

Case study

Ultra-high-performance fiber-reinforced concrete. Part II: Hydration and microstructure



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ABSTRACTS

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Ultra-high-performance concrete (UHPC) refers to cement-based materials exhibiting a compressive strength higher than 150 MPa, high ductility, and excellent durability. Besides, over the last twenty years, remarkable advances have taken place in the research and application of Ultra-High-Performance Fiber-Reinforced Concrete (UHPFRC). Therefore, a comprehensive investigation of the durability characteristics of UHPC is essential to provide fundamental information for material testing requirements and procedures and expand its practical applications. Part I reviewed the developments, principles, and raw materials of the UHPFRC. This Part II covers the hydration and microstructure of the UHPFRC. Part III covers the fresh and hardened properties of the UHPFRC. Part IV covers the durability properties, cost assessment, applications, and challenges of the UHPFRC. This review is expected to advance the fundamental knowledge of UHPC and promote further research and applications of UHPC.

1. Introduction

Concrete is the most widely “used synthetic material on the globe, and it will remain in high demand for the near future. It is estimated that global concrete output is over 6 billion cubic meters per year, with China now utilizing approximately 40 % of global concrete production [1–7]. Concrete’s superior properties, such as its strength and durability, capacity to be laid in a variety of forms, and low cost, have made it the most well-known and vital material in the building industry. Concrete is generally employed because of its high compressive strength [8–11]. Over the last few decades, considerable progress has been made in the field of concrete development. Intensive scientific attempts to improve concrete’s compressive strength began” in the 1930s

Ultra-High-Performance Concrete (UHPC) “is an innovative cement-based composite material that outperforms traditional concrete in terms of mechanical and durability [12–16]. UHPC is gaining popularity in research and commercial applications. Although

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UHPC applications have been successfully proven in many nations, mainstream adoption remains a challenge. Several impediments are identified, including a lack of understanding of structural behavior, material characterization processes, and generally accepted design codes. The ability to design lightweight and slender structures is one of the driving elements behind increased utilization [17–24]. Others include lower costs, a smaller environmental footprint, and fewer maintenance requirements.

Existing codes for conventional “concrete production and structural application do not fully apply to UHPC. Several nations, including Germany [25], Switzerland [26], Australia [27], Canada [28], Spain [29] and Japan [30], are developing design guidelines or recommendations for UHPC. Each of these nationally evolving design guidelines has various material characterization needs, and each takes a different approach to the design process. Already in 2002, the Association Française de Génie Civil (AFGC) issued design recommendations for UHPC [31]. In 2016, a version of this was adopted in France as a national appendix [32–37] to the ordinary concrete design” code (Eurocode 2).

Generally these different properties of fiber yield different effects when added to their respective concretes. For the microstructure of concrete, Marković [38] indicated that the micro fiber (shorter than 0.1 mm) has a more homogenous distribution in concrete, leading to a higher packing density of cement matrix. Keer [39] reported that synthetic fiber increases the permeability of concrete due to their porous interfacial transition zone (ITZ). As far as the mechanical performances of concrete are concerned, various researchers [40–45] have studied the fibers’ effect on concrete under compression or tension. They have reported that the fibers increase the tensile strength of concrete, but not necessarily its compressive strength. They have also found that the macro fiber has an efficacious capacity against the macro cracking of concrete in the post-peak phase. Nataraja, Dhang and Gupta [46] reported that fibers with a greater ratio of L/f yield a higher compressive strength in the concrete. Zheng and Feldman [47] showed that fibers with higher tensile strength and higher elastic modulus could significantly improve the mechanical performance of concrete.

Many researchers have conducted studies on UHPC, but information on the materials and structural properties of UHPC are still limited. “This review includes four parts. Part I reviewed the developments, principles, and raw materials of the UHPFRC. This Part II covers the hydration and microstructure of the UHPFRC. Part III covers the fresh and hardened properties of the UHPFRC. Part IV covers the durability properties, cost assessment, applications, and challenges of the UHPFRC. This review is expected to advance the fundamental knowledge of UHPC and promote further research and applications of UHPC. The purpose of this review is to summarize previous research and to suggest some needs for future” research.

