

PROPERTIES OF CEMENTITIOUS COMPOSITES AT HIGH TEMPERATURES

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Abstract:

Cementitious composites subjected to high temperatures undergo chemical reactions which result in decomposition of some of the original compounds of the cement gel. The reliable knowledge of these reactions and their consequences for both the cement matrix and pore space is of crucial importance for understanding the behavior of this type of composites at high temperatures. In this paper, properties of several characteristic cement-based composites are analyzed both after and during high-temperature exposure and their relation to the thermal decomposition processes is analyzed.

Keywords:

Cement-based composites, high temperatures, properties

INTRODUCTION

Thermal and hygric properties of cementitious composites such as concrete, cement mortar and cement paste are measured at room temperature in standard conditions, in most cases. For many applications of concrete in building structures is it quite sufficient as usual environmental exposure is within the range from about -20°C to $+50^{\circ}\text{C}$. However, some concrete structures can be exposed to elevated or high temperatures during their lifetime. Fire resistance problems of concrete structures can be considered probably as the most important example in this respect, but special industrial applications of concrete such as in blast furnaces, nuclear safety related structures or heat pipes also become of great significance. In such conditions, high temperature values of thermal parameters are to be determined to analyze the behavior of the particular structures already in the design phase in a proper way.

Concrete is a material that can survive severe thermal conditions. There are examples of concrete structures that were exposed to a major fire but after reconstruction they were quite serviceable (for instance the Great Exhibition Palace in Prague). Therefore, it may also be useful to know its hygric and thermal properties after high-temperature exposure, in order to assess its serviceability after a fire.

In this paper, properties of several characteristic types of cement-based composites are analyzed both during and after high-temperature exposure.

EFFECT OF HIGH TEMPERATURES ON STRUCTURE AND COMPOSITION OF CEMENT-BASED COMPOSITES

There are numerous methods for investigation of concrete structure and composition which can be utilized in the analysis of the effect of high temperatures on the cement matrix and pore space. Thermal analysis and mercury intrusion porosimetry belong to the simplest but very effective

methods of this type. Therefore, we will use them for the demonstration of basic processes taking place in concrete subjected to high temperatures.

