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Physicochemical, mineralogical, and morphological characteristics of concrete exposed to elevated temperatures

S.K. Handoo*, S. Agarwal, S.K. Agarwal

National Council for Cement and Building Materials, A-135 Defence Colony, New Delhi 110 024, India

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Abstract

Concrete cubes prepared from ordinary Portland cement (OPC) of known chemical, mineralogical, and physical performance characteristics and fired to various temperature regimes up to 1000 °C in steps of 100 °C for a constant period of 5 h have been studied by using X-ray diffraction (XRD) and DTA/TGA to establish the effect of elevated temperatures on the mineralogical changes occurring in the hydrated phases of concrete. The changes in physical state of concrete were studied by measuring ultrasonic pulse velocity (UPV) and consequent deterioration in the compressive strength with increase in temperature. Scanning electron microscopy (SEM) studies showed distinct morphological changes corresponding to deterioration of concrete exposed to higher temperatures. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Temperature; Microstructure; Thermal analysis; Compressive strength; Concrete

1. Introduction

Over the years, it has been noticed that structural material is really not "inert" during service and gets affected either by the service environment to which it was exposed or physical–chemical causes due to the reasons residing within. The reduction in engineering properties of concrete such as strength, elastic modulus, and durability occur due to variety of chemical and physical causes such as corrosion of reinforcements, sulfate and sea water attack, carbonation, freezing and thawing, thermal effects, abrasion, and nature of materials (e.g., type of aggregate and cement blend) [1–4].

Subjecting concrete to high temperature (e.g., due to accidental fire etc.) leads to severe deterioration and it undergoes a number of transformations and reactions, thereby causing progressive breakdown of cement gel structure and consequent loss in its load-bearing capacity, reduced durability, increased tendency of drying shrinkage, structural cracking, and associated aggregate color changes [4–7]. Assessment of the condition of concrete and extent of damage after the fire is an important requirement for taking possible corrective measures for its rehabilitation. Therefore, systematic parametric studies on simulated conditions of temperatures such as that generally experienced during an accidental fire in concrete structures are of utmost importance. The present study considered the thermal effects on concrete and reported the physicochemical, mineralogical, and morphological changes in pre- and postfired concrete.

2. Methods

M-20-grade concrete was designed as per Indian Standard IS:10262 (1982) [8] using standard siliceous aggregates and ordinary Portland cement (OPC) of known characteristics as given in Table 1. The concrete cubes of 100-mm size were cast and cured under moist conditions at ambient temperature for 48 h and after demolding, the cubes were cured in water at temperature of 27 ± 2 °C for 28 days as per IS:516 (1959) [9]. The water-cured cubes were dried in air at a temperature of 27 ± 2 °C with relative humidity (RH) > 90% prior to getting exposed to a high-temperature regime up to 1000 °C in steps of 100 °C in a hot-air oven/muffle furnace for a constant retention period of 5 h. The air-dried pre- and postfired concrete cubes were assessed for their physical deterioration by ultrasonic pulse velocity (UPV)

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* Corresponding author. Tel.: +91-129-4312-423; fax: +91-129-5242-100.

E-mail address: nccbm@giasd101.vsnl.net.in (S.K. Handoo).

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Table 1
Physicochemical characteristics of OPC cement

Oxide constituents (%)

LOI	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	IR	CaO_f
2.69	61.38	21.27	5.16	4.08	2.36	2.29	1.59	0.28

Physical characteristics

	Compressive strength[a] (N/mm^2)			Setting time (min)		Soundness	
Blain's (m^2/kg)	3 days	7 days	28 days	IST	FST	Le-chatier (mm)	Autoclave (%)
330	23	34	47	50	160	1	0.01

IST: Initial Setting Time; FST: Final Setting Time.

[a] Measured on 1:3 mortar cubes as per IS:4031 (1988).

measurement by cross-probing method using portable ultrasonic nondestructive digital indicator tester as per IS:13311-Part I (1992) [10]. The fired cubes after cooling to ambient temperature were immersed in water for 48 h before testing for compressive strength [9]. DTA/TGA and X-ray diffraction (XRD) studies were carried out on the mortar part of the cubes drawn from areas representing the exposed surface as well as the core, using simultaneous Mettler thermoanalyzer TA-1 system and Rigaku's X-ray diffractometer with CoKα radiation ($\lambda = 1.791$ Å), respectively. Scanning electron microscopic (SEM) studies were carried out on gold-coated fractured surfaces of fired concrete mortar samples on Philips SEM-515.

3. Results and discussion

The chemical analysis of OPC used in the casting of concrete cubes indicating the presence of main constituent oxides are listed in Table 1 along with minor constituents 2.29% SO_3, 1.59% insoluble residue (IR), 0.28% free lime, and 2.36% MgO, which conform to IS:269 (1989) [11]. Total alkali content (Na_2O equivalent) in OPC was found to be 1.59%. Physical characteristics of OPC determined as per IS:4031 (1988) [12] showed 3-, 7-, and 28-day compressive strength of 23, 34, and 47 N/mm^2, respectively. Pre- and postfired concrete cubes were characterized for the physical properties, mineralogy, morphology, and thermal behavior, and the results are discussed in the following sections.

