Volume 10, Number 4 (August 2017) p. 838 – 863 • ISSN 1983-4195
http://dx.doi.org/10.1590/S1983-41952017000400004

REVISTA IBRACON DE ESTRUTURAS E MATERIAIS
IBRACON STRUCTURES AND MATERIALS JOURNAL

Microstructure of concrete subjected to elevated temperatures: physico-chemical changes and analysis techniques

Microestrutura do concreto submetido a altas temperaturas: alterações físico-químicas e técnicas de análise




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Abstract

The exposure of concrete to high temperatures, such as in a fire, leads to physical and chemical changes, which may cause deterioration of mechanical properties, cracking and spalling. This paper presents a critical review of microstructural changes in concrete exposed to high temperature. The transformations developed in the cement paste, aggregates and interfacial transition zone were studied, as well as the experimental techniques of microanalysis presented in recent related researches. Lastly, a critical analysis of experimental results from literature was performed. It was verified that microstructural changes are related to concrete properties and the heating process. The experimental techniques has a potential use for assessment of thermally damaged concrete, however, these techniques must be applied simultaneously and specific methods must be established.

Keywords: microstructure, concrete, concrete structures, high temperatures.

Resumo

A exposição a altas temperaturas, como as de um incêndio, promove alterações físicas e químicas no concreto, provocando deterioração das propriedades mecânicas nas estruturas, fissuração e desplacamento. O presente trabalho consiste em uma revisão crítica das alterações microestruturais que incidem no concreto submetido a altas temperaturas. As transformações desenvolvidas na pasta de cimento hidratada, nos agregados e na zona de transição foram estudadas, bem como as técnicas experimentais de microanálise utilizadas em recentes pesquisas desenvolvidas na área. Por fim, uma análise crítica dos resultados de estudos experimentais apresentados pela literatura foi realizada. Verifica-se que as alterações da microestrutura estão relacionadas com as características constitutivas do concreto e com processo do aquecimento. Constata-se a potencialidade das técnicas microestruturais para as etapas de na inspeção e recuperação de estruturas incendiadas, entretanto verifica-se a necessidade de combinação de técnicas e o estabelecimento de métodos padronizados.

Palavras-chave: microestrutura, concreto, estruturas de concreto, altas temperaturas.

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Received: 29 May 2016 • Accepted: 09 Feb 2017 • Available Online: 27 Jul 2017

1. Introduction

Concrete, when exposed to high temperatures, can react quite well due to its incombustibility and low thermal diffusivity. From a research that encompassed more than a hundred concrete structures damaged by fire, Tovey and Crook [1] concluded that most of these constructions performed well and that most of them could be repaired to preserve their initial performance.

Exposure to high temperatures promotes changes in the concrete physical and chemical properties, resulting in reduction in mechanical properties such as compressive strength and modulus of elasticity, fissures, spalling, and transient creep [2–5], jeopardizing the resistant capacity of elements and the structural system's overall stability. Deterioration of these properties is directly connected to material-related factors (aggregate and cement type, water/cement ratio, additions and fibers) and to the environment (exposure time, heating rate, applied load and humidity) [4–6]. Analysis of this degradation - and evaluation of the steel reinforcement residual properties - helps in the diagnosis of the structure and definition of a therapy strategy, be it repair, reinforcement or even demolition [7, 8].

Postfire residual strength of concrete is linked to the heating profile. Under real conditions, not all structural element faces will be submitted to the heating action [9], as they are usually inserted in walls or facing other structural elements. This fact, in addition to the low thermal conductivity of concrete, induces temperature gradients among the consecutive section layers, promoting differential changes in the element [8, 10]. Therefore, compressive strength testing on specimens from a fire damaged structure must be used with caution in the diagnosis, since they might not be representative because of the heterogeneous due to temperature distribution in the cross-section [9, 11, 12] and, consequently, the changes in the mechanical properties of the concrete.

Changes in the properties of concrete exposed to high temperatures are related to changes in the material microstructure [6]. Thus, the residual strength of the material can be verified through testing procedures able to identify these physical, chemical, and mineralogical changes. Techniques such as scanning electron microscopy, X-ray diffraction, thermogravimetric analysis, mercury intrusion porosimetry, colorimetry, and petrography are widely used in the study of concrete degradation after exposure to high temperatures [2, 8, 9, 12–18].

Despite the great quantity of studies in this area, transformations in the micro- and nanostructure of concrete, which drive the macroscopic behavior, are not completely characterized and disseminated [19]. In Brazil, despite the reduced number, important researches of such a type have been developed [20–25].

This article intends to contribute to the study of concrete structures exposed to high temperatures by undertaking a literature review on this theme, addressing aspects related to the effect of high temperatures on the microstructure (physicochemical changes) and microstructural techniques to evaluate the damaged concrete.

2. Effects of high temperatures on concrete microstructure

Deterioration of concrete exposed to high temperatures is attributed to three factors: physicochemical changes in the cement paste, in its aggregates, and the thermal incompatibility between them. Fire-related factors, such as temperature and heating rate, and structural element conditions, such as applied load and humidity, also play a role in concrete deterioration [5]. Therefore, it is important to discuss the effects of high temperatures on concrete focusing on the microstructural changes in the aggregates, the hydrated cement paste, and the transition zone. Transformations occurring until the temperature of 1200 ºC – when concrete starts to melt – will be examined[5]. It is important to highlight that real fire can reach temperatures over 900 ºC, however, it is limited to the superficial layers of structural elements, while the internal temperature keeps relatively low[11].

2.1 Effects of high temperatures on aggregates

The nature and microstructure of aggregate affect the stability and thermal conductivity of concrete, changing the residual strength and fluid transport mechanisms [6, 25–27]. When exposed to high temperatures, physicochemical changes affect aggregates, promoting expansion, fractures on their crystalline microstructure, and even melting, at temperatures over 1000 ºC. These effects are related to the aggregate thermal stability, i.e., its susceptibility to chemical and physical changes when exposed to high temperatures. This feature, as well as the verified degradation, changes according to the type of used aggregate[4, 6].

Siliceous aggregates and sand, having quartz in their composition, undergo significant changes at high temperatures; the most known being the volumetric expansion of 5.7% at 573 ºC, due to the transformation of the quartz crystalline form from α to β [6]. Despite the reversibility of this transformation, radial cracks around the aggregate may be verified due to this expansion [9].

