

SPECIFIC HEAT CAPACITY OF CEMENTITIOUS COMPOSITES IN HIGH-TEMPERATURE RANGE

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Abstract

Specific heat capacity c of several cementitious materials, namely cement mortar, three types of glass fiber reinforced composites and two types of carbon fiber reinforced composites, is determined in the temperature range of 25⁰C to 800⁰C. Two basic types of $c(T)$ functional relationships are identified. The first characteristic for materials with siliceous aggregates is an increasing function up to about 600⁰C, which then begins to decrease. The second is a decreasing function in the whole studied temperature range.

Key words: cementitious composites, specific heat capacity, high temperatures

1 Introduction

Fiber reinforced cement composites are produced by incorporating a small amount of fibers in cement mortar to overcome the traditional weakness of inorganic cements, namely poor tensile strength and brittleness. The length and content of the fiber reinforcement can be chosen to meet the strength and toughness requirements of the product. Also, the type of aggregates can be varied in order to control thermal properties.

Glass fiber reinforced cement composites (GFRCC) have found their place as versatile and commercially viable materials for use in construction industry in the beginning of 1970s [1]. Currently, they are frequently applied in wall systems, utilized in form work, pipework, used for surface bonding and rendering, etc. They can also replace asbestos cement products as fire protection materials. More detailed survey of GFRCC applications can be found e.g. in [1]-[3].

Carbon fiber reinforcement has found its application first in polymeric matrices for automotive and aircraft industry. It partially replaced previously used glass fibers in such situations where superior strength properties, very low tensile strains and mass savings were necessary. The initial phases of utilization of carbon fibers in the production of composite materials were affected by its high price. Carbon fiber is produced by the controlled oxidation, carbonization and graphitization of carbon-rich organic precursors, which are already in fiber form. In the beginnings of carbon fiber production the most often used precursor was PAN (polyacrylonitrile) that gave

superior carbon fiber properties but was quite expensive. The appearance of low cost pitch based carbon fibers in 1980s has led to a significant increase of various applications of carbon fibers. In the construction industry it resulted in an increasing use of carbon fiber reinforced cement composites (see, e.g., [4] for details). A comprehensive survey of both properties and processing of carbon fibers and of the various types of carbon fiber reinforced composites can be found in [5].

In the current research practice, the mechanical properties of fiber reinforced cement composites (FRCC) are in the center of interest of most researchers working on those materials. This is quite logical taking into account why they were developed, i.e. to improve the tensile and flexural strength of cement based composites. However, there are numerous applications of fiber reinforced composites that require a good knowledge of thermal parameters. For instance, lightweight FRCC can be used as thermal insulation materials, other FRCC can be employed as fire protection materials, etc. Therefore, the knowledge of thermal properties of FRCC particularly in high temperature range is very important.

In this paper, specific heat capacity of several carbon and glass fiber reinforced cement composites is determined in a wide temperature range and compared with cement mortar.

2 Method for the determination of specific heat capacity

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 by Toman and Černý (see [6] for details) was employed for the determination of temperature-dependent specific heat capacity. We will present the main idea of the method in what follows.

The nonadiabatic calorimeter that we used has a mixing vessel with a volume of 2,5 liters. The volume of the measuring fluid (water in this case) is about 1 liter. The maximum volume of the measured samples is 1 liter. The amount of heat loss of the nonadiabatic system is determined using a calibration. The calorimeter is filled with water, whose temperature is different from the ambient air. Then, the relation of water temperature to time, $T_c(t)$, is measured.

The tests show that the calibration curve $T_c(t)$ is nearly exponential; small differences in measuring conditions cause only small changes in the calibration curve. The experiments have a replicability better than 1%.

The measuring method itself is based on well-known principles. The sample is heated to a predetermined temperature T_s in a muffle furnace and then put into the calorimeter with water. Then, the relation of water temperature to time $T_w(t)$ is measured, the water being slowly stirred all the time, until the temperatures of the measured sample and the calorimeter are equal. The duration of temperature equilibration achieves typically several hours, depending on the thermal conductivity and size of the material being measured.

The heat balance of the sample-calorimeter system can be written in the form:

$$mc(T_s - T_e) = (K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r, \quad (1)$$

where m is the mass of the sample, T_s the temperature of the sample prior to being put into the calorimeter, c the specific heat capacity of the sample in the temperature interval $[T_e, T_s]$, K the heat capacity of the calorimeter, m_w the mass of the water, c_w the specific heat capacity of water, T_{wo} the initial water temperature, L the latent heat of evaporation of water, Q_r the reaction heat of a possible hydrolysis, Δm the mass of evaporated water.