3.1. UPV measurements

UPV measurements carried out on fired concrete cubes show a reduction of velocity from 4.05 to 0.33 km/s with the increase in temperature from 100 to 700 °C and consequent gradual deterioration in the quality of concrete (Table 2). Pulse transmission pattern across the cubes shows gradual decrease in its velocity with rise in temperature, and beyond 300 °C, it decreases rapidly due to the sharp deterioration in the physical state of fired concrete (as shown in Fig. 1). At 800 °C, the pulse could not be transmitted through the cubes indicating total deterioration in their physical state.

3.2. Evaluation of compressive strength

The average compressive strength of concrete cubes after curing in water for 28 days was found to be 36 N/mm^2. Concrete cubes exposed to different temperature regime for a constant period of 5 h have negligible effect on their compressive strength up to 400 °C but suffer a significant loss of strength subsequently, due to the loss of crystal water resulting in the reduction of the $Ca(OH)_2$ content, besides the changes in the morphology and microcrack formation. Khoury [4] has made a similar observation that compressive strength of unsealed "concrete" declines sharply above 300 °C. The reduction in the average compressive strength with temperature shows distinct distress beyond 800 °C (Table 3). Similar pattern of reduction in strength of concrete specimens has also been reported earlier [13–17].

Table 2
UPV across concrete cubes exposed to different temperatures for 5 h

Temperature (°C)	UPV (km/s)	Average value (km/s)	Condition of concrete[a]
Ambient	4.54, 4.76, 4.34, 4.54, 4.34, 4.54	4.51	excellent
100	4.00, 4.16, 4.00, 4.00, 4.00, 4.16	4.05	good
200	3.85, 3.85, 3.70, 3.70, 3.85, 3.85	3.80	good
300	3.57, 3.57, 3.44, 3.57, 3.58, 3.70	3.57	good
400	2.94, 3.12, 3.00, 3.00, 3.20, 2.98	3.04	medium
500	1.78, 2.56, 2.50, 2.50, 2.56, 2.50	2.40	poor
600	1.40, 1.53, 1.49, 1.11, 1.53, 1.14	1.36	poor
700	0.46, 0.28, 0.41, 0.30, 0.33, 0.20	0.33	poor
800	pulse does not pass through the sample		

[a] As per IS:13311-Part 1 (1992).

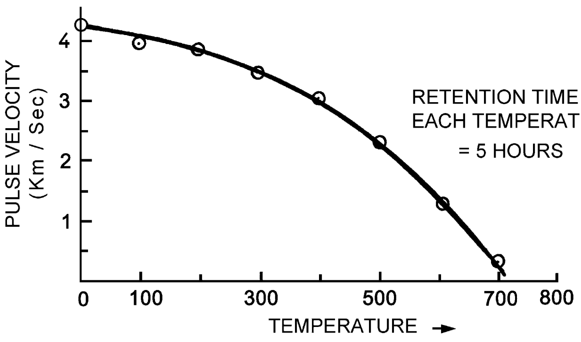

Fig. 1. Decrease in UPV across the concrete cubes with increasing temperature.

3.3. XRD studies

Phase analysis of mortar part of hardened concrete cured at ambient temperature prior to exposed to high temperatures by XRD shows the presence of usual hydrated phases such as Portlandite $Ca(OH)_2$, calcium silicate hydrate (C-S-H), ettringite, etc. along with α-quartz due to siliceous aggregate used in concrete. Multiple XRD patterns of mortar samples drawn from core as well as surface of concrete cubes and subjected to different temperature regimes, i.e., from 100 to 1000 °C, were recorded and presented in Fig. 2a and b, which corresponds to the diffraction line ($d = 4.90$ Å) for $Ca(OH)_2$, and Fig. 3a and b, which corresponds to the diffraction line ($d = 3.03$ Å) for $CaCO_3$. Fig. 2a and b showed the gradual reduction in $Ca(OH)_2$ content with increase in temperature indicating gradual deterioration in concrete quality. As expected, a gradient exists between the amount of $Ca(OH)_2$ at the surface and in the core of concrete samples exposed to higher temperature as shown in Fig. 2a and b. The variation in intensities of diffraction line ($d = 4.90$ Å) is found to be more predominant in surface sample as compared to the core. Since the intensity of diffraction line ($d = 4.90$ Å) in the core and surface samples was almost same at ambient temperature, it was assumed that a negligible amount of leaching of $Ca(OH)_2$ has taken place. An almost similar intensity of diffraction line ($d = 3.03$ Å) at ambient temperature indicates a negligible carbonation at the exposed surface due to atmospheric CO_2 (Fig. 3a and b).

3.4. Thermal analysis

Harmathy [18] demonstrated the use of differential thermogravimetric technique for gauging the temperature to which concrete could have been exposed during an accidental fire. Raina et al. [19] and Handoo et al. [20] have also reported the application of DTA/TGA technique for assessing fire-damaged concrete.