Carbonate rocks, such as dolomite, become unstable at temperatures higher than 700 °C due to the transformation of calcium carbonate ($CaCO_3$) into calcium oxide (lime - CaO) and carbon dioxide (CO_2). Reaching its peak at 800 ºC and finishing at 898 ºC, this process is endothermic and tend to retard the temperature progress on concrete [4, 6, 27]. In calcareous aggregates, this phenomenon begins at 600 ºC due to the decomposition of calcium carbonate [29]. Basalt aggregates have a great thermal stability and start to melt at temperatures above 1000 ºC. During this process, they expand and release gases held inside the rock. [6].

2.2 Effect of high temperatures on the hydrated cement paste

The behavior of the hydrated cement paste at high temperatures depends on factors such as water/cement ratio, the ratio between C/S (CaO/SiO_2 or calcium oxide / silicon dioxide), quantity of $Ca(OH)_2$ (portlandite / CH) formed, hydration degree and humidity [6, 27].

Under high temperatures, the degradation process begins with the decomposition of ettringite, which happens at 80 ºC approximately [4, 13, 30]. Subsequently, the cement paste dehydrates, and this is associated with the microstructural changes in the material. Initially, the capillary water (free water), which is not influenced by the Van der Waals attraction forces, evaporates,

followed by the evaporation of lamellar and adsorbed waters, due to a physical process. Lastly, the water chemically associated with C-S-H (calcium silicate hydrate) is lost [4, 6, 29]. This C-S-H dehydration is a physicochemical process that causes the relaxation of microtensions and is responsible for transient creep. It begins at 100 ºC (212 ºF) and starts cement paste loss, together with the cracking and porosity increase, in addition to accumulation of water vapor in the pores, which in turn contributes to spalling. At 700 ºC, C-S-H decomposes into β-C_2S (belite), βCS (wollastonite) and water, leading to shrinkage of cement paste and strength reduction. The loss of water associated with C-S-H promotes an increase in porosity, also contributing to strength loss [4, 6, 29, 30].

Portlandite crystals also undergo a process of dehydration at temperatures over 420 ºC, contributing to increased shrinkage and microcracking in the cement paste. In this process, $Ca(OH)_2$ decomposes into CaO (calcium oxide) and water. Another change is the decarburization of calcium carbonate ($CaCO_3$), which decomposes into CaO and CO_2 at temperatures higher than 650 ºC [6, 30].

High temperatures also affect non-hydrated clinker grains, existent in the hydrated cement paste, promoting their expansion. This phenomenon, combined with shrinkage of cement paste caused by changes in C-S-H and CH, promotes differential thermal expansions among the materials, that results in microcracking in the concrete, increasing its porosity [32]. When temperatures exceed 1200 ºC, the cement paste starts to melt [5].

Porosity is also influenced by high temperatures, growing nonlinearly, mainly due to the progressive C-S-H dehydration process. From 20 ºC until 300 ºC, the increase in porosity is reduced, lower than the verified mass loss. This relation reverses beyond 300 ºC, with significant increase in porosity and intensification of microcracks. Another peak of porosity increase happens beyond 900 ºC[6]. In conditions where the cement paste does not lose humidity to the environment rapidly, as in the interior of large concrete sections, heating may lead to the appearance of C-S-H or other crystals, depending on the CaO/SiO_2 ratio [4, 5].

After exposure to high temperatures, cooling also promotes changes in the cement paste. The cementitious products in the paste may rehydrate, forming new gels or crystalline components. The formed lime also rehydrates and expands, creating new fissures [33].

2.3 *Effect of high temperatures on the transition zone*

The interface between aggregates and cement paste, usually 50 µm thick [34], is regarded as the "weak link" in concrete, due to the great volume of voids and fissures in the region, besides the presence of weak C-S-H crystals and portlandite and ettringite secondary crystals [28].

Concrete heating leads to a differential thermal expansion between the aggregate and the cementitious matrix. Due to dehydration, the paste suffers an intense shrinkage process during heating, whereas the aggregates undergo an expansion process (Figure 1). This leads to cracks, which initially appear in the transition zone due to its higher fragility [4, 6, 9].

Transition zone weakening can also lead to concrete spalling at high temperatures, according to Bolina [29] experimental observations. Induced by vapor pressures from the material interior, the interface maximizes the phenomenon [2-5], promoting a reduction in the cross-section of elements and decreasing their resistant capacity; which happens in the initial moments of exposure, when spaling starts [29].

3. Evaluation of concrete after exposure to high temperatures

One of the fire protection engineering concerns is to assess the safety of a structure exposed to fire, aiming at the definition of a therapy strategy [7]. For such purposes, careful inspection is fundamental for a proper diagnosis of the affected structure. In case of reinforced concrete, the inspection must encompass aspects related to concrete – the focus of this text – and to steel reinforcement. Different techniques, destructive and nondestructive, can be used in postfire assessment. A summary of these techniques applied to

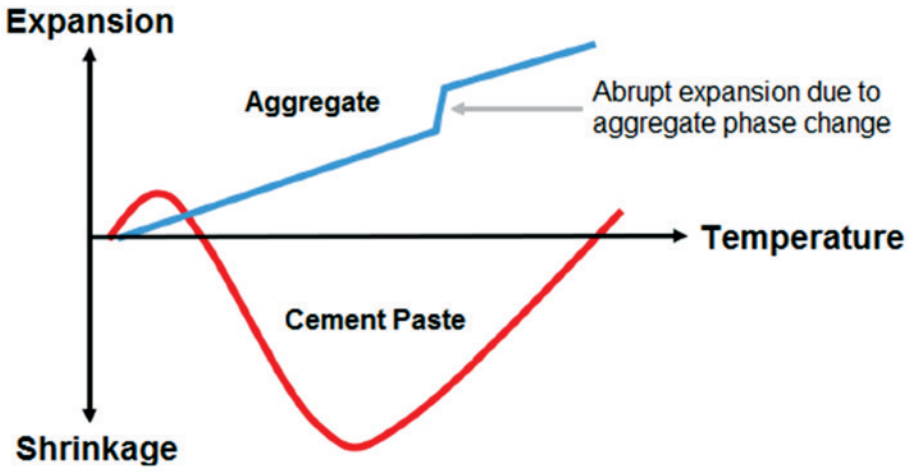

Figure 1
Thermal incompatibility between aggregate and hydrated cement paste (adapted (6))

