

Effect of elevated temperature on texture, composition and properties of fiber reinforced cement composites

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Abstract

Behavior of four types of fiber reinforced cement based composites was studied after thermal load up to 1000° C. As the reinforcement were used glass and PP fibers, PVA fibers, aramid fibers and carbon fibers. The effect of thermal load on the texture and composition of the samples was evaluated; behaviour of the used fibers was compared. The moisture diffusivity of the loaded samples and the reference sample (unloaded) was measured. It was found that three independent degradation process take place when the composites are thermally loaded. The effect of thermally unstable fibers (PVA, aramid) on moisture diffusivity is less important than effect of the cement matrix thermal degradation.

Introduction

Fiber reinforced cement based composites are recently widely studied materials because some better properties of them compared to conventional concrete. The study of effect of elevated temperature on fiber reinforced composites is motivated by possible damage of these materials by fire or other extreme conditions. It is necessary to evaluate and predict behavior of fiber composites under elevated temperature. Such behavior of conventional concrete is well known but here also to fibers play a role. Many types of fibers were applied as concrete reinforcement; four of them were studied within this work. The fibers differ in their ability to resist to elevated temperature. This property joins to other concrete's properties which influence its behaviour under elevated temperatures.

Materials

The effect of elevated temperature was studied on four types of fiber reinforced cement based materials (**Tab. 1**). Two types of matrix were used, cement CEM I 52.5 was used. Samples SC (alkali proof glass + polypropylene fibers) and K (polyvinylacetate fibers) were mixed with low w/c ratio and added superplasticizer, fine quartz sand was used as aggregates. Samples UC (carbon fibers) and T (aramid fibers) were mixed with high w/c ratio and quartz and wollastonite were used as aggregates. Small amount of microsilica was added to all materials.

The measurements were performed by reference sample and by annealed samples. The annealed samples were exposed to gradual temperature increase up to 600, 800 and 1000° C during two hours, then left for next 2 hours at the given temperature and then were slowly cooled down. All the specimens were dried at 110° C before each measurement, hence the reference (unloaded) samples are considered as loaded at 110° C.

Tab. 1 Composition of studied fiber reinforced cement composites (mass %).

		SC	K	UC	T
CEM I 52.5		54	54	40	36
w/c		0.33	0.32	0.85	0.9
Microsilica		3	3	2	4
Aggregates					
	Quartz	40	40	17	17
	Wollastonite	-	-	40	39
Fibers					
	Glass 12 mm	3			
	PP 30 mm	0.3			
	PVA 6+12 mm		1.8		
	Carbon			1	
	Aramid 1.5+6 mm				4

Experimental

The texture of studied materials was characterized by density ρ , bulk density ρ_b , and pore size distribution. Density was determined by means of helium pycnometer Pycnomatic (Porotec, Germany). Bulk density was calculated from mass of dried sample and its geometrical volume (prismatic specimens were used). These two values provide porosity and total pore volume V_p [1]. The pore size distribution was determined by mercury intrusion porosimetry (MIP) by instruments Pascal 140 and 440 (Thermo, Italy). The surface tension of mercury was assumed to be 480 mN m^{-1} and contact angle 130° .

The phase composition of SC samples was studied by X-ray diffraction analysis (XRD) performed by means of X'pert PRO (PANalytical, Netherland) instrument. Data were evaluated by software Highscore 1.0d (PANalytical, Netherland) using database JCPDS PDF2 (International center for diffraction data, USA).

The apparent coefficient of moisture diffusivity κ_{app} [$\text{m}^2 \text{s}^{-1}$] was determined by help of imbibition experiment [2]. The content of water in sample (in kg m^{-2}) was recorded automatically and plotted as function of square root of time. The slope of linear part of the dependence signed A was used to calculation of κ_{app} as follows (Eq. 1) where w_{sat} is the saturated water content.

$$\kappa_{\text{app}} = \left(\frac{A}{W_{\text{sat}}} \right)^2 \quad (\text{Eq. 1})$$

Results

The simplest way of observation of thermal degradation of cement based materials is measurement of porosity upon thermal load (**Fig. 1**). The two types of matrix – with low and high w/c ratio resulting to higher and lower porosity – are clearly distinguished. The higher w/c ratio leads to higher content of gel pores. The thermal load causes increase of porosity of all the tested materials, the slope is roughly the same for each type of matrix, regardless the type of fibers.