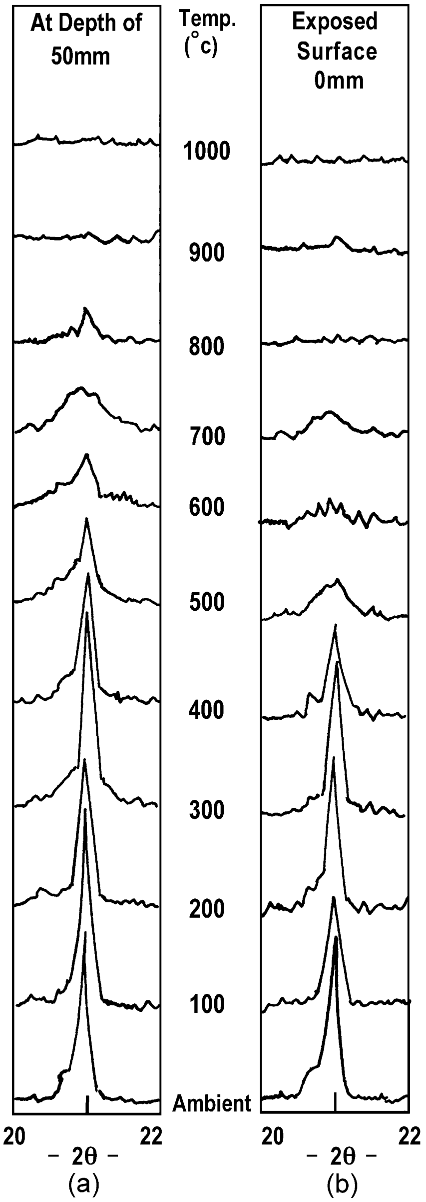

Fig. 2. X-ray diffractograms of mortar samples of concrete monitoring $Ca(OH)_2$ fired at different temperature regimes: (a) core, (b) surface.

DTA/TGA studies on the mortar samples of temperature-affected concrete and drawn depth-wise representing the surface and the core confirm that concrete at the surface

Table 3
Decrease in compressive strength of concrete with temperature

	Temperature (°C)									
	Ambient	200	300	400	500	600	700	800	900	1000
Comp. strength (N/mm^2)	36	36	36	35	32	16	15	13	10	nil

suffered more damage compared to the core at all temperatures as evident from thermograms shown in Fig. 4. The almost equal amount of $Ca(OH)_2$ content at the surface (6.01%) and at the core (6.04%) as given in Table 4 and determined by the corresponding TG loss in mortar samples of the hardened concrete cubes at ambient temperature indicates negligible leaching of $Ca(OH)_2$ in curing water, which collaborated with the XRD studies. The change in $Ca(OH)_2$ content reveals that at 700 °C, it is reduced from 6.01 to 1.27 wt.% at the surface and from 6.04 to 3.20 wt.% in the core (Table 4). Beyond 700 °C, $Ca(OH)_2$ could not observed in DTA in the exposed surface samples of the concrete. However, the rate of dehydration in the core at a

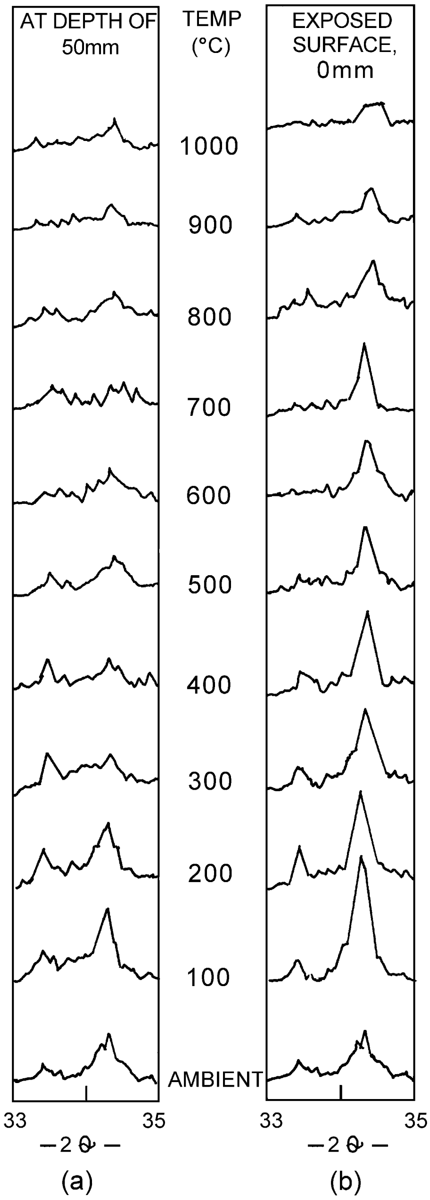

Fig. 3. X-ray diffractograms of mortar samples of concrete monitoring $CaCO_3$ fired at different temperature regimes: (a) core, (b) surface.