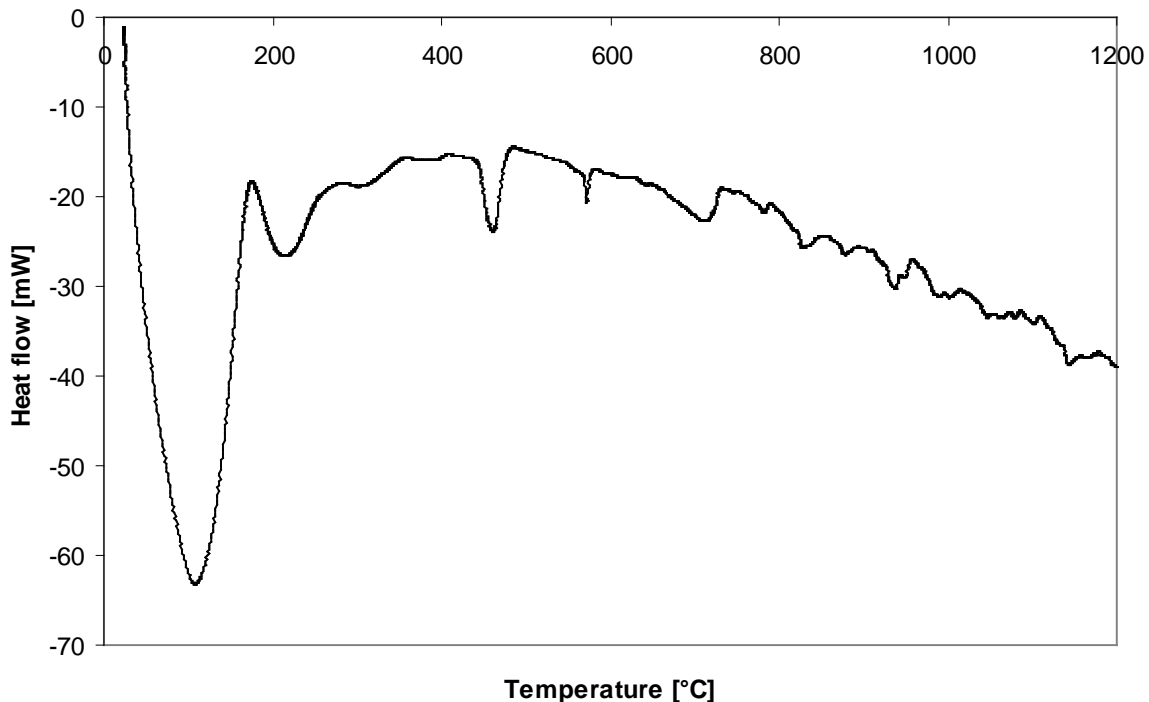


Figure 1 DTA of Portland cement mortar

Fig. 1 shows a typical differential thermal analysis (DTA) curve of Portland cement mortar. The first very pronounced endothermic peak (a minimum) at 107°C represents the evaporation of pore water. This peak probably also includes the decomposition of CSH gels that should take place between 120°C and 140°C [1] and the decomposition of ettringite around 120°C [1]. The second endothermic peak at 212°C corresponds to the decomposition of the aluminate phase $4\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 13\text{H}_2\text{O}$ and sulfoaluminate phases $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ and $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$ [1]. The third significant endothermic peak at 460°C represents the decomposition of $\text{Ca}(\text{OH})_2$ [1]. The sharp endothermic peak at 573°C is apparently not related to the processes in cement. It shows the α/β phase transition of aggregate SiO_2 . The wide endothermic peak with a minimum at 710°C can be assigned to the decomposition of calcium carbonate CaCO_3 which appeared in the material due to the carbonation of calcium hydroxide. The other small peaks in the range of 800–1200°C are difficult to identify because their explanation was not reported yet — as far as the author knows — in the literature.

Fig. 2 shows a typical thermogravimetric (TG) curve of Portland cement mortar which was dried before the TG analysis. The total mass loss observed was 16.25%. The first remarkable mass loss below 200°C is approximately 1 mg (i.e., 2.5% of the mass of the sample) and corresponds to the loss of nearly free water from the pore space and water released from CSH gels and ettringite. Further slower mass decreases on the TG curve up to approximately 400°C can be attributed to the decomposition of aluminate and sulfoaluminate phases. It amounts to 0.93 mg (2.33% of mass) and corresponds to the loss of water from these phases. The fast mass decrease between 450 and 470°C is due to the decomposition of calcium hydroxide. The amount of water released during this decomposition was 0.786 mg (1.97% of mass), which corresponds to 3.23 mg of $\text{Ca}(\text{OH})_2$ in the

sample (i.e., 8.07%). The remarkable mass loss between 600 and 710°C (3.13 mg; i.e., 7.83% of mass) can be assigned to the decomposition of calcium carbonate. The amount of released CO₂ corresponds to 5.26 mg of originally present CaCO₃. The slow mass loss at temperatures higher than 710°C cannot be exactly identified; it is not discussed in detail in the literature.

