; ×329).

days, no significant difference was noticed on the surface of the fibres, indicating that the unidentified material was not caused by the mechanism suspected. Fig. 5 shows an SEM micrograph of the micro carbon fibres before and after exposure to 200°C for 2 days.

The gel-like amorphous nature of this unidentified material suggests that it may result from a reaction between silica fume and sodium hydroxide (NaOH) released early during the hydration process. This probability is supported by the very high silica fume content of groups 3, 4, 6, and 7 and the absence of this unidentified material in the other groups which had a relatively small silica fume content.

The potential implications of the new material on the engineering behaviour of UHPC are unknown, but will depend on its composition, the amount present, and the long-term stability. Further work is clearly needed to identify this material.

3.1.5. Role of carbon fibres in UHPC

The enhancement of the mechanical properties of UHPC mixtures can be attributed to the role of micro carbon fibres
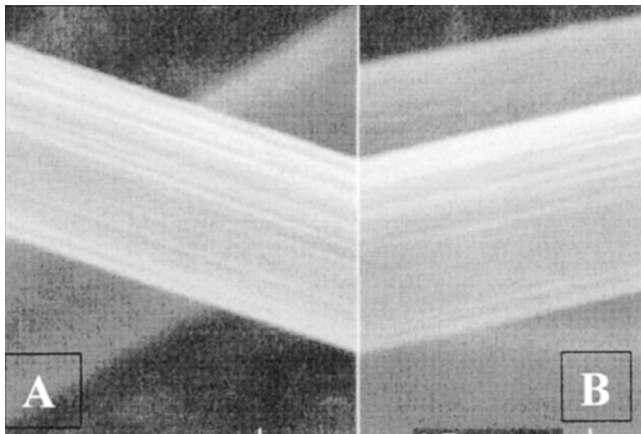

Fig. 5. SEM micrograph showing the micro carbon fibres (*A*) before and (*B*) after exposure to 200°C for 2 days (×5000).

in addition to the microstructural improvements of the concrete matrix. This can be verified from Table 4 by comparing the compressive strengths of UHPC groups including micro carbon fibres (groups 3, 4, 6, 7, 9, 10, 11, and 12) with those that do not include carbon fibres (groups 1, 2, 5, and 8). A statistical analysis using the student t-distribution has been performed on this experimental data to examine the significance of micro carbon fibre incorporation on the compressive strength of UHPC groups. The numerical increase in compressive strength due to incorporation of micro carbon fibres is not as large as that associated with oven-curing, but is nevertheless statistically significant. According to the concept suggested by Rossi and Renwez [8], fibres in cement composites can act at both the material and structural levels. On the material level, the fibres can enhance the ductility and strength of the cement composite, whereas on the structural level the fibres can improve the bearing capacity of the composite by transferring force across the large cracks in the cement composite.

In contrast with the known microstructure of conventional fibre-reinforced concrete [9], no additional transition zones were found in the region of the reinforcing fibres, no special air entrapment was observed in the fibre vicinity, nor was there inefficient packing of particles. Fig. 6 shows a schematic diagram of the fibre transition zone model developed by Bentur and Mindess [10]. The existence of such transition zones should result in a weak matrix/fibre link [11].

The main reason for using strong fibres (carbon fibres) in a brittle matrix (concrete) is to enhance both strength and ductility. The insignificant increase in the composite strength of most conventional fibre cementitious composites has been attributed to the small fibre fraction used (<2% of the cement matrix by volume) and the weak bond between the fibre and the cement matrix. This latter is the stress transfer medium in conventional fibre cementitious matrices [12] and if easily broken restricts stress transfer between the fibres and the matrix.