Table 1
Non-destructive testing applied to fire damaged concrete (adapted (10))

Concrete cover analysis	Point-by-point analysis of small samples	Special techniques
Hammer tapping	Small-scale mechanical testing	Ultrasonic Pulse Velocity (UPV)
Schmidt rebound hammer	Differential thermal analysis (DTA)	Impact echo
Windsor probe	Thermogravimetric analysis (TGA)	Sonic tomography
CAPO test	Dilatometry (TMA)	Modal analysis of surface waves (MASW)
BRE internal fracture	Thermoluminescence	Electric resistivity
–	Porosimetry	–
–	Colorimetry	–
–	Petrographic analysis	–
–	Chemical analysis	–

Table 2 (Part 1)
Summary of research that used microanalysis techniques

Author (reference)	Year	Sample type*	T. max (°C)	SEM**	XRD**	MIP**	DTA/ TGA**	COL**	PET**	Others
Rostásy, Wei and Wiedemann [41]	1980	Lab.	900	–	–	X	–	–	–	–
Piasta, Sawicz and Rudzinski [42]	1984	Lab.	800	–	X	X	X	–	–	Infrared spectroscopy
Chan, Peng and Chan [43]	1996	Lab.	1200	–	–	X	–	–	–	–
Saad *et al.* [44]	1996	Lab.	600	–	X	–	–	–	–	–
Lin, Lin and Powers-Couche [45]	1996	Lab.	900	X	–	–	–	–	–	–
Luo, Sun and Chan [46]	2000	Lab.	800	–	–	X	–	–	–	–
Short, Purkiss and Guise [47]	2001	Lab.	700	–	–	–	–	X	–	–
Poon *et al.* [48]	2001	Lab.	800	–	–	X	–	–	–	–
Handoo, Agarwal and Agarwal [18]	2002	Lab.	1000	X	X	–	X	–	–	–
Castellote *et al.* [30]	2004	Lab.	620	–	–	X	X	–	–	Neutron diffraction
Alarcon-Ruiz *et al.* [49]	2005	Lab.	800	–	–	–	X	–	–	–
Georgali and Tsakiridis [2]	2005	Est.	–	–	–	–	–	–	X	–
Lima [20]	2005	Lab.	900	X	X	–	X	–	–	Dilatometry
Wang, Wu and Wang [50]	2005	Lab.	500	X	–	–	–	–	–	–
Wendt [51]	2006	Lab.	900	–	–	–	–	X	–	–
Peng and Huang [17]	2008	Lab.	800	X	X	X	–	–	–	–

* Lab. = Amostra confecionada em laboratório; Est. = Amostra retirada de elemento estrutural
** SEM = Scanning Electron Microscopy; XRD = X-Ray Diffraction; MIP = Mercury Intrusion Porosimetry; DTA = Differential Thermal Analysis; TGA = Thermogravimetric Analysis; COL = Colorimetry e PET = Petrography

concrete – the focus of the present study - can be seen in table 1 [7, 10].

An important factor for residual strength verification of the element is the temperature gradient between consecutive layers of the material cross section, formed due to the low thermal conductivity of concrete [9, 10]. This factor, added to the material heterogeneity, makes the structure assessment after exposure to high temperatures a complex process[8].

This complexity also influences the performance of tests applied to structure inspection. The compressive strength test, the most usual and straightforward method for *in situ* concrete strength testing, offers little information as to the material residual strength, due to the variation of the damage along the sample profundity [7, 11, 12]. Annerel and Taerwe [9] emphasize that these tests, when applied to samples of structures submitted to high temperatures, are not representative. Thus, techniques allowing quantification of physical, chemical, and mineralogical changes, as well as the temperature reached in the structural element, are more efficient [6, 9]. These techniques can and should be applied along with other tests, including compressive strength test. The more techniques are used for concrete integrity characterization, the more precise the diagnosis and the more efficient and affordable the therapy of the fire damaged structure will be.

Table 2 presents a summary of the research using microstructural techniques for characterization of the concrete exposed to high temperatures. A prevalence of laboratory tests is observed; with few cases where the techniques were applied to elements and damaged structures. Four main techniques were observed: scanning electron microscopy (SEM), X-ray diffraction (XRD), mercury intrusion porosimetry (MIP), and differential thermal analysis (DTA) and thermogravimetric analysis (TGA). It is important to emphasize that most of the research uses multiple methods for experimental analysis.

Table 2 (Part 2)
Summary of research that used microanalysis techniques

Author (reference)	Year	Sample type*	T. max (°C)	SEM**	XRD**	MIP**	DTA/ TGA**	COL**	PET**	Others
Biolzi, Cattaneo and Rosati [52]	2008	Lab.	750	X	–	X	–	–	–	–
Annerel and Taerwe [9]	2009	Lab.	550	X	–	–	–	X	–	Fluorescent Microscope
Arioz [36]	2009	Lab.	1200	X	–	–	–	–	–	–
Fall and Samb [53]	2009	Lab.	600	X	–	X	X	–	–	Capillary Absorption
Sousa [23]	2009	Lab.	600	X	–	–	–	–	–	–
Menéndez and Vega [54]	2009	Est.	–	X	X	–	X	–	–	–
Annerel and Taerwe [14]	2011	Lab.	100	–	–	–	–	X	–	–
Britez [25]	2011	Est.	–	–	X	–	X	–	–	–
Ruschel [39]	2011	Est.	–	–	X	–	–	–	–	–
Ibrahim, Hamid and Taha [55]	2012	Lab.	700	X	X	–	X	–	–	BET
Hager [8]	2013	Lab.	800	–	–	–	X	X	–	–
Akca and Zihnioglu [56]	2013	Lab.	900	X	–	X	X	–	–	–
Heap *et al.* [57]	2013	Lab.	1000	X	X	–	X	–	–	–
Heikal *et al.* [58]	2013	Lab.	800	X	X	–	–	–	–	–
Zhang, Ye and Koenders [15]	2013	Lab.	1000	X	X	–	–	–	–	Nitrogen Adsorption
Kim, Yun and Park [37]	2013	Lab.	1000	X	X	–	–	–	–	X-ray Computed Tomography
Carré, Hager and Perlot [16]	2014	Lab.	1000	–	–	–	–	X	–	–
Lim e Mondal [19]	2014	Lab.	1000	X	X	–	X	–	–	Atomic Force Microscopy
Wang *et al.* [38]	2014	Lab.	800	X	X	X	X	–	–	–