2. Advantages and disadvantages of UHPC

UHPC has compressive “strengths ranging from 150 to 810 MPa [48–51], which is approximately 3–16 times that of normal concrete. The ductility and energy absorption of UHPC are typically 300 times better than that of HPC when steel fiber is used. Carbon dioxide, chlorides, and sulfates are nearly impermeable to UHPC. Its enhanced durability results in a longer service life with less maintenance. Bridge decks and industrial floors benefit from increased abrasion resistance, while places with poor or harsh weather conditions benefit from increased corrosion resistance [52]. Under cracking circumstances, a sizable percentage of unhydrated cement in the completed product gives self-healing capacity. Because of their ultra-high compressive strength, UHPC buildings weigh just one-third or one-half of their ordinary concrete counterparts under the same load. This weight reduction results in more thin construction, more usable floor space in high-rise buildings, and lower total expenses. The elimination of steel reinforcement bars

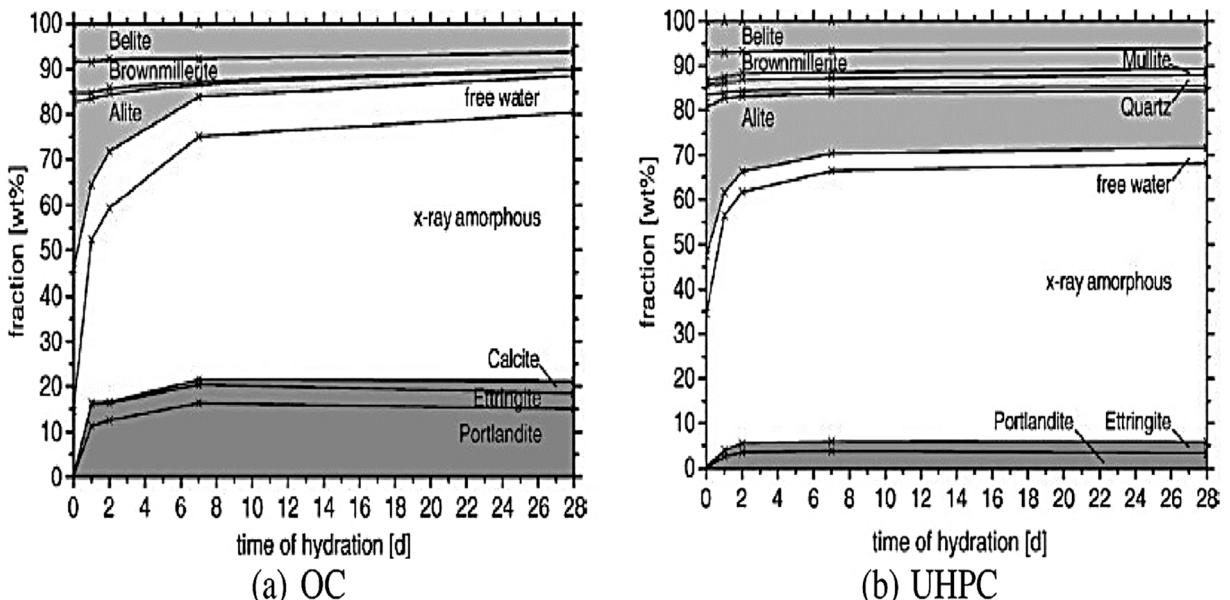


Fig. 1. Time-dependent phase development in OC and UHPC [68].

decreases labor costs and increases architectural freedom, giving architects and designers virtually limitless structural member shapes and" forms [52–56].