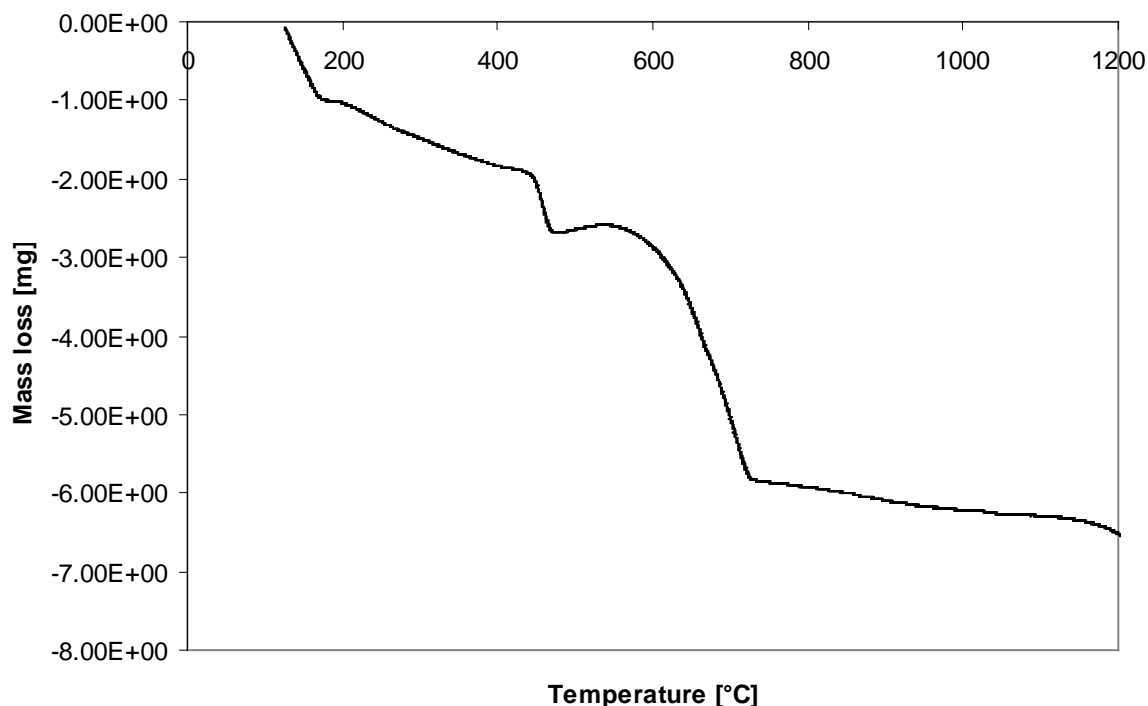


Figure 2 TG of Portland cement mortar

The effect of high temperatures on the pore structure of Portland cement mortar is illustrated in Table 1 and Fig. 3. Table 1 shows global characteristics of the porous space of reference Portland cement mortar and the same mortar which was pre-heated to 800°C for two hours before the measurement; V_p is the total intrusion volume, A_p the total pore area, r_v the median pore radius by volume, ρ the bulk density. Apparently, the effect of thermal load was very pronounced. The median pore radius increased about 15 times compared to the reference specimen, V_p increased by almost 70% and even ρ decreased by 8%.

Table 1 Global characteristics of the pore space of Portland cement mortar

Material	V_p [cm ³ /g]	A_p [m ² /g]	r_v [μm]	ρ [kg/m ³]
Reference mortar	0.073	13.62	0.038	2200
Pre-heated to 800°C	0.122	5.46	0.565	2020

Fig. 3 shows a comparison of pore distribution functions of the reference- and 800°C pre-heated Portland cement mortar specimens. The thermally loaded specimen exhibited a very significant increase of pore volume in the region 0.1 μm - 5 μm compared to the reference mortar but a remarkable decrease was observed in the region of smaller pores, $r < 0.1$ μm.

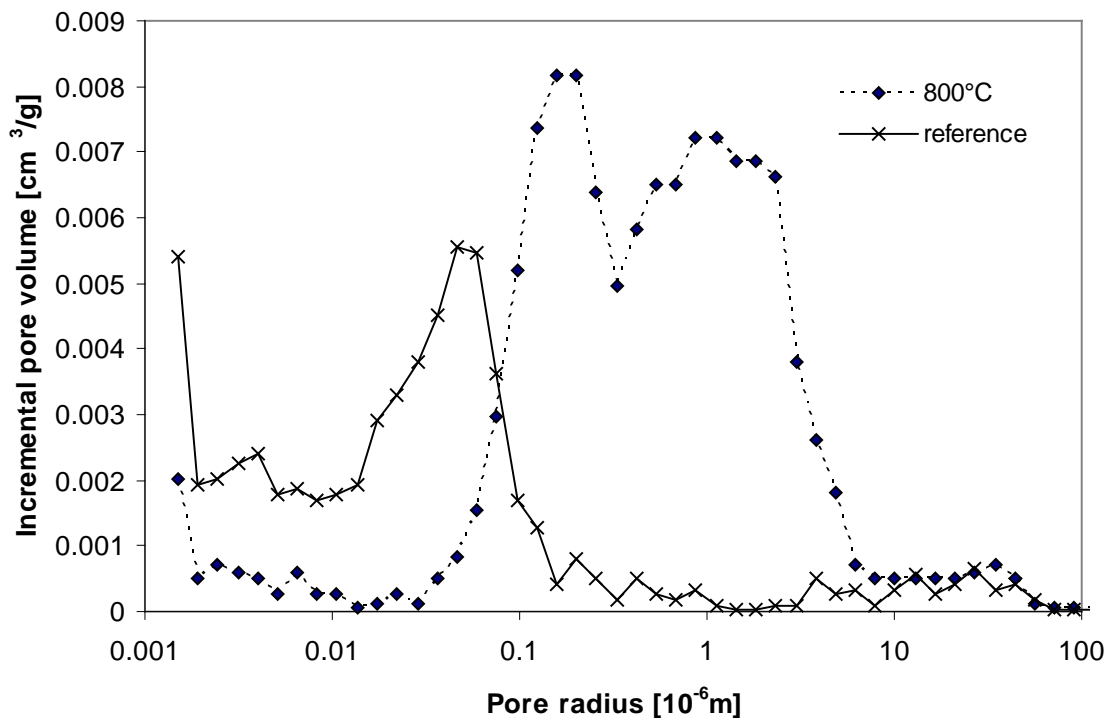


Figure 3 Incremental pore volume of Portland cement mortar

The characteristic example of thermally induced changes in the composition and porous structure of cement mortar presented above gives evidence that the damage of both the matrix and pore space can be quite serious. The rather significant mass loss together with the increase of pore volume and the shift of the major peak of pore distribution curve to the μm range are certainly supposed to result in major changes in principal material parameters. As for the composition and pore structure the material subjected to high temperatures reminds the original Portland cement-based composite only marginally. We will illustrate the effect of high temperatures on hygric and thermal properties of selected Portland cement-based composites, namely cement mortar, high-performance concrete, three types of glass fiber reinforced composites and a carbon fiber reinforced composite material, in what follows.