* Lab. = Amostra confecionada em laboratório; Est. = Amostra retirada de elemento estrutural
** SEM = Scanning Electron Microscopy; XRD = X-Ray Diffraction; MIP = Mercury Intrusion Porosimetry; DTA = Differential Thermal Analysis; TGA = Thermogravimetric Analysis; COL = Colorimetry e PET = Petrography

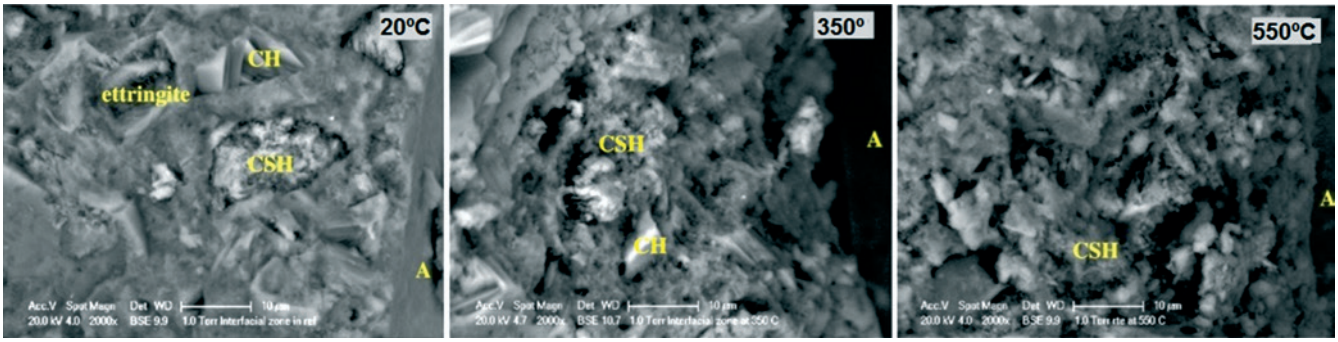

Figure 2
Micrograph of transition zone of ordinary concrete subjected to 550 °C (adapted (9))

3.1 Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) provides information on the material morphology with a usual magnification of 10,000 times and a resolution between 2 and 5 nm. A distinctive feature is the possibility to have a large depth of focus, forming a 3D-like image, with possible combination with a chemical microanalysis, [35]. Handoo, Agarwal and Agarwal [18] used this technique in ordinary concretes with siliceous aggregate and compression strength of 47 MPa under temperatures up to 1000 ºC, which enabled them to identify that the morphological changes started at 300 ºC and become more intense at 600 ºC, showing great deformation of portlandite crystals and calcium silicate hydrate, besides the presence of voids and fissures.
This increase in voids was also observed in the Peng and Huang [17] experimental program. They investigated changes in the microstructure of concretes with compressive strength of 40 MPa, 70 MPa and 110 MPa, heated from 400 ºC until 800 ºC for up to 8 hours. The authors observed a great increase in porosity at 600 ºC, due to the formation of microcracks - one of the main causes of concrete strength reduction.

Annerel and Taerwe [9] assessed the microstructure in the transition zone of conventional concretes with siliceous aggregate, a/c ratio of 0.47 ratio and compressive strength of 52.8 MPa, exposed to temperatures of 350 ºC and 550 ºC. The micrographs are presented in Figure 2. It was observed that at room temperature the transition zone presented an intact matrix, constituted by ettringite, portlandite and calcium silicate hydrate. It was also possible to observe that the ettringite and portlandite crystals disappeared at 350 ºC and 550 ºC respectively. The authors points out that the ettringite dehydration process started at 70 ºC but it could not be visualized because micrographs were not collected at temperatures below 350 ºC .
The micrographs obtained by the experimental program of Arioz [36] allowed the identification of microcracks, voids, and partial deterioration of CH and C-S-H in concretes with calcareous aggregate and compressive strength of 76.6 MPa, submitted to 800 ºC. The author also analyzed samples submitted to 1200 ºC, completely deteriorated (Figure 3).
Kim, Yun, and Park [37] studied the behavior of mortars with 0.5 w/c ratio, submitted to elevated temperatures. In the obtained

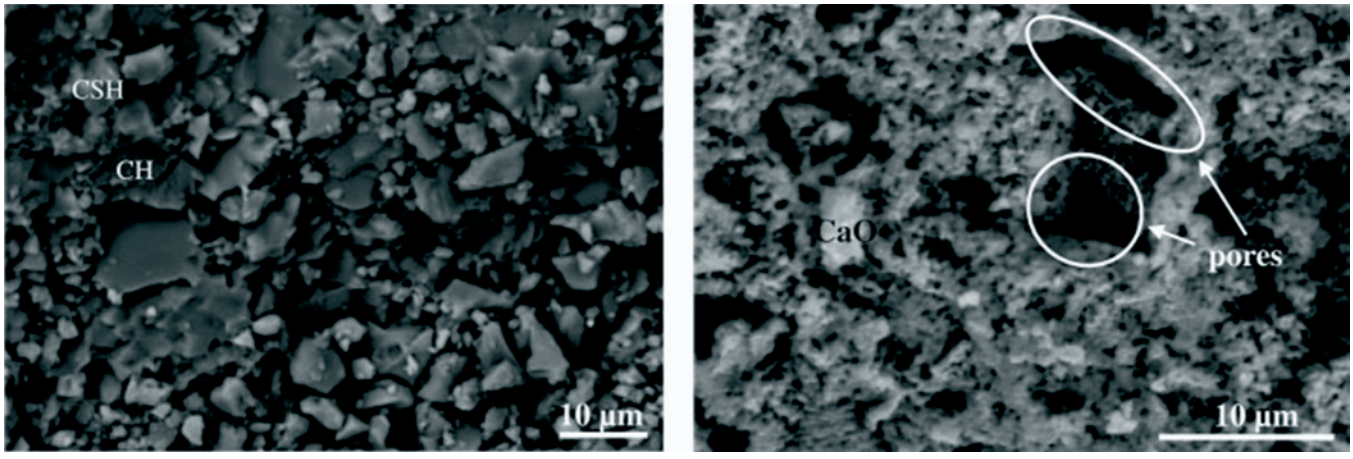

Figure 3
Changes in concrete subjected to 1200 ºC (adaptaed (36))

micrographs, the authors pointed out that at 500 ºC the hexagonal CH crystals started to deform, and that at 700 ºC they were completely decomposed, as well as C-S-H. Zhang, Ye and Koenders [15], who also researched the behavior of cement pastes with 0.5 w/c ratio, have seen in the micrographs that until 400 ºC the changes in the paste are minimal and that from 500 ºC until 1000 ºC fissures start to show in the region, along with pores, interconnected by these fissures.