The disadvantages associated with "UHPCs, however, include its high cement content (950–1000 kg/m³), which increases production costs, and its high silica fume (100–250 kg/m³) [57], which increases CO₂ emissions and global warming [58–63]. Furthermore, the sensitivity to the amount of water-to-cementitious materials, superplasticizers-to-cementitious materials, chemical properties of materials, and distribution of fine particles (needed for mixers with higher rotation speed) are other disadvantages associated with UHPCs. In addition, if fibers are not used, the UHPCs like other high-strength materials would be very brittle accompanied by a high modulus of elasticity (about 45–60 GPa), which is not much desirable. Such problems might be effectively addressed by using such mineral cement replacements as slag, rice husk ash, zeolite, fly ash [64], and metakaolin [65–67]. In addition, "supplementary cement materials can be used in UHPCs to reduce production costs and enhance customer appeal encouraging more extensive applications.

3. Hydration

In UHPC, "cementitious ingredients hydrate similarly to conventional concrete. Portland cement first hydrates to produce calcium silicate hydrate and calcium hydroxide, and then mineral admixtures (such as silica fume) react with calcium hydroxide to produce calcium silicate hydrate (C-S-H). The time-dependent phase development in OC and UHPC at room temperature is depicted in Fig. 1 [68]. It can be noticed that the content of crystalline phases was significantly higher in OC, whereas fewer amorphous phases were found in UHPC. The discrepancy is due to the pozzolanic reactions caused by the relatively elevated levels of silica fume and fly ash. After the second hydration day, the consumption of portlandite becomes noticeable and is substantially lower than that of conventional concrete after 28 days, indicating that pozzolanic reactions are still incomplete. The absence of calcite identified by X-rays in UHPC after 28 days may be interpreted as a lack of significant phase carbonation in this specimen. The differences in ettringite content development between the first and second hydration days suggest that some ettringite can be converted to the monosulfate phase and that a large quantity of aluminate can reach the X-ray amorphous C-S-H" phases [68–72].

Water is consumed during "hydration, resulting in pozzolanic activity and the formation of voids within the matrix. The formation of diverse hydration products does not entirely fill the remaining space, and voids remain in the matrix. The empty areas between the various concrete constituents create weak zones, making the concrete more prone to failure. However, the development of voids inside the matrix is limited in UHPC due to the following factors: (1) a lower amount of water [73], (2) a finer size of SCM that increases the particle-to-particle contact surface area and thus improves the uniform stress distribution [74], and (3) the absence of large and coarse aggregates (restraining the growth of the ASR). These considerations explain why the UHPC matrix has less ettringite, less ASR, and fewer voids. Taking all of these aspects into account, the insertion of stiff thin fibers interacts with the dense UHPC paste to disclose varying degrees of improvement in hardened characteristics. The characteristics of UHPC improved by fiber are strongly influenced by the fiber's characteristics (steel, mineral, or synthetic), geometry (macro fiber vs. microfiber), and tensile strength [75]. When utilizing fibers less than 0.1 mm long, the distribution of fiber in the paste is uniform, which aids in increasing the matrix's packing density [38]. When utilizing synthetic fiber, however, the permeability of the matrix rises due to the porous ITZ formed by these" materials [39].

Increased "curing temperature hastens cement hydration and enhances secondary hydration between mineral admixtures and Ca(OH)₂ [76]. At 90 °C, hydration products remain amorphous. In the absence of an external SiO₂ source, the hydration of C3S and C2S in the autoclave results in the creation of crystalline adicalcium silicate hydrate. A hydrogarnet phase is formed from tricalcium aluminate (C3A) and tetracalcium alumino-ferrite (C4AF). These two phases' bonding properties are relatively unfavorable. A pozzolanic reaction occurs in the presence of finely ground quartz and/or other SiO₂ sources, giving crystalline 1.1 nm tobermorite (C₅S₅H₅) as the major product of the process at temperatures between 150 and 200 °C. At even greater temperatures, xonolite C-S-H (I), C-S-H (II), and a-C2SH can develop [77]. Crystalline Ca(OH)₂ and some unidentified hydration products were also discovered in 1-day Portland cement (PC) paste at 150 °C. Crystalline C2SH (A) was found in 5-day PC paste. Only Ca(OH)₂ and C2SH(A) were found in the 15-day PC paste. CSH (B) and xonotlite were the primary hydration products for alkali-blast furnace slag cement (ABSC) paste.