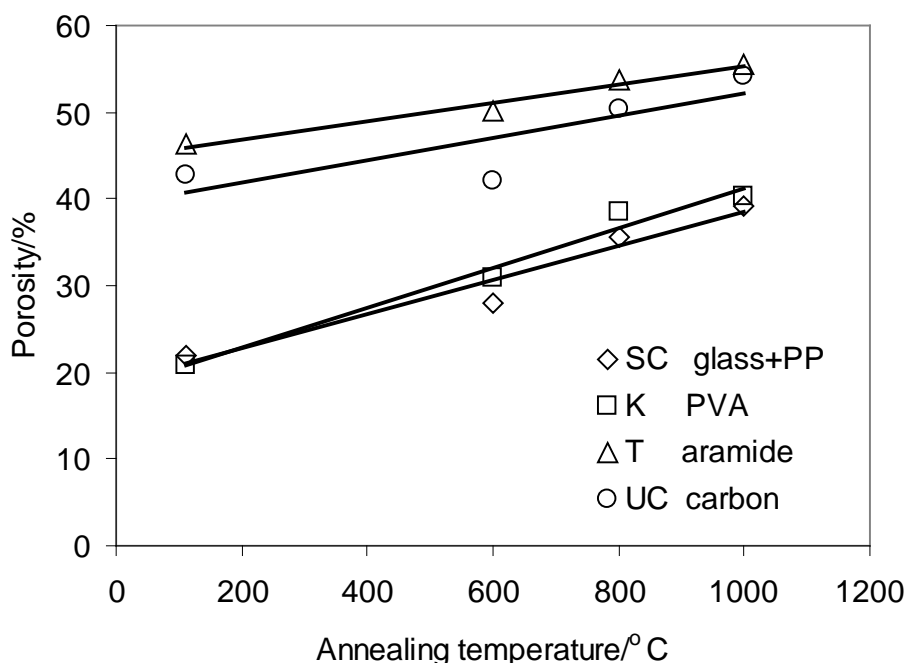


Fig. 1 Porosity of thermally loaded fiber composites.

In order to explain the increase of porosity of fiber reinforced composites, the effect of thermal load on pore size distribution and composition of samples was studied.

The XRD reveals that the thermal load induces two processes taking place in the cement binder. Portlandit $\text{Ca}(\text{OH})_2$ decomposes to CaO and water vapor. The equilibrium decomposition temperature of portlandit is 520°C but the process probably starts at somewhat lower temperature. The decomposition of portlandit causes the destabilization of phase equilibrium in hydrated cement binder which leads, together with high temperature, to disintegration of binding CSH and CAH structures and consequently to loss of their binding ability. The diffractograms of loaded samples contain calcite CaCO_3 (forms from CaO in air) and clinker minerals (C_2S , C_3A etc.) as products of decomposed CSH and CAH hydrates. This is the reason for the strength reduction of thermally loaded cement based materials.

The results of pore size distribution measurements of loaded materials are presented in **Fig. 2 a** and **b**. The general trends are of pore size distribution evolution are similar in all of the materials. The pore system of cementitious

materials is formed by three groups of pores. The smallest are gel pores formed in cement binder. The second group is called capillary pores and the largest are technological pores and voids.

The plots show that the volume of smallest (diameter 0.001 to 0.1 μm) pores – gel pores – is reduced with increasing annealing temperature. It corresponds to the XRD results; the gel structure decomposes to calcite and clinker minerals what is accompanied by the sintering of the gel fine porous texture. At 1000° C are practically all the gel pores gone. The diminishing of gel pores may be observed also by measurement of specific surface area of the samples [3].