Degradation of cementitious compounds has also been observed by Wang *et al*., [38] who studied cement pastes with compressive strength of 42 MPa and 0.4 w/c ratio, heated to 400 ºC , 600 ºC and 800 ºC. The authors indicated that at 400 ºC portlandite and calcium silicate hydrate were in good conditions. At 800 ºC the hydration products were completely decomposed, producing voids and cracks.

Lim and Mondal [19] researched the micro- and nanostructure of cement pastes with 0.35 w/c ratio, heated until 1000 ºC. The micrographs are shown in Figure 4. It is possible to observe that at room temperature the portlandite and C-S-H crystals remained intact. At 300 ºC the degradation of these solids started, in addition to the appearance of non-hydrated cement particles. Microcracks appeared at 500 ºCat their interface and got more intense at 700 ºC and 900 ºC, increasing the paste porosity.

In Brazil, SEM has been used by Lima [20] and Sousa [23]. The former studied high strength concretes with basaltic and granitic aggregates with a w/c ratio of 0.3, heated from 200 ºC to 900 ºC. The main changes seen were the rough aspect and the interconnectivity of fissures, at temperatures of 600 ºC and 900 ºC. Sousa [23] studied ordinary concretes with calcareous and gneissic aggregates, 0.5 w/c ratio and 35 MPa compressive strength, submitted to 100 ºC, 300 ºC and 600 ºC, observing an increase in the number of pores and microcracks from 300 ºC on. At 600 ºC the author identified the presence of sintered areas, cracks, and small ettringite crystals, probably formed after the samples were cooled.

3.2 X-Ray Diffraction (XRD)

X-ray diffraction analysis allows the identification of the crystalline

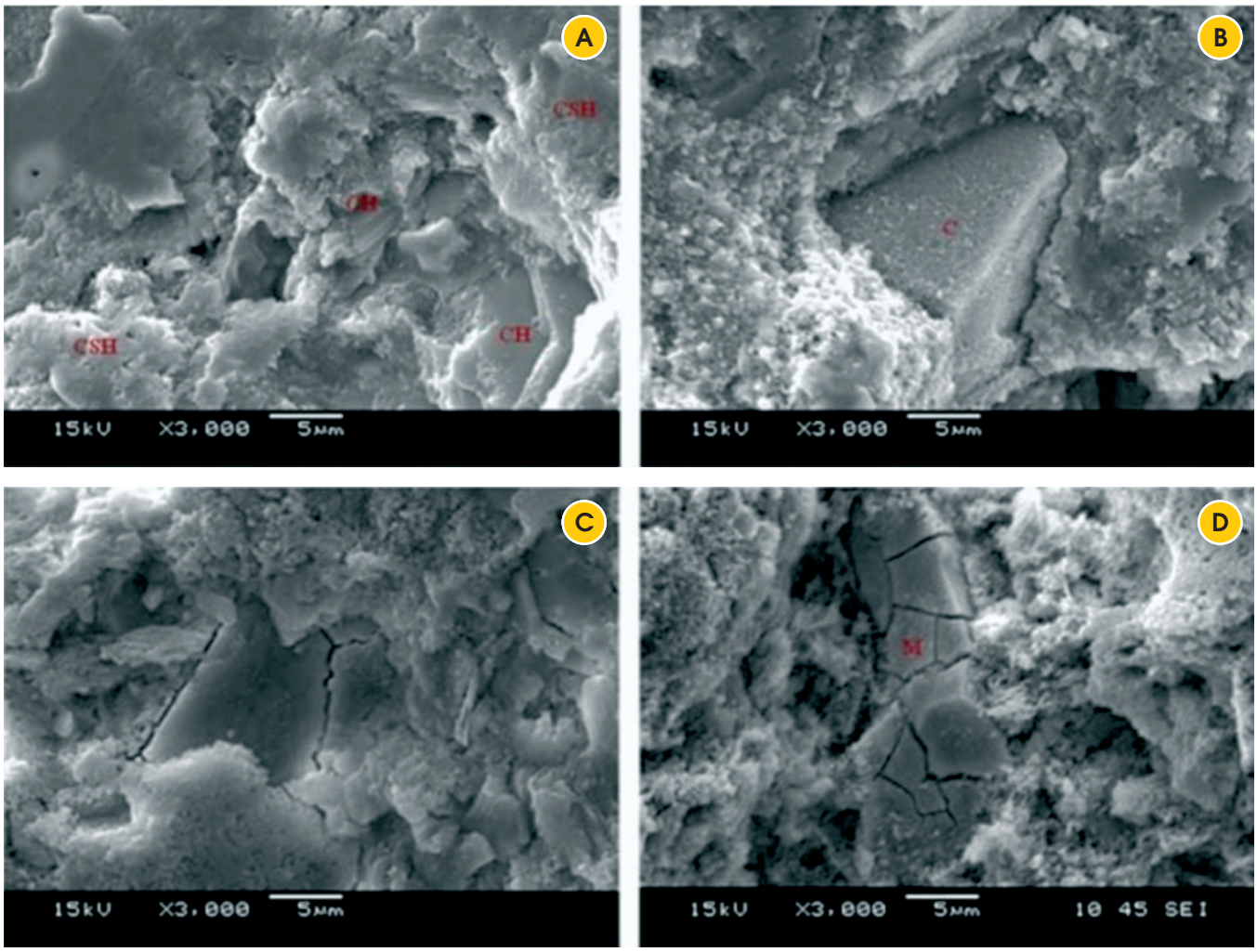

Figure 4
Micrographs of cement paste at ambiente temperature (a), 300 ºC (b), 500 ºC (c) e 900 ºC (d) (adapted (19))