Determining the specific heat capacity c directly from equation (1) we would obtain a mean value of specific heat capacity, c_{mean} , in the interval $[T_e, T_s]$ by

$$c_{mean} = \frac{(K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r}{m(T_s - T_e)}. \quad (2)$$

However, from the physical point of view, it is more correct to determine the value of the specific heat capacity "pointwise", in accordance with the basic physical definition of the specific heat capacity,

$$c(T) = \frac{\partial h(T)}{\partial T}. \quad (3)$$

Using relation (3) to determine the specific heat capacity, we have to specify the zero-point of the enthalpy scale, i.e., we have to ensure that all the enthalpy calculations are related to a certain constant temperature. This reference temperature can be, for example, $T_k = 0^{\circ}\text{C}$. Upon adding

$$Q = mc_o(T_e - T_k), \quad (4)$$

where c_o is the mean specific heat capacity of the sample in the temperature interval $[0, T_e]$, to both sides of equation (1), and dividing by m , we obtain

$$h(T_s) = \frac{(K + m_w c_w)(T_e - T_{wo}) + \Delta m \cdot L - Q_r}{m} + c_o(T_e - T_k). \quad (5)$$

The value of c_o is considered to be constant, taking into account the condition

$$T_s - T_e \gg T_e - T_k \quad (6)$$

and it can be measured, for example, using the classical adiabatic mixing method.

Performing a set of measurements for various sample temperatures T_i , we obtain a set of points $[T_i, h(T_i)]$. A regression analysis of this pointwise given function results in a functional relationship for $h = h(T)$ and, using relation (3), also in the function $c = c(T)$ as the first derivative of h with respect to T .

3 Materials and samples

The experiments were done with several different types of cementitious materials, cement mortar, three types of glass fiber reinforced composites and two types of carbon fiber reinforced composites.

The samples of cement mortar had the following composition (i.e. the mixture for one charge): Portland cement ENV 197 - 1 CEM I 42.5 R (Kráľův 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 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 Mokra), 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 1 (the percentage is calculated among the dry substances only, water corresponding to the water to cement ratio of 0.8 is to be added to the mixture).

Table 1 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 specimens (denoted as CC I and CC III) had the composition shown in Table 2 (again calculated among the dry substances only). Portland cement CEM I 52.5 Mokra was used for CC I, aluminous cement Alcoa CA-14M for CC III, 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 for CC I, 0.73 for CC III.

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

	Cement	Micro-dorsilite	Plasti-cizer	Carbon fiber	Wolla-stonite	Methyl-cellulose	Defoamer	Microsilica
CC I	39.71	16.50	0.98	0.98	39.6	0.11	0.16	1.96
CC III	40.00	28.40	0.80	1.00	29.50	0.10	0.20	-

The dimensions of the specimens were 71x71x71 mm.

4 Experimental results and discussion

The results of specific heat capacity measurements carried out using the nonadiabatic method described in Section 2 are shown in Fig. 1. Two basic types of $c(T)$ functional relationships can be identified. The first is characteristic for cement mortar, GC I and CC III. Here $c(T)$ is an increasing function up to about 600°C, and then it begins to decrease. For GC II, GC III and CC I $c(T)$ is a decreasing function in the whole studied temperature range.

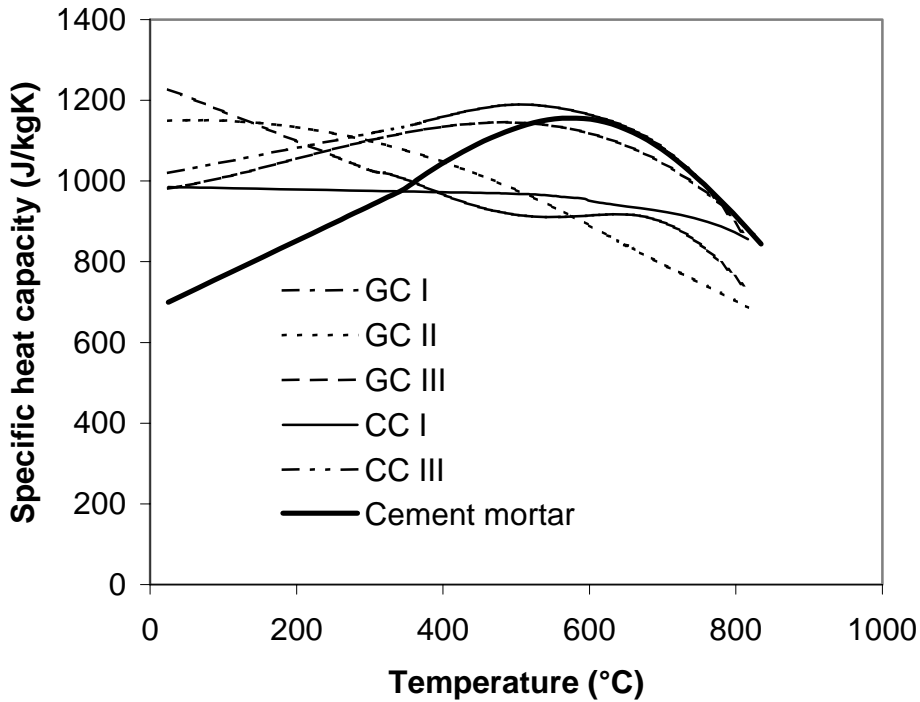


Fig. 1 Specific heat capacity of studied cementitious composites

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 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 on cement mortar can be observed on GC I which has a 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 cannot 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 are the chemical reactions in cement gel after heating that result in fact in our case in a determination of specific heat capacity for a set of different materials.

5 Conclusions

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 (see, e.g., [7]) was observed for the materials with siliceous aggregates, and only up to 600⁰C. 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.

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