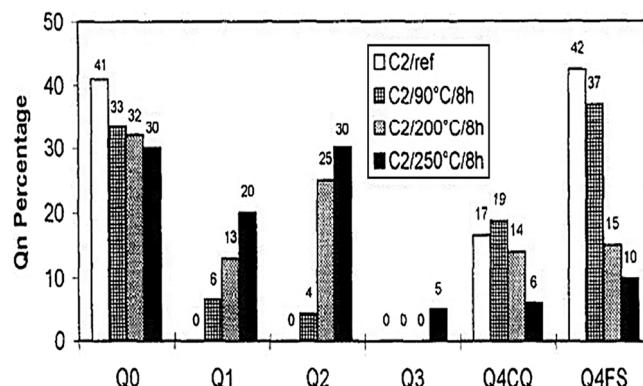
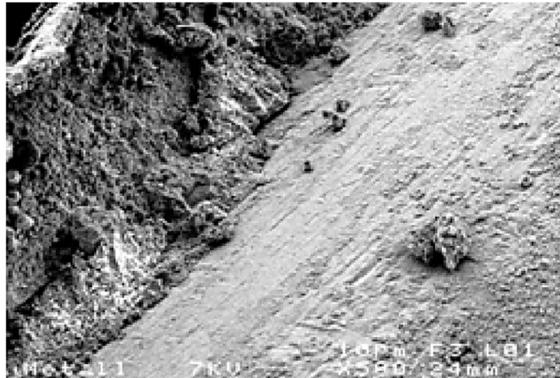
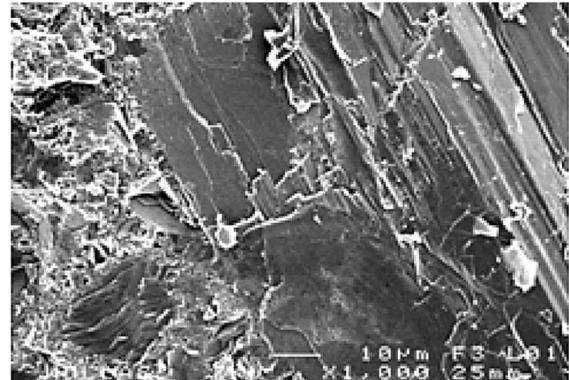


Fig. 2. Q⁰ to Q⁴ percentages for samples with heat treatment at 90 °C, 200 °C, and 250 °C for 8 h [83].

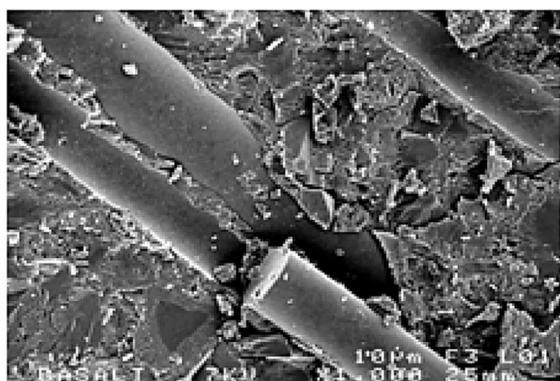
After 5 days, the $3\text{CaOMgO}_2\text{SiO}_2$ in the slag had vanished. In alkali-phosphorus slag cement (APSC) paste, only CSH (B) and tobermorite were found [78]. The formation of both 1.1 nm tobermorite and xonolite is favorable for the strength development of autoclaved material [79]. Xonotlite formed with a Q^3 peak at 250 °C, as shown in Fig. 2 [80]. The H/C (H_2O to CaO) ratio of C-S-H of OC is approximately one, while the H/C of xonotlite is 1/6, and the xonotlite is only formed in the inner part of the concrete specimen [81]. The formation of xonotlite in heat cured UHPC was due to local, large water vapor pressures. However, lower (3 Pa) dynamic equilibrium vapor pressures could totally suppress the formation of crystalline hydration products, even if no xonotlite or other crystalline hydration products formed" even at 250 °C [82].