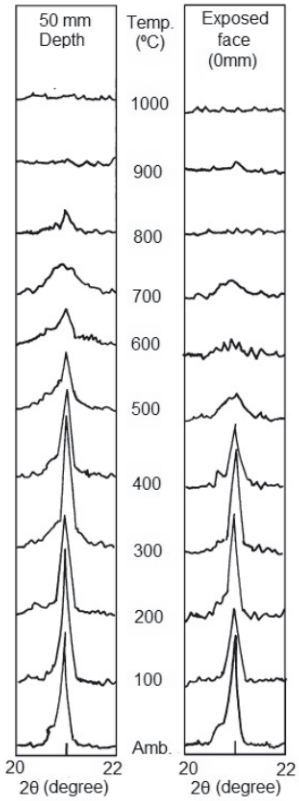

Figure 5
Diffractograms identifying portlandite behaviour (adapted (18))

phases of a material, providing information on the structure, composition, and state of the sample. The technique consists in projecting an X-ray beam onto the sample, which interacts with the ray through its atoms, creating the diffraction phenomenon [35]. Diffracted rays are captured and processed by the equipment and the result is plotted in a graph with the intensity of radiation diffracted by diffraction angles [20].

Handoo, Agarwal and Agarwal [18] tested with XRD the behavior of ordinary concrete with siliceous aggregate and 47 MPa compressive strength, heated until 1000 ºC. The obtained diffractograms showed a gradual reduction of $Ca(OH)_2$ from 400 ºC on until its complete extinction at 800 ºC (Figure 5). Peng and Huang [17] obtained diffractograms of their samples and veryfied (Figure 6) that the intensity peaks related to calcium hydroxide and calcium carbonate started to decrease at 500 ºC , indicating its decomposition. Calcium silicate hydrate started to decompose at 600 ºC, the same level where an intense presence of pores was observed through SEM.

In Kim, Yun, and Park [37] diffractograms, the main transformation happens with CH, which starts to be reduced at 400 ºC and disappeared at 1000 ºC (Figure 7). This phenomenon is consistent with the transformations observed in the micrographs. In the cement paste samples with 42 MPa compressive strength and 0.4 w/c ratio analyzed by Wang *et al*. [38], as shown in Figure 8, there was a reduction in the peaks of portlandite and C-S-H from 600 ºC on.

Lim and Mondal [19] cement paste (w/c ratio of 0.35) analysis (Figure 9) shows that until 300 ºC there were no visible changes in the intensity peaks of the hydration products. From 500 ºC on, disappearance of the C-S-H peak was observed, along with the appearance of a β-C_2S peak. At 500 ºC there was a decrease in the CH peaks and the emergence of CaO peaks. The authors mention the emergence and disappearance of $CaCO_3$, resulting from the reaction of CaO with CO_2 present in the furnace at 700 ºC and 900 ºC, respectively.

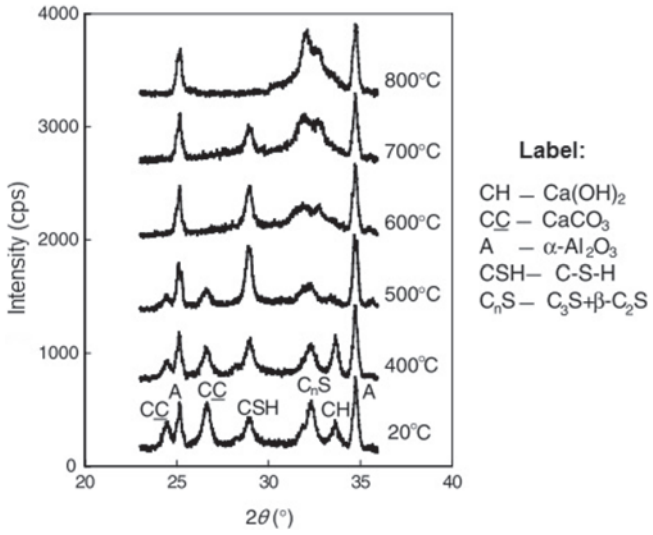

Figure 6
Diffractograms of cement paste heated up to 800 ºC (adapted (17))

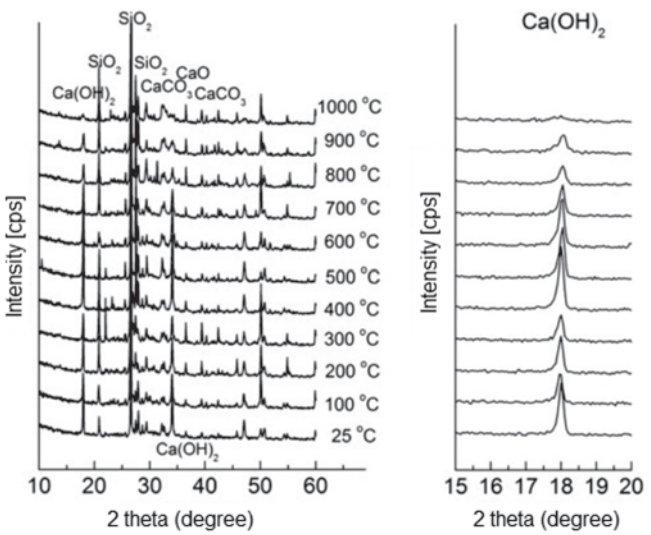

Figure 7
Diffractograms of cement paste heated at different temperatures (adapted (37))

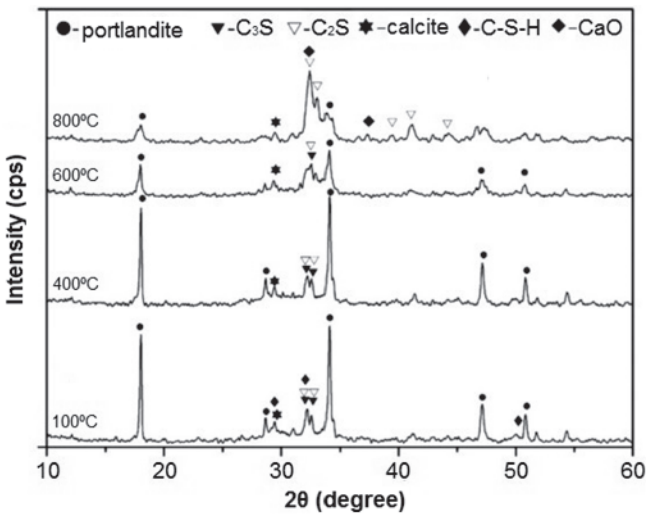

Figure 8
Diffractograms of cement paste heated up to 800 ºC (adapted (38))