MATERIALS

The samples of cement mortar (CM) had the following composition (i.e. the mixture for one charge): Portland cement ENV 197 - 1 CEM I 42.5 R (Králov Dvůr, CZ) – 450 g, natural quartz sand with continuous granulometry I, II, III (the total screen residue on 1.6 mm 2%, on 1.0 mm 35%, on 0.50 mm 66%, on 0.16 mm 85%, on 0.08 mm 99.3%) - 1350 g, water – 225 g.

The composition of the high performance concrete (HPC) was as follows: Cement 42.5 R (Mokrá, CZ) - 499 kg/m^3 , sand 0/4 size fraction - 705 kg/m^3 , gravel sand 8/16 size fraction - 460 kg/m^3 , gravel sand 16/22 size fraction - 527 kg/m^3 , water - 215 kg/m^3 , plasticizer - 4.5 l/m^3 .

The samples of glass fiber reinforced cement composites denoted as GC I, GC II, GC III were plate materials with Portland cement matrix (cement CEM I 52.5 Mokrá), which was reinforced by alkali-resistant glass fibers (CEM-FIL 2 250/5B Tex 2450 30 mm for GC I, CEM-FIL 70/30 6 mm for GC II and GC III), the materials GC II and III contained vermiculite and

wollastonite. The basic composition of GC I, II, III is shown in Table 2 (the percentage was calculated among the dry substances, water corresponding to the water to cement ratio of 0.8 was added to the mixture).

Table 2 Composition of glass fiber reinforced cement composites in %.

	Cement	Sand	Plasticizer	Glass fiber	Wollastonite	Vermiculite	Microsilica
GC I	47.99	47.99	0.62	3.40			
GC II	47.60		0.45	3.84	38.50	9.61	
GC III	56.88		0.92	7.66	8.68	21.51	4.35

The carbon fiber reinforced cement composite (denoted as CC) had the composition shown in Table 3 (again calculated among the dry substances only). Portland cement CEM I 52.5 Mokra was used for CC, carbon fiber was pitch based with 10 mm length. Water in the amount corresponding to the w/c ratio of 0.8 was added to the mixture.

Table 3 Composition of carbon fiber reinforced cement composite in %.

Cement	Micro-dorsilite	Plasti-cizer	Carbon fiber	Wolla-stonite	Methyl-cellulose	Defoamer	Microsilica
39.71	16.50	0.98	0.98	39.6	0.11	0.16	1.96

EXPERIMENTAL DETAILS

Moisture diffusivity, thermal conductivity and specific heat capacity were chosen as hygric and thermal parameters most characteristic for the demonstration of the effect of high temperatures on cementitious composites after thermal load. The specimens were heated to either 600°C or 800°C in a furnace, left for two hours at the final temperature and then slowly cooled. The measurements were then done at room temperature on dry specimens.

Thermal conductivity λ and specific heat capacity c in room temperature conditions were determined using the commercial device ISOMET 2104 (Applied Precision, Ltd.). ISOMET 2104 is a multifunctional instrument for measuring thermal conductivity, thermal diffusivity, and volume heat capacity. It is equipped with various types of optional probes, needle probes are for porous, fibrous or soft materials, and surface probes are suitable for hard materials. The measurement is based on analysis of the temperature response of the analyzed material to heat flow impulses. The heat flow is induced by electrical heating using a resistor heater having a direct thermal contact with the surface of the sample.

Moisture diffusivity κ was determined using a simple gravimetric method [2] based on the common sorptivity experiment and the assumption that κ can be considered as piecewise constant with respect to the moisture content. Contrary to the most frequently used methods for κ determination, the method from [2] is very fast even for materials with low κ , and in addition it exhibits a reasonable precision. Therefore, its application for cement based materials is very suitable. The saturated moisture content by mass u_{max} was measured by the capillary saturation

method. The specimen was dried at 110°C and weighed, then left for 24 hours in water, weighed again and its moisture content by mass calculated. Water vapor diffusion permeability δ was measured by the common dry cup method [3].

Specific heat capacity, thermal diffusivity and linear thermal expansion coefficient were measured in the temperature range up to 1000°C. As the adiabatic methods are not very suitable for measuring high-temperature specific heat capacity of building materials, mainly because of the necessity to use relatively large samples, a nonadiabatic method [4] was employed for the determination of temperature-dependent specific heat capacity. The measurements of high-temperature thermal diffusivity were done using the double integration method [5]. The thermal diffusivity was determined using the results of experimental measurements of temperature fields in the sample at one-sided heating in the solution of the inverse heat conduction problem. The measurements of linear thermal expansion coefficient were performed by the method described in [6]. This method consists in using a comparative treatment with a known material. A set of strain values corresponding to the given temperatures is determined and the linear thermal expansion coefficient calculated as the first derivative of the strain vs. temperature function with respect to temperature.