In the light of the microstructural investigation of these UHPC mixtures, the latter reason seems to be more significant. Examination of the micro carbon fibres under SEM (Fig. 5) has shown these fibres to have a nonsmooth surface. In conjunction with the dense and homogeneous microstructure in the fibre vicinity, this should be able to provide
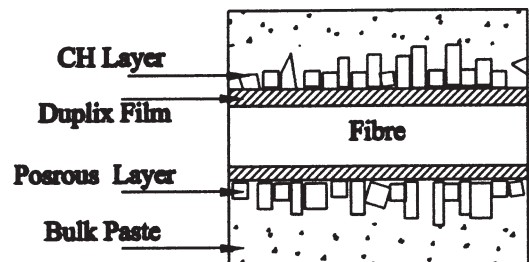

Fig. 6. Schematic representation of the fibre transition zone in conventional fibre reinforced concrete [10].
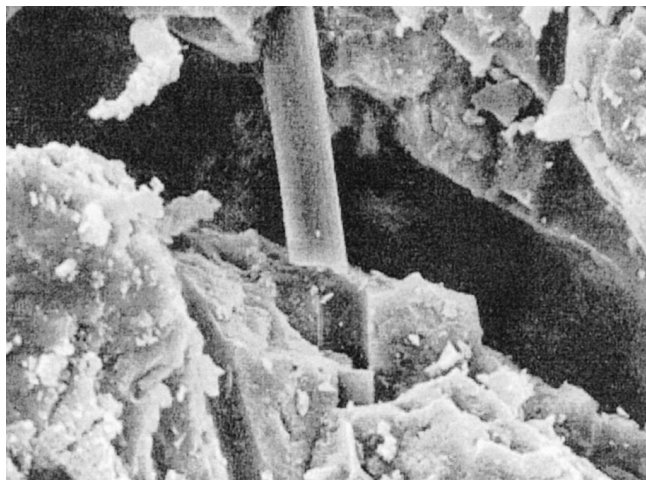
Fig. 7. SEM micrograph showing a ruptured micro carbon fibre bridging a microcrack (group 9; ×138).

better bond between the fibres and the cement paste. The excellent bond developed allows good shear transfer throughout the composite system.

When microcracks propagate through the cement paste due to loading, the fibres can bridge the microcracks and as a result the specimen can continue to carry load after cracking. The high bond strength between the micro carbon fibre and the enhanced cementitious material potentially allows stress transfer up to the fibre maximum tensile capacity (3600 MPa) [13]. This seems to prevent crack widening and provides the UHPC composite with its ultra high compressive strength.

Given the 3–6-mm fibre length, we expected fibre pullout to be more dominant than fibre fracture during the postpeak behaviour due to the short anchorage length available. However, the high fibre matrix bond may reduce fibre pullout. Different micrographs show both fibre fracture and fibre pullout. Banthia [14] also observed both fracture mecha-

nisms, as did Beaudoin [15]. He performed experiments on autoclaved wood fibre-reinforced cement mortars and attributed both fibre pullout and fracture to the very strong bond strength between the fibres and the cement paste matrix. Fig. 7 shows a ruptured micro carbon fibre bridging a microcrack in one of the UHPC mixes.

It is quite clear that the small anchorage length of the micro carbon fibres does not detract from the ability of the material to withstand high compressive stresses, but does limit strain capacity when compared with conventional fibre-reinforced cement based composites. This was reflected in the limited enhancement of the fracture toughness of the UHPC mixtures. Fig. 8 shows a comparison between the load displacement (P-Δ) under flexural loading of both UHPC group 7 and a 100-MPa HPC mixture. Although the fracture toughness (the area under the curve) of the UHPC mixture is approximately three times that of the HPC mix, there is only a limited enhancement of the post-peak behaviour of the UHPC mixture.

3.2. XRD analysis

The main observation from the XRD analysis was that the strongest portlandite (CH) peaks at 2.63Å and 4.90Å were absent on diffractograms of the UHPC mixture examined, with the exception of groups 3 and 7. This confirms the conclusion from the SEM micrographs that CH was largely consumed by the pozzolanic reaction and converted to strong C-S-H gel.