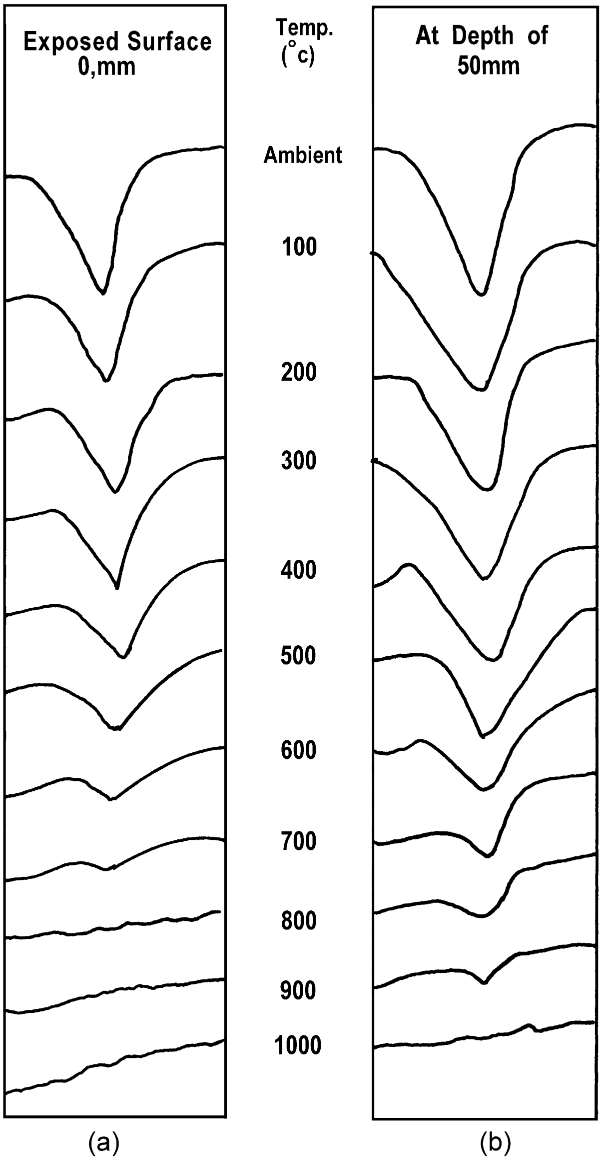

Fig. 4. DTA patterns of mortar samples of concrete fired at different temperatures: (a) core, (b) surface.

Table 4
Reduction in $Ca(OH)_2$ content in concrete mortar with temperature

	$Ca(OH)_2$ content (%)	
Temperature (°C)	Surface	Core
Ambient	6.01	6.04
100	6.01	6.04
200	6.00	6.04
300	5.14	5.97
400	4.39	4.80
500	2.52	4.52
600	1.86	4.09
700	1.27	3.20
800	nil	2.67
900	nil	0.08
1000	nil	nil

depth of 50 mm of the cubes was rather slow due to a temperature gradient from the surface. Consequently, the residual $Ca(OH)_2$ in the core samples of the cubes fired at 900 °C was still found to be 0.08 wt.%, i.e., 13.2% of the content at ambient temperature.

This decrease in the $Ca(OH)_2$ content with the temperature gradient from the exposed surface to the core of the concrete cubes can possibly be used for determining the temperature to which concrete has got exposed to and consequent extent of damage depth-wise during the exposure to temperatures like in accidental fire [21]. Such data can also be useful for making necessary recommendations for possible rehabilitation or otherwise of the fire-damaged concrete structure.