RESULTS AND DISCUSSION

Tables 4-9 show the thermal and hygric parameters of studied cement based composites after thermal load. The decrease of room temperature thermal conductivity after exposure to high temperatures that was observed for all materials (except for the high performance concrete where these measurements were not performed) is a consequence of decomposition processes in the Portland cement matrix described before. The decomposition of calcium hydroxide was apparently the most important process from this point of view because the decrease of thermal conductivity was faster between 25°C and 600°C than between 600°C and 800°C. The decrease of thermal conductivity after thermal load was much higher for cement mortar (about 4-5 times) than for fiber reinforced composites (less than 50% in all cases) although the density decrease was quite comparable. This is clearly a positive effect of fiber reinforcement that was able to keep the cement matrix together even after significant decomposition processes and prevent it from the formation of wide cracks, which play the most important role in the decrease of thermal conductivity. This effect was even more pronounced in the moisture diffusivity measurements. While 3 orders of magnitude increase of moisture diffusivity was observed for cement mortar after exposure to 800°C, for GC II, GC III and CC this increase was only about one order of magnitude. High performance concrete exhibited two orders of magnitude increase in moisture diffusivity which was comparable to GC I. The adhesion of fibers to the cement matrix was for GC I probably worse than for the other studied fiber reinforced composites. Water vapor permeability was affected by the high-temperature exposure in a less significant way than moisture diffusivity for all analyzed materials but the changes were important yet; δ increased up to three times compared to the reference specimens. The effect of fibers was not clearly distinguished in this case. The relative increase of water vapor permeability was similar for high performance concrete and fiber reinforced concretes. Apparently, these findings were related to the lower sensitivity of water vapor diffusion to large crack appearance compared to moisture diffusivity and thermal conductivity. While water vapor transport in porous media is more or less related to the volume of open pores, the liquid moisture transport is very sensitive to opening of preferential paths and thermal conductivity of porous materials is highly dependent on the topological characteristics of the porous space.

Table 4 Thermal and hygric parameters of cement mortar after thermal load

Temperature exposure [°C]	ρ_s [kg m ⁻³]	c [J kg ⁻¹ K ⁻¹]	λ [W m ⁻¹ K ⁻¹]	u_{max} [%]	κ [m ² s ⁻¹]	δ [s]
25	2130	850	1.16	8.0	9.70E-9	3.34E-12
800	2020	-	0.27	13.4	1.00E-5	4.03E-12

Table 5 Thermal and hygric parameters of high performance concrete after thermal load

Temperature exposure [°C]	ρ_s [kg m ⁻³]	c [J kg ⁻¹ K ⁻¹]	λ [W m ⁻¹ K ⁻¹]	u_{max} [%]	κ [m ² s ⁻¹]	δ [s]
25	2206	800	1.58	7.0	1.77E-8	3.07E-12
600	2172	-	-	8.8	8.53E-7	1.18E-11
800	2156	-	-	9.8	2.74E-6	-

Table 6 Thermal and hygric parameters of GC I after thermal load

Temperature exposure [°C]	ρ_s [kg m ⁻³]	c [J kg ⁻¹ K ⁻¹]	λ [W m ⁻¹ K ⁻¹]	u_{max} [%]	κ [m ² s ⁻¹]	δ [s]
25	1960	920	1.124	10.6	1.28E-09	4.09E-12
600	1865	920	0.706	15.6	9.57E-08	8.53E-12
800	1820	900	0.666	16.2	1.79E-07	1.35E-11

Table 7 Thermal and hygric parameters of GC II after thermal load

Temperature exposure [°C]	ρ_s [kg m ⁻³]	c [J kg ⁻¹ K ⁻¹]	λ [W m ⁻¹ K ⁻¹]	u_{max} [%]	κ [m ² s ⁻¹]
25	1090	1090	0.275	47.5	2.52E-08
600	1030	1050	0.198	56.8	1.27E-07
800	990	960	0.160	56.8	3.18E-07

Table 8 Thermal and hygric parameters of GC III after thermal load

Temperature exposure [°C]	ρ_s [kg m ⁻³]	c [J kg ⁻¹ K ⁻¹]	λ [W m ⁻¹ K ⁻¹]	u_{max} [%]	κ [m ² s ⁻¹]
25	970	1285	0.274	58.1	3.36E-08
600	900	947	0.198	68.4	1.92E-07
800	900	837	0.159	68.4	3.36E-07

Table 9 Thermal and hygric parameters of CC after thermal load

Temperature exposure [°C]	ρ_s [kg m ⁻³]	c [J kg ⁻¹ K ⁻¹]	λ [W m ⁻¹ K ⁻¹]	u_{max} [%]	κ [m ² s ⁻¹]	δ [s]
25	1610	1020	0.511	25	5.63E-09	1.71E-11
600	1480	930	0.382	28	2.08E-08	2.49E-11
800	1430	870	0.366	28.5	7.67E-08	4.01E-11

The results of specific heat capacity measurements are shown in Fig. 4. Two basic types of $c(T)$ functional relationships could be identified. The first was characteristic for cement mortar, high performance concrete and GC I. Here $c(T)$ was an increasing function up to about 600°C, and then it began to decrease. For GC II, GC III and CC $c(T)$ was a decreasing function in the whole studied temperature range.