Ettringite peaks were not identified on diffractograms of any samples, confirming the SEM observation that ettringite needles were absent. The absence of ettringite may simply reflect the stage of maturity of the samples studied in these mixtures and under the curing conditions used. Under some conditions accelerated curing at elevated temperatures appears to favour ettringite formation at later stages which is known as delayed ettringite formation. Specimens examined in this work were too young for that process to have
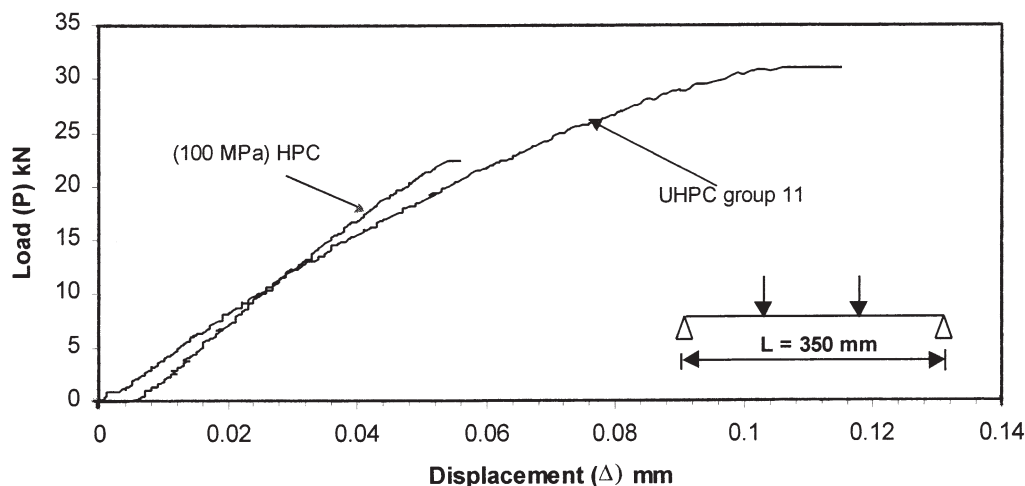

Fig. 8. P-Δ diagram for both UHPC group 11 and 100 MPa HPC.

occurred. Thus, ettringite may be formed at later stages in some of these groups.

The principal calcium silicate hydrate identified was xonotlite (C_6S_6H) with smaller amounts of tobermorite ($C_5S_6H_5$) and scawtite ($C_7S_6\overline{C}H_2$). Xonotlite has been associated with strong and moderately permeable cement.

4. Conclusions

New UHPC mixtures have been developed with excellent compressive strengths up to 240 MPa. These mixtures have very dense microstructures compared to the known microstructures of conventional concrete or even HPC.

UHPC mixtures including calcined bauxite provide excellent mechanical performance and have a very dense microstructure even when no pressure was applied to fresh concrete. This can be attributed to reaction between portland cement and the supplementary cementing materials and to the improved bond between the binder and the aggregate.

UHPC mixtures containing both silica fume and silica flour have generally shown a very dense and uniform microstructure that was observed in the SEM micrographs. No significant portlandite (CH) was detected by XRD. The concrete ingredients used, the very low water/cement ratio, and the elevated temperature curing regime created a favourable environment for pozzolanic reactions that consumed most of the weak CH crystals produced during hydration, and converted them to strong C-S-H.

The transition zone observed in the UHPC mixtures examined was of very small thickness with respect to that of HPC and conventional concrete. The microcracks in the vicinity of the aggregate particles were very small with no CH crystals in this vicinity.

The main hydration products identified had d-values in the range of 2.5 Å and 3.5 Å. Different phases of crystallized C-S-H were observed. Very strong and moderately permeable Xonotlite (C_6S_6H) was a major product in mixtures cured at elevated temperatures.

No additional transition zones were found adjacent to reinforcing micro carbon fibres. The bond between the micro carbon fibres and the cement paste seems to be very good and the microstructure observed in the fibre vicinity was shown to be very dense and homogeneous.

An unidentified microstructure was observed near the fibre/cement paste interface in some UHPC mixtures (groups 3, 4, 6, and 7). The materials found were gel-like and amorphous in nature. It is suggested that the material may have resulted from a reaction between silica fume and sodium hydroxide (NaOH) released during hydration.

The micro carbon fibres incorporated in these innovative UHPC mixtures seem to enhance both the strength and the fracture toughness of the matrix with a limited postcracking behaviour. The examination of micro carbon fibres under SEM has shown these fibres to have a nonsmooth surface, which favours a better bond between these fibres and the cement paste.

The short length (3–6 mm) of the micro carbon fibres used provides little anchorage, which allows high compressive stresses, but limits strain capacity with respect to conventional fibre reinforced cement based composites.

Acknowledgments

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