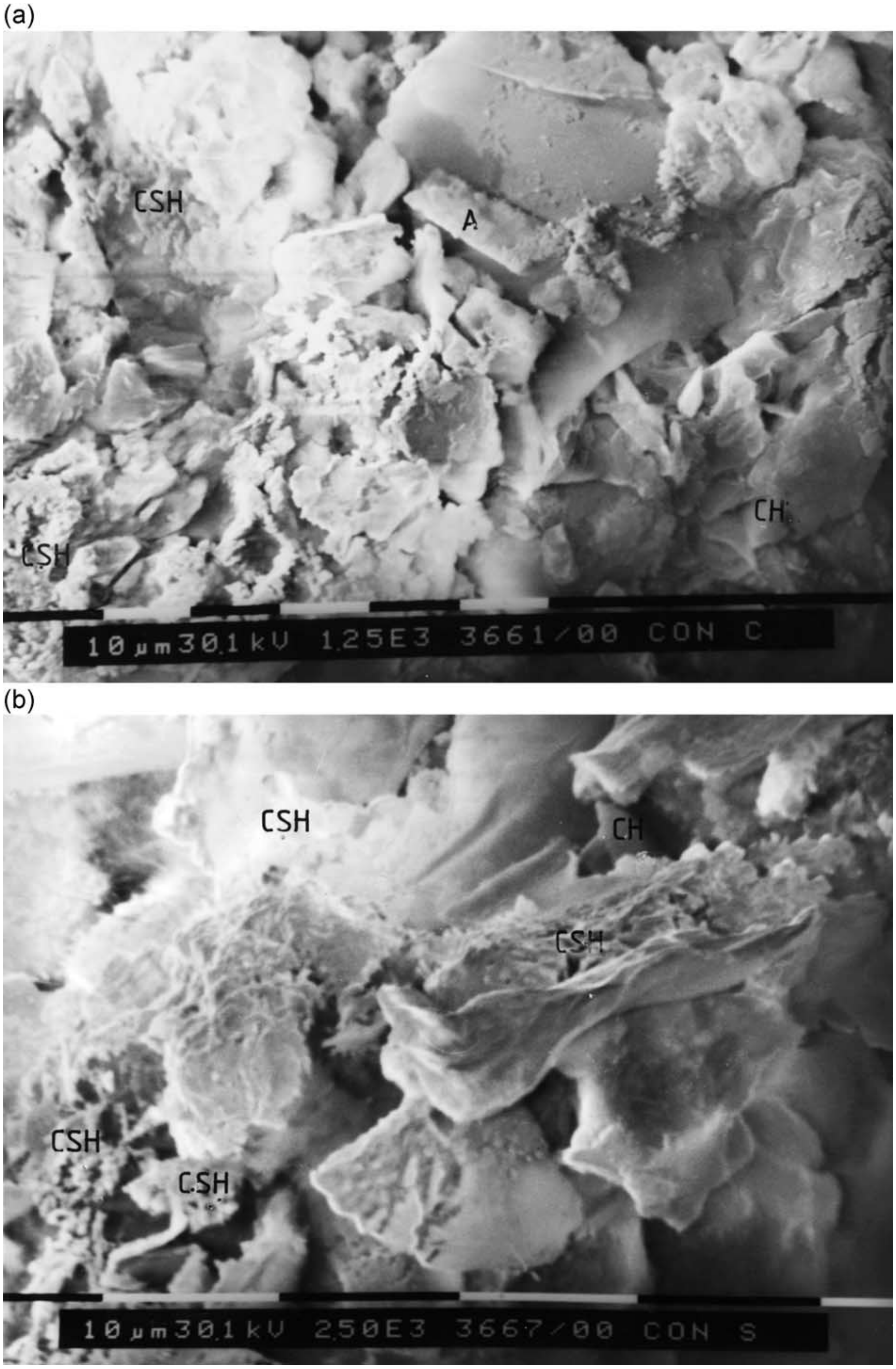

Fig. 5. SEM micrographs of hardened concrete at ambient temperature: (a) core, (b) surface.

3.5. SEM studies

SEM investigations on hardened concrete shows distinct changes in the morphology as a consequence of exposure to elevated temperatures. The samples again drawn from the surface and the core of concrete specimens were examined. A number of SEM micrographs illustrating various characteristics features of pre- and postfired concrete up to 800 °C are shown in Figs. 5–9. SEM micrographs of hardened concrete at ambient temperature as shown in Fig. 5a and b for core and surface, respectively, reveal well-developed hydrated phases such as $Ca(OH)_2$ crystals (marked "CH") intermixed with C-S-H (marked "CSH") and calcium aluminate crystals (marked "A") as shown in upper-half part of Fig. 5a. Similar findings were reported earlier by Sidney [22] in 1972 over neat cement paste. SEM micrograph of concrete samples exposed to moderate temperature, i.e., up to 200 °C, did not show any distinct change in the morphology, while at 300 °C, the morphology of effective concrete showed deformed $Ca(OH)_2$ crystals, C-S-H gel, voids (marked "V"), and the transformation of $Ca(OH)_2$ into $CaCO_3$ (marked "C") (as shown in Fig. 6a and b). Further increase in temperature to 500 °C leads to the predominance of microcracks (as indicated by arrow mark) intermingled with voids due to increase in porosity, distorted $Ca(OH)_2$, and C-S-H gel as shown in Fig. 7a and b.