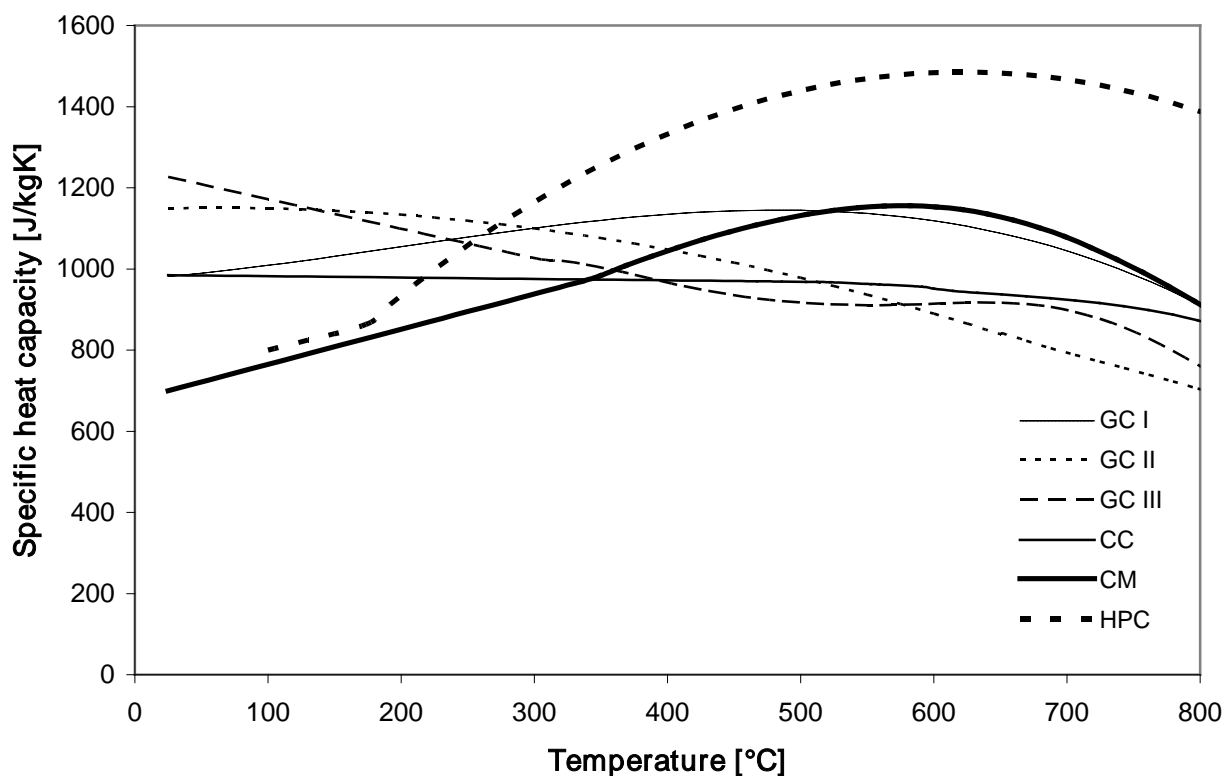


Figure 4 Specific heat capacity of cement based composites

The relatively fast increase of specific heat capacity of cement mortar in the temperature range of 25-600°C can be attributed probably to the effect of siliceous aggregates. Silicon dioxide has at 25°C the specific heat capacity of 730 J/kgK while at 575°C it is 1380 J/kgK [7]. This is in basic accordance with our results because the cement to sand ratio for the cement mortar was 1:3, for high performance concrete 1:3.4, so that the effect of aggregates on the specific heat capacity (which is an additive quantity in the sense of the theory of mixtures) was very pronounced. Similarly we can explain the decrease of the specific heat capacity of cement mortar above 600°C. Silicon dioxide undergoes at 573°C the $\alpha \rightarrow \beta$ transition [7], and the newly formed β form has the specific heat capacity of only 1125 J/kgK [7].

Similar effects to those of cement mortar and high performance concrete could be observed on GC I which had similar composition except for the cement to sand ratio that is 1:1. This might be the reason of the slower increase of the $c(T)$ function in the temperature range of 25-600°C.

As for the remaining materials, their $c(T)$ function behavior could not be explained even in a similar rough and simple way like with cement mortar and GC I because of the lack of reliable data for the specific heat capacities of their particular compounds. Another factor making any statement in this sense even more complicated were the chemical reactions in cement gel after heating that resulted in fact in a determination of specific heat capacity for a set of different materials.