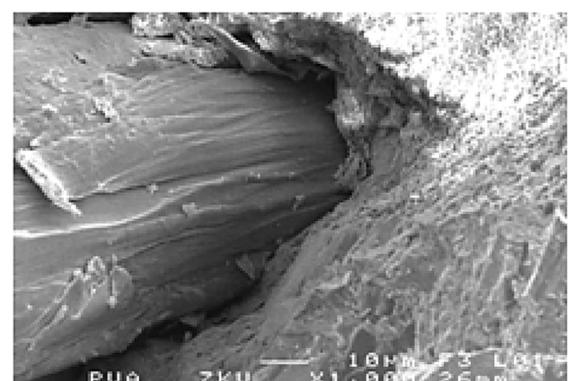
(a) Steel fiber



(b) Wollastonite fiber



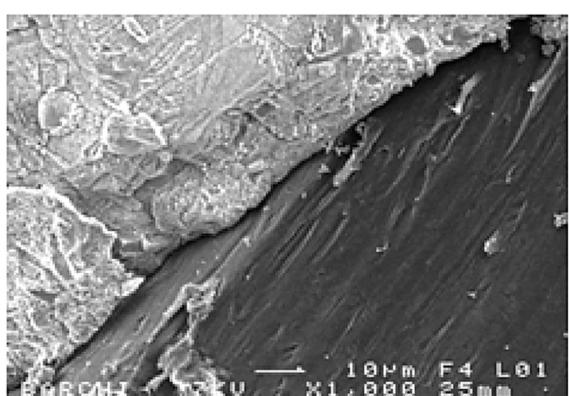
(c) Basalt



(d) PVA fiber



(e) PP-PE fiber



(f) Barchip fiber

Fig. 3. SEM observation of the fiber-matrix bond ($\times 1000$) [75].

4. Microstructure

4.1. Microstructure of UHPC containing supplementary cementitious materials and fiber

The microstructure of UHPC "has been shown in the literature to be highly dense and compact [84,85], as shown in Fig. 3. SEM, energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD) observations reveal the development of C–S–H, calcium hydroxide, ettringite, alkali-silica reactions, and a tight fiber/matrix interfacial zone [86]. Furthermore, due to the hydration process of higher amounts of finer mineral admixtures in the matrix, the possibility of cracks and big voids forming in the microstructure is zero in UHPC. A lower water/cement ratio, the amount of mineral admixture utilized, and the curing method are the key elements contributing to hydration processes in UHPC and UHPFRC. A lower water/cement ratio results in extremely low porosity," pozzolanic materials aid in achieving the optimal packing density, and the curing process influence the ultimate strength of concrete [87]. This hydration phase development is important in designing a better microstructure of UHPC.

C–S–H is the most advantageous hydration product for ensuring a thick microstructure of UHPC. The surfaces of the cement grains represent the active field for C–S–H growth to begin. Several studies have tried to figure out how different forms of C–S–H affects the mechanical properties of cement-based materials [88]. Table 1 shows the elastic modulus of C–S–H.

Nanoindentation can be used to "evaluate the nanomechanical behavior of cementitious materials [89]. The C–S–H properties of the UHPC matrix were published by Sorelli, Constantinides, Ulm and Toutlemonde [90]. It is divided into two phases: low and high-density C–S–H. The computed volume fraction of low-density C–S–H in the UHPC matrix from the statistical nanoindentation technique (SNT) was 14 %, which is quite low. Based on the study of Constantinides and Ulm [91], the Poisson's ratio was considered to be 0.24. The reported homogenized Young's modulus of the C–S–H matrix was 29.9 GPa," which is greater than the 23.8 GPa of regular cement paste.

Furthermore, Taylor, Richardson and Brydson [92] found that the morphology of C–S–H in ordinary Portland cement has a "fibriller" appearance, "whereas SCMs in the mix has a "foil" like shape. This differential in C–S–H morphology may explain some of the "refinement" and better characteristics of blended materials. According to a more comprehensive review published by Stark [93], the characterizations of C–S–H in terms of its nanostructure, thermodynamic properties, solubility (including the impact of aluminum incorporation), electron binding energy, morphology," adsorption, organic molecule intercalation, and mechanical properties are still ongoing.