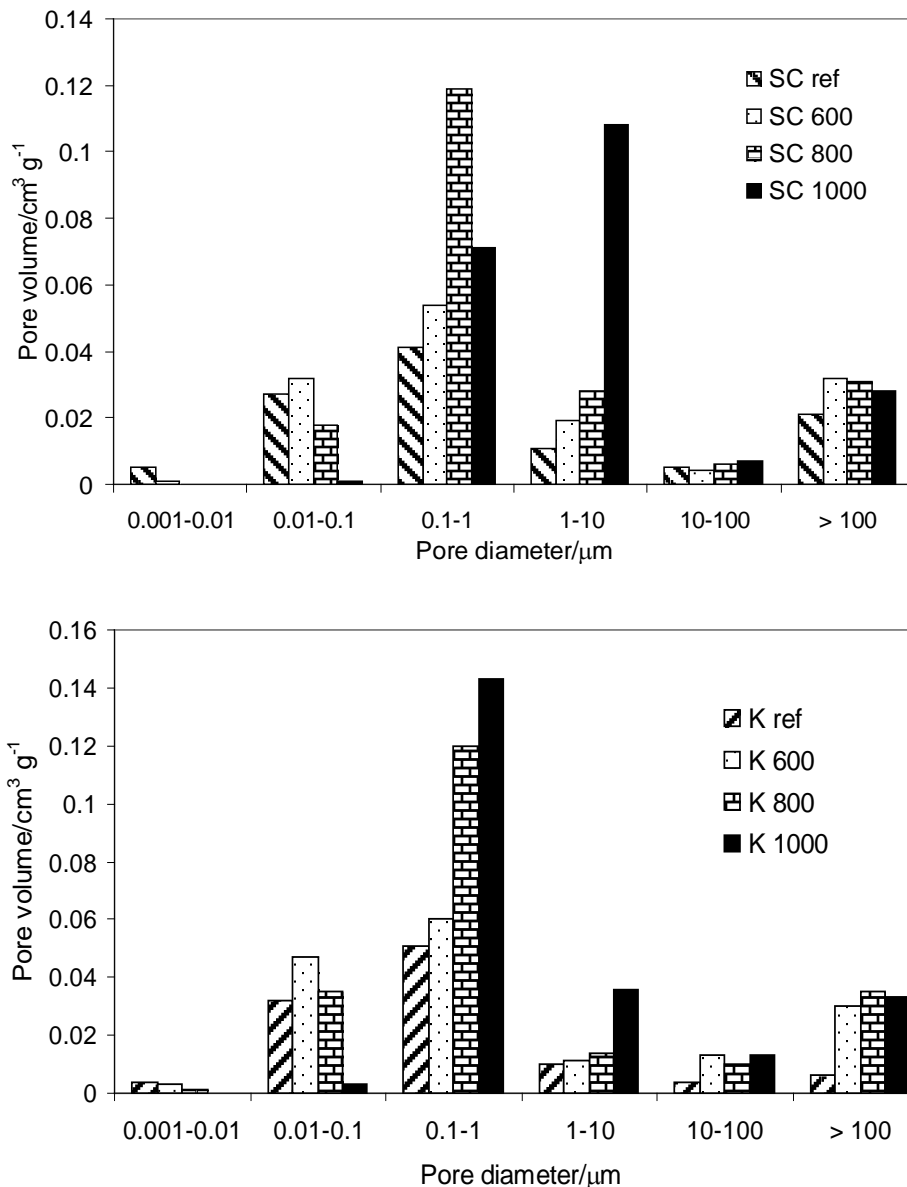


Fig. 2 a Pore size distribution of SC (glass + PP) and K (PVA) composites.

The volume of capillary pores (diameter 0.1 to 100 μm) increases with the thermal load. The explanation has to be searched in thermal dilation of individual components of the materials. The initial (room temperature) quartz modification (α -quartz, specific volume $0,378 \text{ cm}^3 \text{ g}^{-1}$) converts reversibly at 573° C to β -quartz ($0,395 \text{ cm}^3 \text{ g}^{-1}$). Another reversible modification change takes place at 867° C (β -

quartz to β -tridymite; $0,442 \text{ cm}^3 \text{ g}^{-1}$), thus quartz increases its volume by 17 %. Wollastonite aggregates are less sensitive to temperature changes but at approximately 850° C also wollastonite starts to change its volume, β -wollastonite forms [4]. Eventhough these volume changes are reversible, they cause, together with sintering of the binder, the loss of contact between the binder and aggregates which results to formation of new, interconnected to each other, capillary pores between binder and aggregates. The cracks formed between binder and aggregates contribute to the lowering of strength and influences the moisture and heat transport parameters of the material.