The specific heat capacity of the studied cementitious composites exhibited various temperature dependences for different materials. The increasing character of the $c(T)$ functions that is typical for most crystalline solids [7] was observed for the materials with siliceous aggregates, and only up to 600°C. For the other materials the specific heat capacity decreased with temperature. Although this type of $c(T)$ function is not very common, it might be explained in general by the complicity of the studied systems where quite a few chemical reactions and phase transitions occur after the temperature increase.

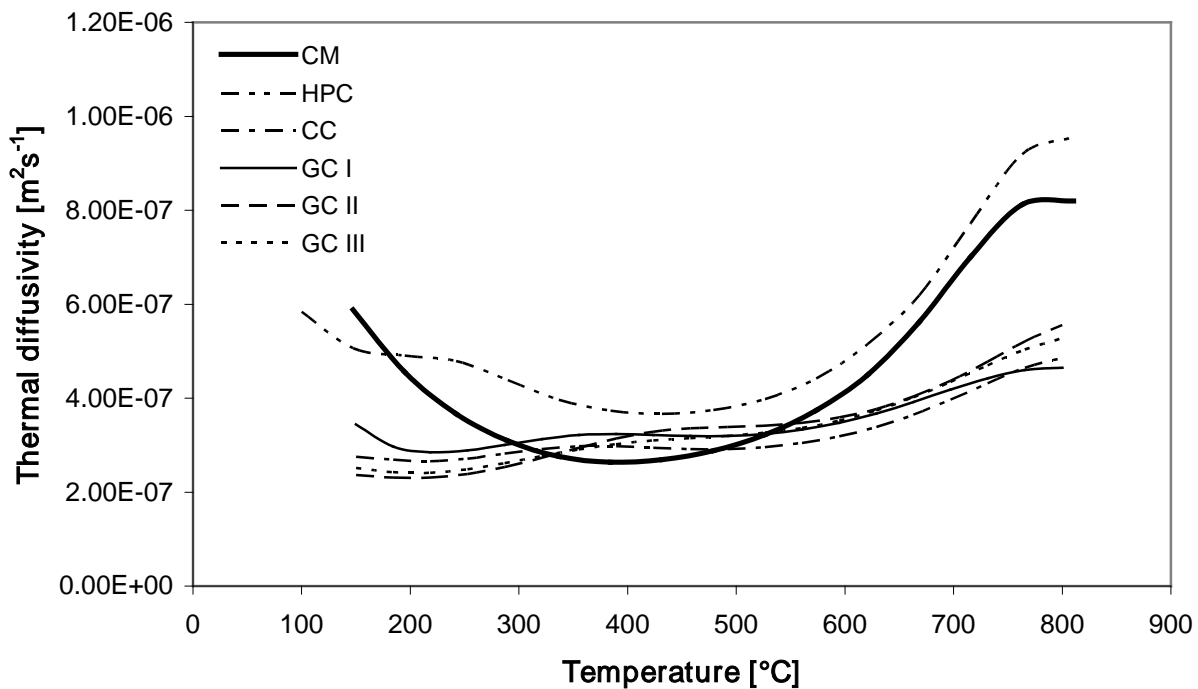


Figure 5 Thermal diffusivity of cement based composites

Fig. 5 shows the results of high-temperature thermal diffusivity measurements. The highest values of thermal diffusivity were achieved in the whole temperature range by high-performance concrete, which is an expected result because it has the highest bulk density (see Tables 4-9). The lighter fiber reinforced composites had significantly lower thermal diffusivity, down to about one half of the values of HPC. The thermal diffusivity of cement mortar was somewhere between these two limits. The character of thermal diffusivity dependence of fiber reinforced composites was different than for HPC and cement mortar without any reinforcement. While the thermal diffusivity of fiber reinforced composites increased in the whole range of temperatures, the thermal diffusivity of HPC and cement mortar first decreased and from 400°C it began to increase. The slower increase of thermal diffusivity of fiber reinforced composites in the range of highest temperatures compared to the cement based materials without any reinforcement can clearly be attributed to the positive effect of the fiber reinforcement that was in certain range able to prevent from opening wide cracks magnifying the convective mode of heat transfer. It should also be noted that the thermal diffusivity of GC I was only slightly higher than of other fiber reinforced cement composites (a higher difference was in the range of lower temperatures up to 400°C) although its density was significantly higher. So, the effect of fiber reinforcement was in the highest temperature range similar for both heavier and lighter fiber reinforced composites. This may be related to the worse mechanical properties of the cement matrix of lighter composites.