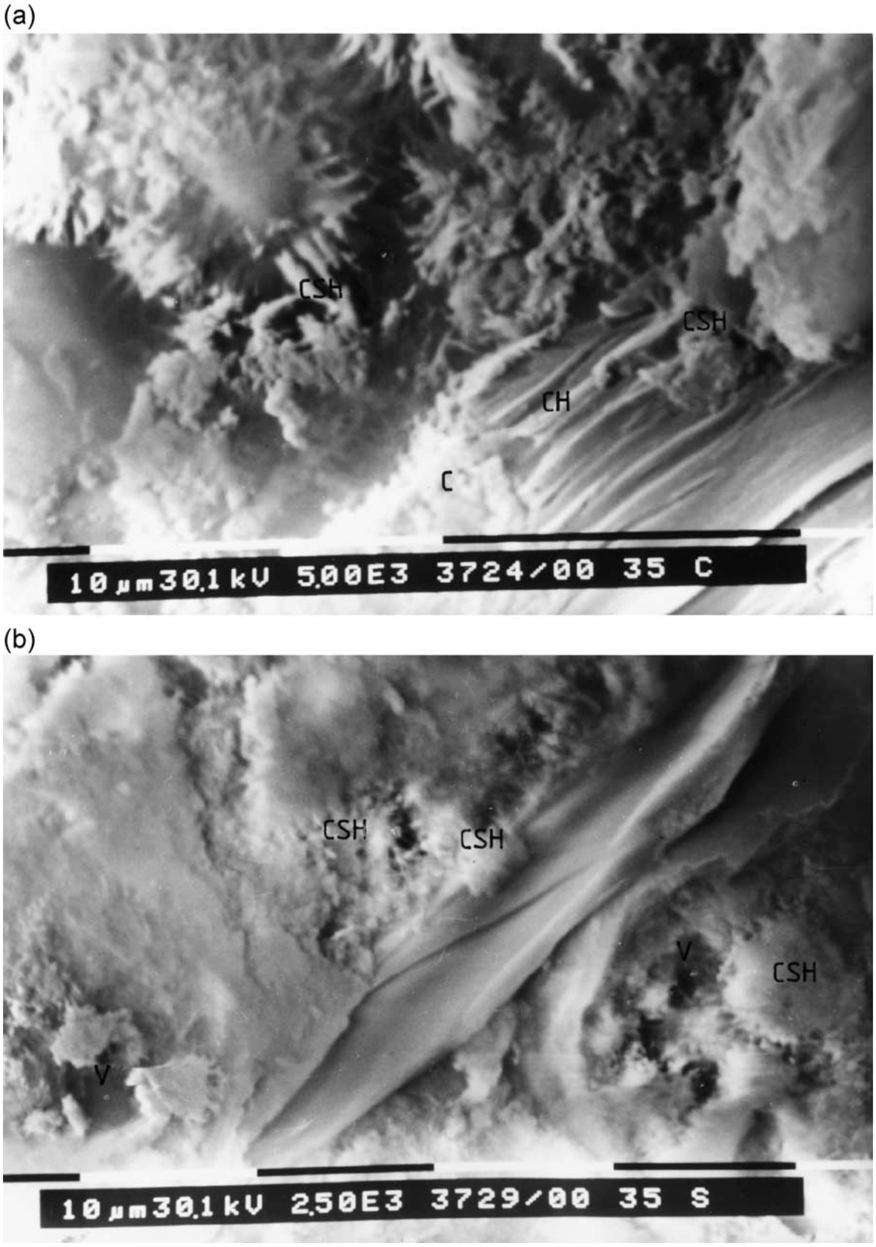

Fig. 6. SEM micrographs of hardened concrete at 300 °C: (a) core, (b) surface.