Pozzolanic compounds such as FA, rice husk ash (RHA), metakaolin (MK), SF, and GGBS have been employed to increase the C–S–H ratio using calcium hydroxide [94]. The calcium hydroxide content of typical concrete materials has increased over time, while SCMs such as RHA and SF in concrete effectively utilize the calcium hydroxide, as illustrated in Fig. 4. "The addition of RHA to a UHPC mix reduced the calcium hydroxide concentration by 45 % after 28 days and 65 % after 91 days, whereas UHPC including SF reduced the calcium hydroxide level by up to 70 % after 28 days and 90 % after 91 days. When compared to RHA, SF has a greater potential to reduce calcium hydroxide at later ages [94]. Furthermore, SF pozzolanic action begins after three days of hydration [95]. Furthermore, microsilica is an exceedingly fine pozzolanic material with a particle size limit of roughly 0.1 m that is now used as the primary constituent in conjunction with a chemical admixture in several RPC/UHPC" systems.

A negative effect has also "been discovered as a result of the hydration-induced production of ettringite and alkali-silica. Several studies have been conducted to assess the development of ettringite in UHPC [96]. Heinz and Ludwig [97] investigated the delayed production of ettringite in UHPC after heat treatment. UHPC had a water-to-cement ratio of 0.2 and a heat treatment temperature range of 65–180 C. XRD, a thermal analysis (DSC/TG), and SEM were used to investigate the phase composition. Ettringite was reported to form between the temperatures of 20 C and 65 C, but not at higher temperatures due to the lack of portlandite in cement paste at higher temperatures. Grabowski, Czarnecki, Gillott, Duggan and Scott [98] discovered that secondary ettringite creation does not result in UHPC" expansion.

4.2. UHPFRC with different curing methods

One of the researchers' goals in "examining the microstructure of UHPC is to speed its hydration reactions because doing so increases C–S–H synthesis while decreasing calcium hydroxide in the microstructure. According to UHPC research, the use of micro silica may be effective in accelerating hydration reactions by employing autoclave, heat, and steam processing methods. The UHPC specimen has a very dense microstructure due to its low water/cement ratio and that the cement products used exhibit significant

Table 1
Elastic Modulus calculated by nanoindentation [99].

Phase				Ref.
Cement (GPa)	Low-density C–S–H (GPa)	High-density C–S–H (GPa)	Calcium hydroxide (GPa)	
–	21.7 ± 2.2	29.4 ± 2.4	38.0 ± 5	[91]
141.1 ± 34.8	19.7 ± 2.5	34.2 ± 5.0	–	[90]
90–150	10–25	25–35	–	[100]
–	18.2 ± 4.2	29.1 ± 4.0	–	[101]
–	19.1 ± 5.0	32.3 ± 3.0	–	[102]
122.20 ± 7.85	22.89 ± 0.76	31.16 ± 2.51	–	[103]

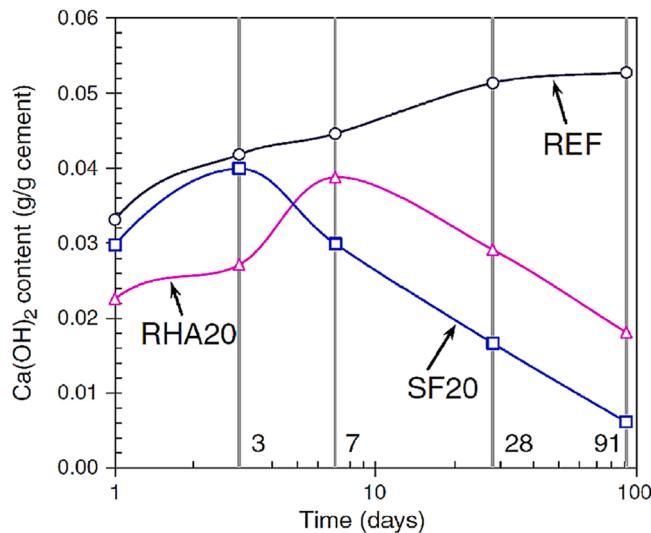


Fig. 4. Ca(OH)₂ content of reference UHPC, 20 % RHA UHPC and 20 % SF contained UHPC with time [94].