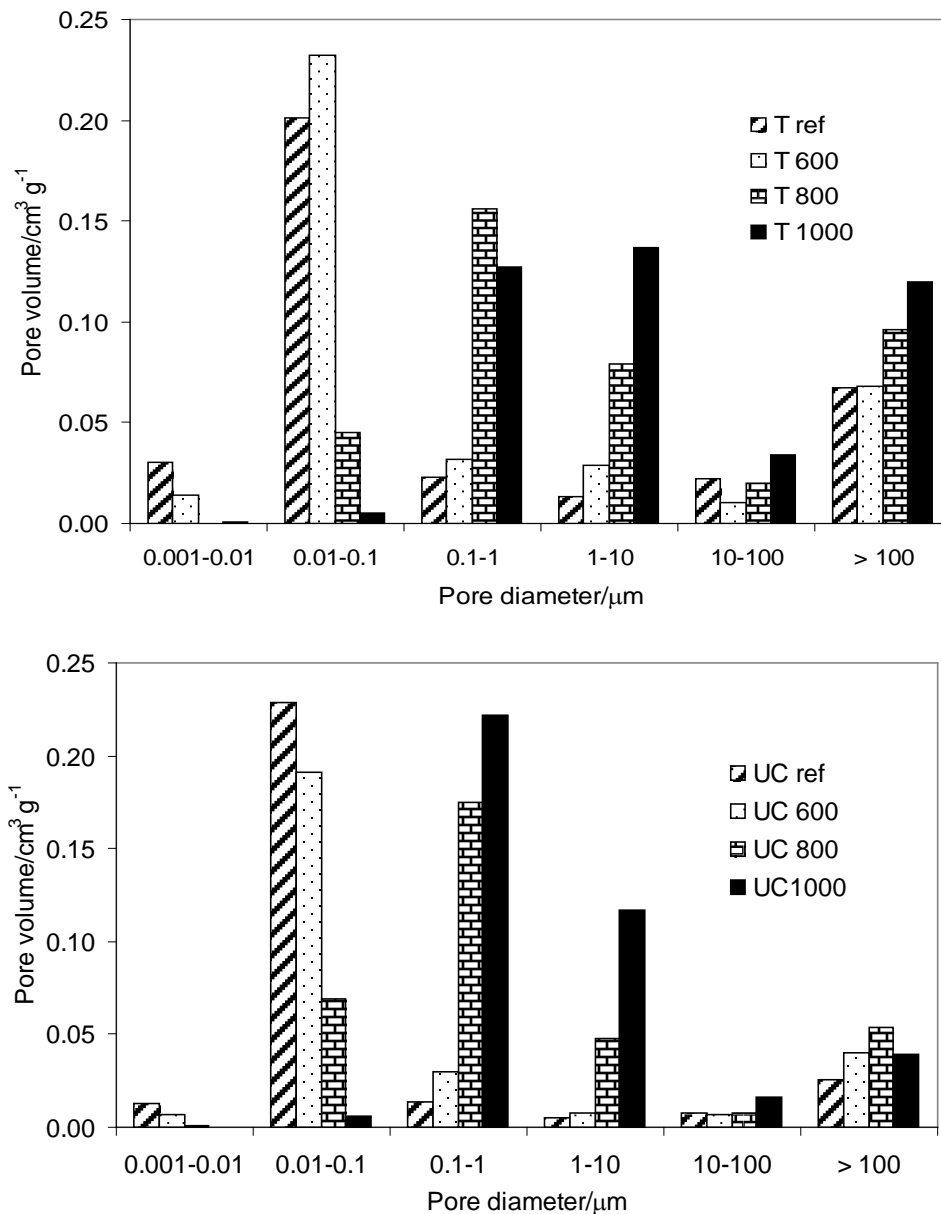


Fig. 2 b Pore size distribution of T (aramid) and UC (carbon) composites.

The volume change of the largest pores in the studied materials may be explained by assuming of different thermal stability of used fibers. Samples SC are reinforced by glass fibers and small amount of PP fibers (0.3 %). The latter obviously burn out at elevated temperature, but the glass fibers should keep their

properties. It was indirectly proved by the MIP measurement (**Fig. 2 a**) where any increase of the largest pores was not observed. The PVA fibers do not resist to elevated temperature. This fact influences significantly the pore size distribution of sample K (**Fig. 2 a**) where one observes high increase of volume of the largest pores due to burn out of the PVA fibers. The aramid fibers (material T) are stable up to cca 500° C where aramid decomposes. Again it has certain influence on the increase of volume of the largest pore fraction in samples T (**Fig. 2 b**). At last, the carbon fibers (UC) incorporated in cement matrix feature good thermal stability (at least at the used experimental conditions) as well as the glass fibers.