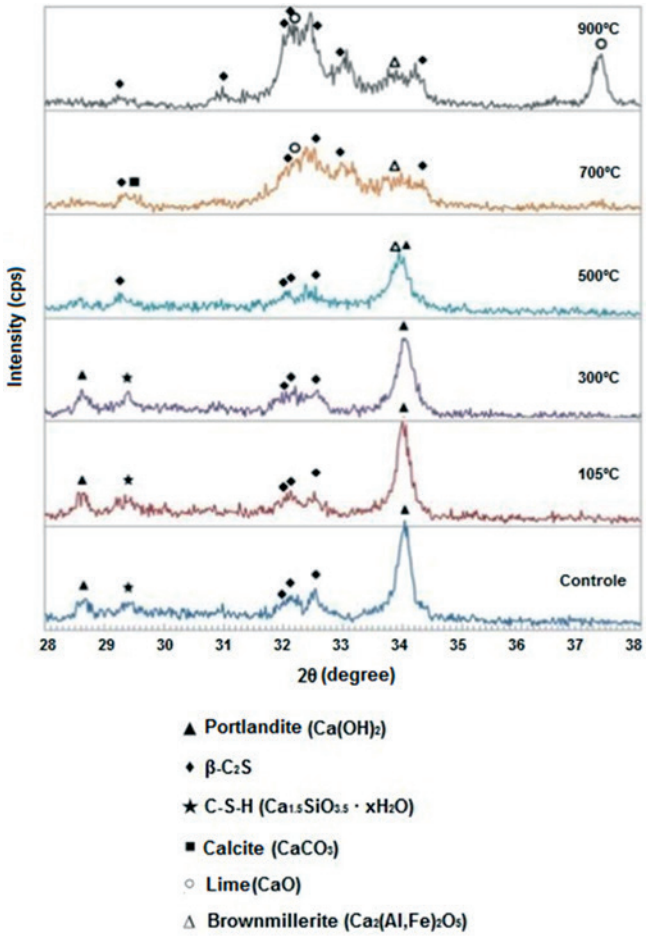

Figure 9
Diffractograms of cement paste after heating (adapted (19))

In Brazil, XRD analysis of concretes exposed to high temperatures was used by Lima [20] and Ruschel [39]. In Lima [20] diffractograms, it is possible to see that ettringite was stable up to 200 ºC and portlandite up to 400 ºC, when it started to transform into calcium oxide until its total disappearance at 900 ºC. This ettringite stability has been observed in other experiments, since this product only starts to dehydrate at 70 ºC. The author emphasizes that this presence may be related to a possible stability of the material in the interior of the collected sample or the result of a concrete rehydration process. Ruschel [39] applied x-ray diffraction in the assessment of a fire damaged structure. He observed in samples from different fire damaged columns a reduction in the peaks of portlandite, mainly at the top of structural elements, where there was accumulation of hot gases and, consequently, a higher concrete degradation.

3.3 Mercury Intrusion Porosimetry (MIP)

The principle of mercury intrusion porosimetry (MIP) is the insertion of a non-wetting fluid – mercury, in this case – able to penetrate into the materials pores, where the fluid pressure and volume are used for the calculation of pore volume. Pore sizes vary from 0.001 µm to 1000 µm, depending on the pressure used [32].
Peng and Huang [17] have verified an increase in the porosity of three samples of concrete with respectively 40 MPa, 70 MPa and 110 MPa compressive strength, heated to 600 ºC. The result confirmed what had been observed in their micrographies. For Zhang, Ye and Koenders [15], who researched the behavior of cement pastes with 0.5 w/c ratio, the total porosity obtained via MIP increased as the temperature got higher. Figure 10 shows that the increase in total porosity was higher after 400 ºC, the point at which portlandite dehydrated.
This significant porosity increase after 400 ºC has also been observed by Wang et al., [38] who studied cement pastes with compressive strength of 42 MPa and w/c ratio of 0.4, heated to 400 ºC and 800 ºC. The authors indicated that at room temperature the

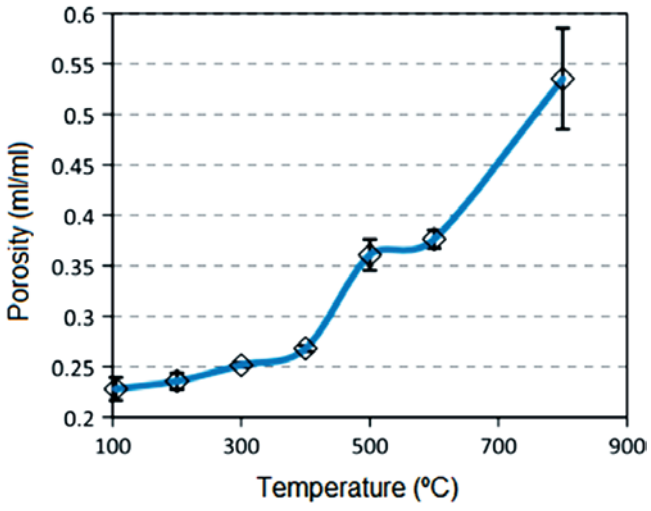

Figure 10
Total porosity of cement paste (adapted (15))

total porosity was 26.9 %. At 400 ºC this value went up to 29.8% and at 800 ºC it jumped to 45.5 %, which explains the marked strength decrease at this point.

3.4 Other experimental techniques

Although the techniques herein reported are predominately used in the characterization of concrete microstructures submitted to high temperatures, other important tools can be used for the analysis of degraded material, such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA). In this kind of analysis, a sample of the concrete is heated in a furnace with a similar inert sample. Changes in the sample mass are monitored during heating to identify the presence of the material components [7].