pozzolanic reactions [89], while its internal transfer zone is much smaller than that of ordinary concrete [104], and no such internal transfer zone is observed in specimens subjected to autoclave curing. The UHPC specimen's relatively tiny internal transfer region suggests a good bond between the cement paste and the aggregates. The difference between standard and autoclave curing conditions may be that amorphous or weak C–S–H is generated in a stiff state in standard curing. Due to the rapid hydration process, which results in increased conversion of calcium hydroxide (CH) to C–S–H, no significant portlandite is found in UHPC specimens treated to normal curing. The SEM pictures also demonstrate that quartz has interacted with cement in autoclave-cured specimens. Furthermore, spherical pores are packed with needle-like tobermorite and gene-like xonotlite. The amount of CH crystals decreases with higher curing temperatures due to the high pozzolanic activity of silica fume and the presence of quartz powder, as seen in Fig. 5, up until a temperature of 250 °C, when no CH crystals remain in the specimens [89]. In general, at elevated temperatures, "UHPC creates a dense microstructure, which leads to the production of crystalline hydrates, which increases the strength of the specimens [83].

4.3. Differences between several types of cementitious materials in affecting the microstructure of UHPC

The microstructure of UHPC data "demonstrates that using cement substitutes (limestone and powdered granulated blast furnace slag), in addition to reducing the amount of unhydrated cement, the ratio of C₂S/C₃S, and the CH, and raising C–S–H, results in a denser and more homogeneous cement matrix [105]. Among the pozzolans (rice husk ash, zeolite, metakaolin, and silica fume), silica fume with reduced porosity, lower calcium-to-silicon ratio (Ca/Si) concentration, and minimum CH content provides the best performance in the UHPC microstructure [11]. As a result, it generates the UHPC's most ideal mechanical specs. In general, fillers like blast furnace slag, lithium slag, and limestone powder reduce the overall porosity of the UHPC matrix and reduce the need for cement. Given that using each of them in optimal percentages increases the mechanical qualities of UHPC while also consuming wastes in the surrounding environment, it cannot be stated that they have a special preference over each other. Furthermore, using nano-silica as a cement substitute may be a suitable choice for improving UHPC mechanical properties because it results in a denser UHPC matrix, less porosity," and more C–S–H [49].

5. Conclusions

Based on the review and discussions above, it can be summarized as follows:

1. Binder hydration in UHPC is "comparable to that in OC. When UHPC is cured at 90 °C, the average C–S–H chain length rises due to binder material hydration. When the curing temperature is raised to 250 °C, C–S–H dehydrates to form xonotlite. However, at low dynamic equilibrium vapor pressures, the formation of crystalline hydration products might be completely suppressed. UHPC has extremely low porosity," particularly after heat curing.
2. Because UHPC is a sort of tailored concrete, "the types, morphologies, and amounts of mineral admixtures, as well as the fibers utilized, have extremely sensitive effects on the material's performance. An optimal amount of a mineral admixture is beneficial for densifying the matrix at the microstructure level. However, an excess percentage of a mineral admixture is left unreactive in the matrix, which is not beneficial for" performance enhancement.
3. High-density C–S–H has an elastic modulus ranging from "34.3–29.2 GPa, whereas low-density C–S–H has an elastic modulus of less than 22.9 GPa. As a result, the presence of higher density C–S–H improves UHPC's" mechanical and durability performance characteristics.