One of the important properties which are highly influenced by the pore structure of the material is moisture diffusivity. In fact, the moisture diffusion coefficient is function of moisture content in the material. Within this work, the apparent moisture diffusion coefficients κ_{app} of studied materials were determined by means of imbibition experiment [5]. The rate of water suction was found to be positively dependent on volume of capillary pores. The reasonable linear fit provided variation on well known Arrhenius plot; the logarithm of measured κ_{app} was plotted as function of reciprocal volume of pores of diameter 1 to 100 μm (**Fig. 3**). This dependences fall into straight lines which are able to be described by semiempirical Eq. 2. The meaning of constants A and B is not physically clear and correct, but it may be assumed, that slope B depends on properties of the material, such are its surface energy and morphology of the pore system.

$$\kappa_{app} = A \cdot \exp \left\{ -\frac{B}{V_{1-100}} \right\} \quad (\text{Eq. 2})$$

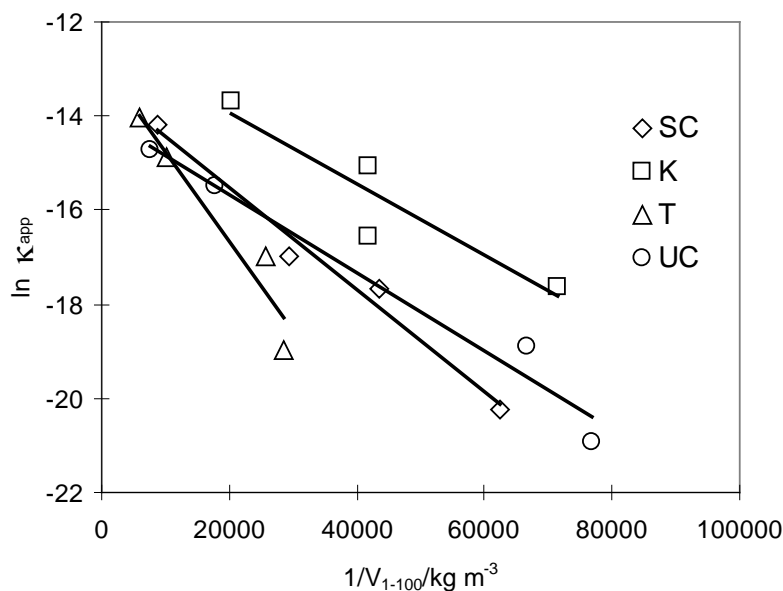


Fig. 3 Measured values of apparent moisture diffusion coefficients plotted as function of capillary pore volume.

Discussion

The characterization of pore system of the studied materials showed that three independent degradation processes are taking place in the materials under thermal load. The binder structure, formed by CSH, CAH and portlandit decomposes thermally and converts to calcite and clinker minerals. The binder

also sinters during the thermal load and the gel pores diminish. On the other hand the aggregates expand during the annealing which causes the loss of contact between binder and aggregates. The thermal decomposition of PVA and aramid reinforcing fibers takes place which results to increase of volume of the largest pore fraction. The carbon and glass fibers were found to be sufficiently stable under the thermal load. The pore size distribution analysis revealed that degradation processes of matrix (gel sintering and aggregates expansion) influence the pore system more significantly than the degradation of thermally unstable fibers. Moreover the channels formed after burn out of the fibers are too large to contribute to capillary action. The thermal stability of fiber reinforced composites could be enhanced by applying of principles used in production of refractory cement: employing of aluminate cement and some aggregates with lower thermally induced volume changes than quartz.

The experimentally determined apparent coefficients of moisture diffusivity were correlated by volume of capillary pores found in the materials. Very simple semiempirical equation describing this relationship was proposed. The physical meaning of the constants in this equation has to be clarified in future.

Conclusions

Three independent degradation processes were identified in thermally loaded fiber reinforced cement composites. The decomposition of cement binder was observed by means of chemical changes as well as by parallel sintering of the gel structure. When the samples were loaded at 1000° C the gel pores diminished completely. The most important – from the point of view of transport properties – is the second degradation process what is loss of contact between binder and aggregates due to the thermal expansion of aggregates. It leads to formation of high amount of interconnected capillary pores which enable intensive transport of liquid water through the material. The decomposition of thermally unstable fibers (PVA, aramide) is responsible for the formation of large channels in the composites, but their contribution to enhanced transport of liquid water is negligible because of the large diameter of these channels. Their contribution to vapor transport would be more important.

Acknowledgement

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