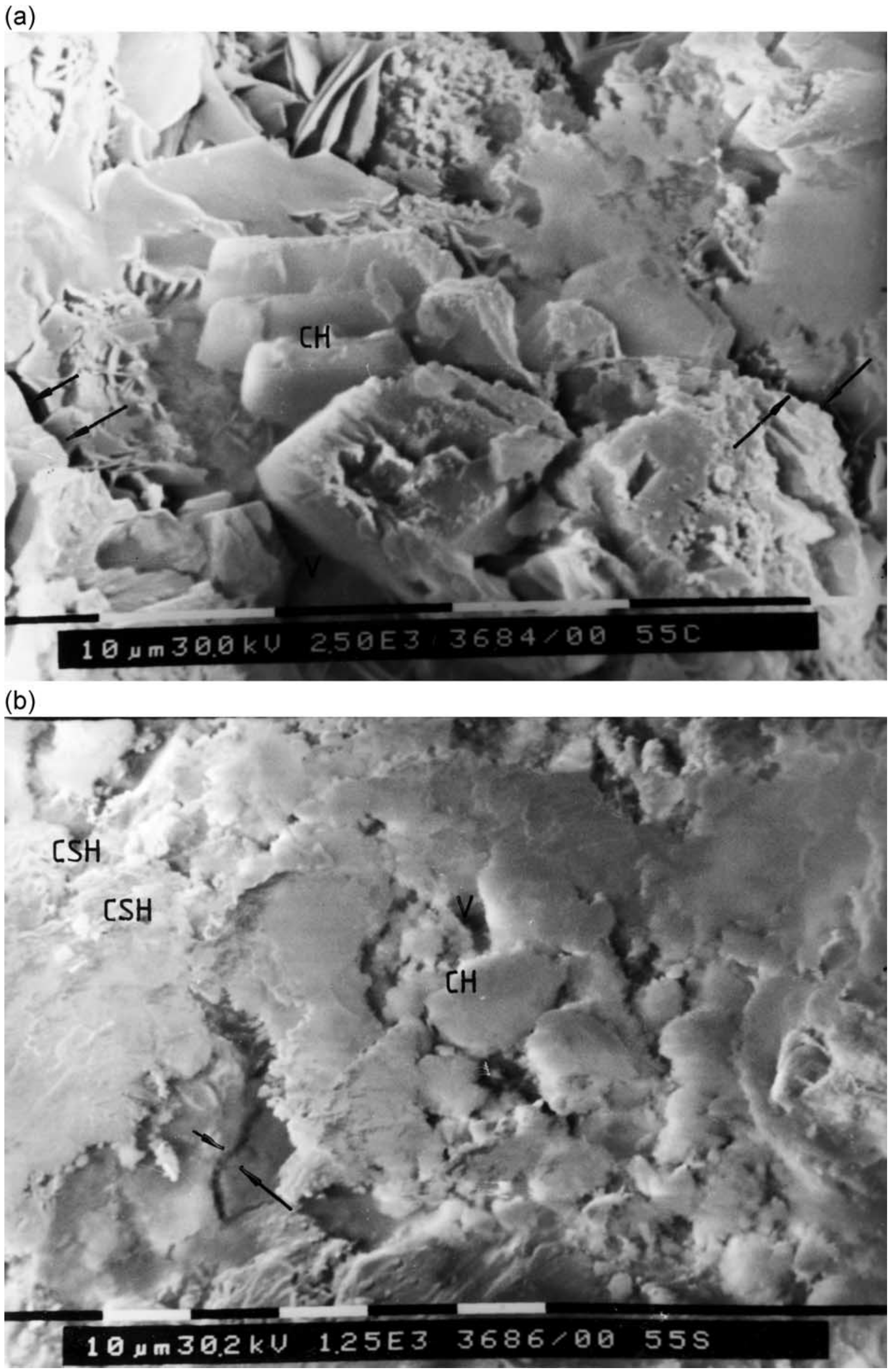

Fig. 7. SEM micrographs of hardened concrete at 500 °C: (a) core, (b) surface.

Further SEM investigation on concrete samples exposed to 600 and 800 °C revealed massive changes in the morphology of effected concrete due to the predominance of microcracks, voids increasing the porosity of concrete-deformed $Ca(OH)_2$ crystals, and disrupted C-S-H phase boundaries. Therefore, the observed loss of strength at increasing temperatures may be related to the loss of bound water, increased porosity, and consequently, increased permeability, which makes the concrete progressively more susceptible to further destruction.

4. Conclusions

1. The drastic reduction in pulse velocity across the concrete cubes between 300 and 700 °C from 3.57 to

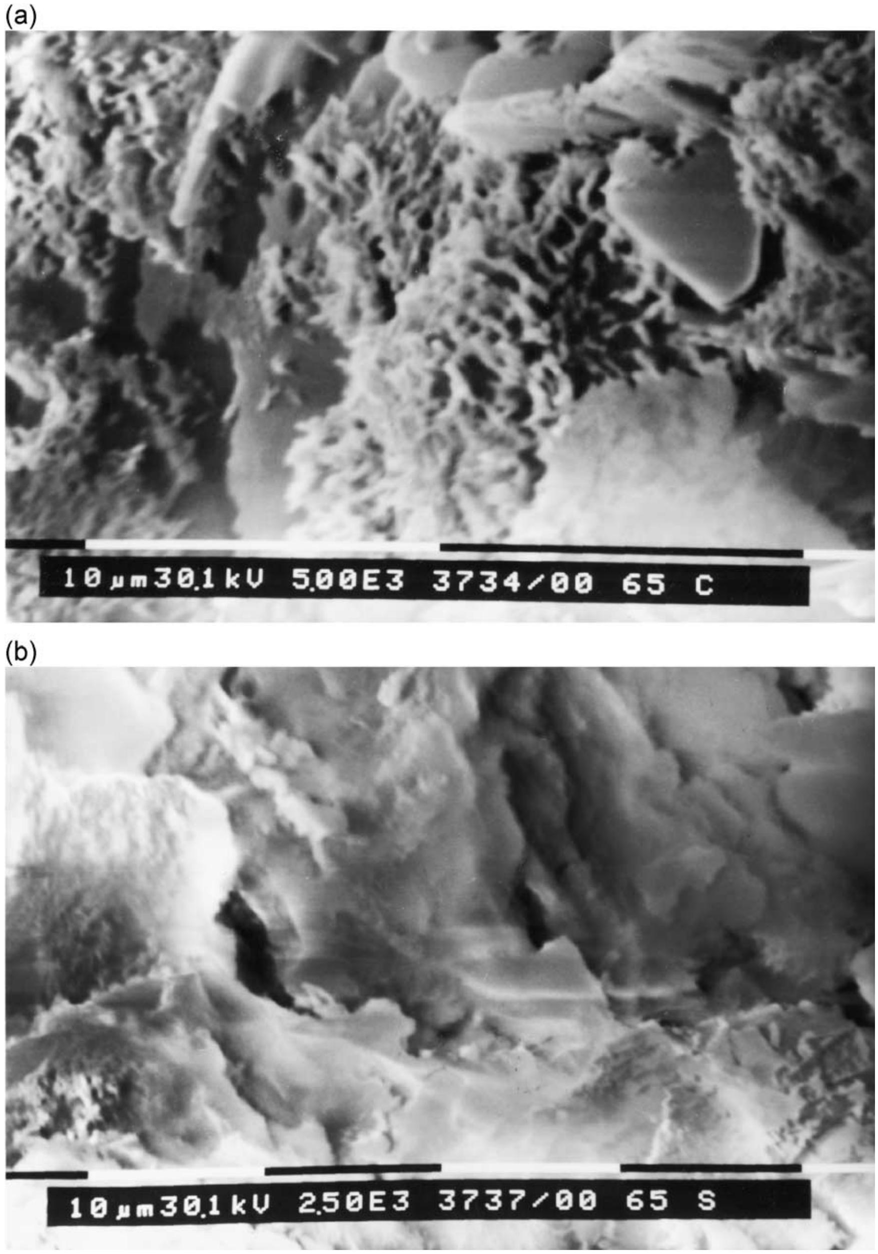

Fig. 8. SEM micrographs of hardened concrete at 600 °C: (a) core, (b) surface.