Handoo, Agarwal and Agarwal [18] applied these thermal analyses to the evaluation of conventional concrete with 47 MPa compressive strength, heated to 1000 ºC. The authors reported a reduction in the portlandite quantity from 300 ºC on, until its disappearance at 800 ºC. In Brazil, Lima [20] performed tests of this nature with cement paste and verified the decomposition of ettringite at 50 ºC, dehydration of portlandite at 500 ºC and reduction of carbon dioxide, resulting from the dehydration of calcium carbonate, at 800 ºC.

Since heating promotes changes in the concrete color, some authors have used techniques centered on colorimetry. Annerel and Taerwe [14] used spectrophotometry and a table scanner for analysis, observing changes in the cement paste from grey to red (300 ºC – 600 ºC), whitish grey (600 ºC – 900 ºC) and brown (900 ºC – 1000 ºC). Hager [8] also used a table scanner to analyze the changes in the material color. Figure 11 shows some images obtained by the author, who emphasizes that these changes are directly linked to alterations in both the aggregate and the paste physical and chemical properties.

Georgali and Tsakiridis [2] used optical microscopy in the analysis of a concrete structure submitted to real fire. Absence of portlandite crystals was observed inside the superficial samples of the structural element, as well as the transformation of carbonate aggregates into CaO, an indication that the temperature reached 900 ºC on the exposed face of the element.

3.5 Discussion

From the techniques studied in the reviewed works it is possible to say that they show great potential for identification of physical, chemical, and mineralogical changes in the concrete submitted to high temperatures. In general, the techniques are convergent to each other and allow confirming the main known transformations in heated concrete. However, some aspects must be observed in the use of these experimental techniques.

The first aspect is the samples nature in the studied experimental programs. Of the 35 works reviewed in Table 2, only 4 studied the behavior of concretes derived from real-scale structural elements. This difference is significant, most in terms of the developed thermal gradients, which vary substantially depending on the dimensions of the specimen and the structural element. This variability is also affected by the sample heating method, whether it is laboratorial (heating rate, curve, and heated faces, among others) or real (fire).

Still related to the sample, the studied experimental programs did not present specific details on its preparation, nor did they indicate if any standard was followed. For example, the sample used in x-ray diffractometry is in the form of powder and the grinding method used in the reviewed studies was not explained. These procedures should be standardized and norms must be followed in order to achieve greater reliability in results.

The same standardization question applies to the process of sample collection in the case of fire damaged structures. For example, one of the options for sample collection is the extraction of core samples via diamond saw. This process may introduce deleterious effects in the core sample[40], such as additional cracks, which may influence the scanning electron microscopy and mercury intrusion porosimetry results.

Another aspect to be pointed out is that despite the knowledge of the main inflicted changes and their respective temperature levels [19], a direct relation between micro and macro still has not yet been completely established, due to the complexity of the phenomena involved, the variability and diversity of studied concretes, as well as the disperse and isolated nature of high temperature tests [6].

In any case, microstructural experimental methods are an important tool for the diagnosis of fire damaged structures and future work should focus on establishing methods and normative procedures with the purpose of application in real fire cases, as well as on identifying the relations between the microstructure and properties of concrete.

4. Conclusion

This work performed a review of the techniques for analysis of the microstructure of concrete submitted to high temperatures. It con-

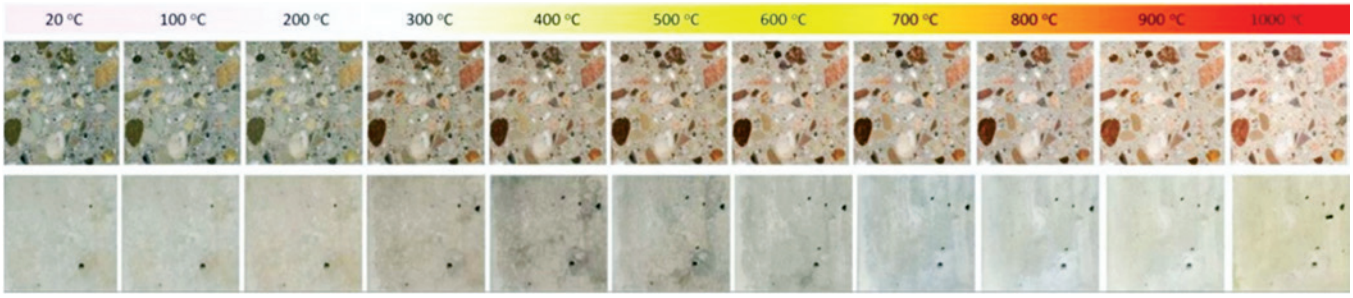

Figure 11
Color change as a function of temperature (adapted (8))

firmed that concrete degradation is directly linked to the concrete features and the heating process. In the case of aggregates, temperature promotes their expansion and may even lead to phase changing, depending on the temperature level. As to the hydrated cement paste, temperature causes chemical changes in the hydration products, leading to the appearance of cracks, voids and intense paste shrinkage. These effects, added to the differential movement between the paste and aggregates, promote intense degradation of concrete properties.

These microstructural changes can be observed and detected through experimental techniques. SEM allows the observation of cracks, voids and morphological changes in the hydrated products. XRD allows the identification of the degradation of concrete elements, mainly in terms of portlandite reduction, which can be used both as a damage and temperature evolution indicator. MIP helps to identify the paste porosity increase, and these values can be directly related to the reduction of mechanical compressive strength and to other microstructural observations. Other techniques, such as colorimetry, DTA and DTG provide complementary information that helps in the diagnosis of concrete submitted to high temperatures.

Despite the outstanding potential, some aspects must be observed in the application of these techniques. Most of the reviewed experimental works use small-scale samples, heated in laboratories, which does not include the diverse variables of a real structure submitted to real fire. Another relevant factor is the absence of standardized procedures for collection and preparation of samples for these analyses. It is necessary to establish specific procedures for inspection of fire damaged structures, describing places for collecting samples, and how to collect and prepare them.

Technique standardization for structure inspection will lead to more reliable results, contributing to the diagnosis of damaged structures and definition of therapy strategies. In any case, the techniques are an important diagnosis tool for structures damaged by high temperatures, especially when applied jointly, given the agreement between results. The experience achieved with their application will contribute to a better understanding of these techniques and to their improvement.

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