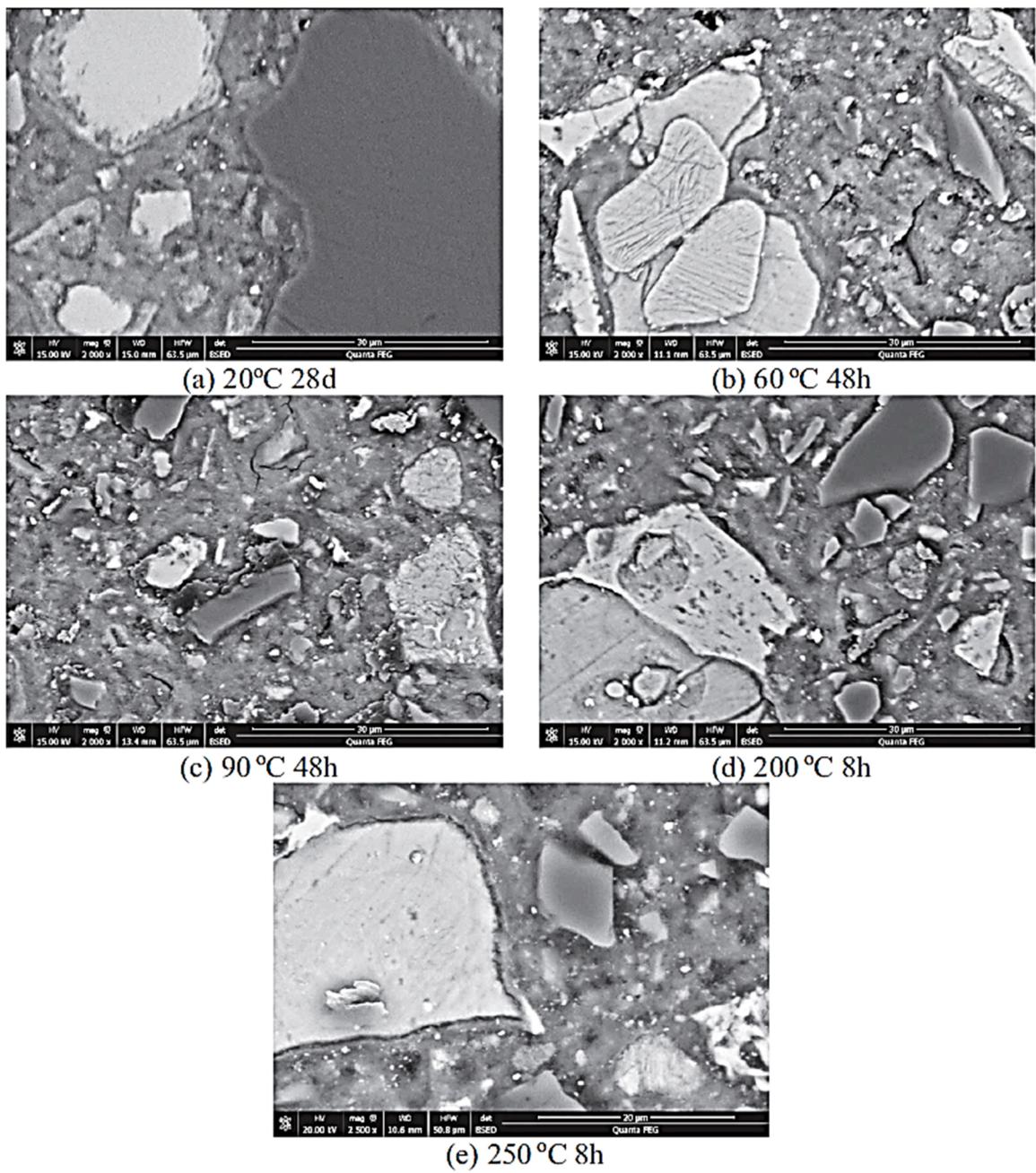


Fig. 5. Images of UHPC backscattered electrons (BSE) under various cure regimes [89].

4. High-temperature curing increases the microstructure and so results in better strength by promoting pozzolanic interactions between CH from cement hydration and extra cementitious ingredients such as silica fume. It also lengthens the chain of C–S–H.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

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