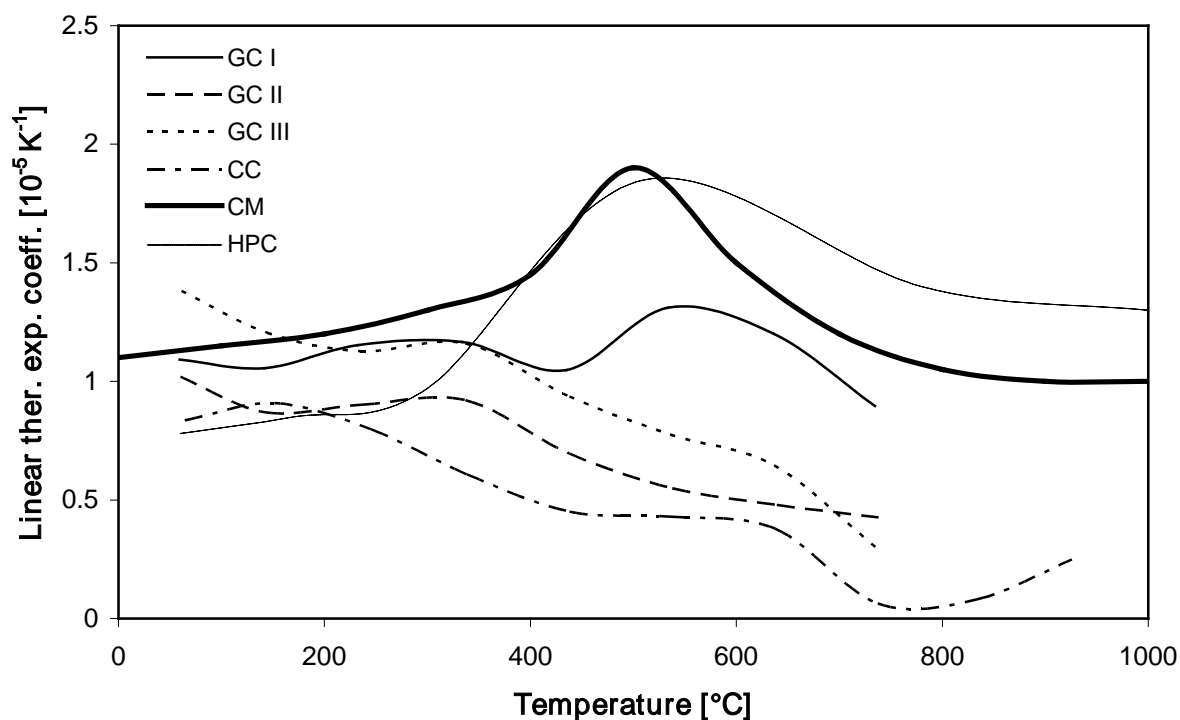


Figure 6 Linear thermal expansion coefficient of cement based composites

The results of measurements of the linear thermal expansion coefficient in the high temperature range (Fig. 6) exhibit once again the positive effect of fiber reinforcement. The linear thermal expansion coefficient of cement mortar and high performance concrete was significantly higher compared to the fiber reinforced composites and markedly increased with temperature up to about 500-600°C. For GC II, GC III and CC the linear thermal expansion coefficient even decreased with temperature in almost whole the temperature range studied. Apparently, the fibers were for these composites able to prevent the matrix from an excessive volume increase due to their good adhesion – contrary to GC I where the linear thermal expansion coefficient was almost constant up to about 600°C. The decrease of linear thermal expansion coefficients in the highest temperature range for most materials is clearly related to the decomposition processes in the cement matrix, where the main role play the decomposition of calcium hydroxide at 460°C and calcium carbonate in the temperature range between 700-800°C.

CONCLUSIONS

Three main factors were shown to affect the hygric and thermal properties of cementitious building materials exposed to high temperatures. The first was the decomposition processes in the cement binder and was clearly negative. The worsening of hygric properties after high-temperature exposure induced by the increase in open porosity and wide crack opening can have fatal consequences for durability of a cement-based material. Presence of fibers as the second factor had in all cases positive consequences; they could partially keep the cement matrix together even after significant decomposition of cement hydration products. However, their positive effects were limited to the moment when glass fibers were melted and carbon fibers exposed to the oxygen from the air after crack opening. The third factor was the composition of the composite. Using vermiculite instead of sand aggregates was clearly positive because of its porous character.

Wollastonite was better choice than sand because of its fibrous character that could partially magnify the effect of fiber reinforcement.

The problem of significant changes in hygric and thermal properties of cementitious composites induced by high temperatures can be regarded with another horizon yet. These changes can serve as sensitive indicators of damage which may not seem apparent in some cases. In particular, the water transport properties may be considered as reliable tool in that respect. Moisture diffusivity is subject of substantial increase if any preferential paths for the transport of liquid water appear; these can be formed even by very small cracks.

ACKNOWLEDGEMENT

This research has been supported by the Czech Science Foundation, under project No 103/06/1474.

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