0.33 km/s establishes that the physical state of concrete deteriorates rapidly beyond 300 °C.

2. Reduction in the compressive strength of concrete exposed to beyond 500 °C is quite rapid. Complete decomposition of portlandite beyond 700 °C at the surface and beyond 900 °C at the core results in total deterioration of concrete.
3. Morphological studies confirm clear deformation of well-developed calcium hydroxide crystals and C-S-H gel beyond 600 °C.
4. The decrease in portlandite content and consequent reduction in compressive strength with increase in temperatures can be used for assessing the condition of building elements subjected to accidental fires.
5. After a fire, if the temperature is found to have reached beyond 500 °C in a structural element, a detailed survey should be carried out to determine its structural integrity.

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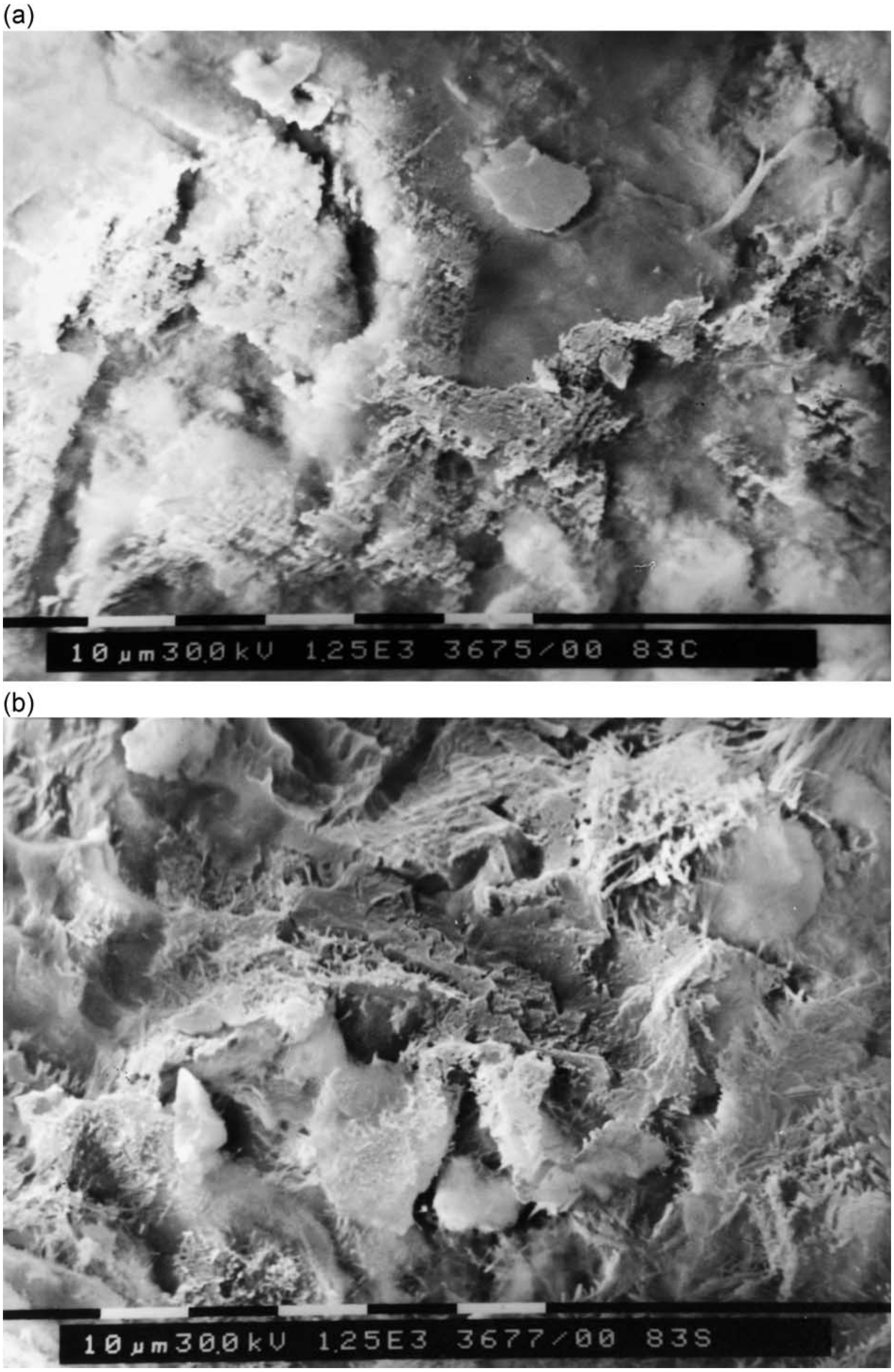

Fig. 9. SEM micrographs of hardened concrete at 800 °C: (a) core, (b) surface.

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