SPECIFIC HEAT CAPACITY OF BUILDING MATERIALS AT HIGH TEMPERATURES

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1. Introduction

Many building materials contain components undergoing chemical reactions not only in the production phase but also after their incorporation in a building structure. Hydration and carbonation of cement containing materials can be considered as a typical example of such reactions. Occurrence of chemical reactions can change thermal behavior of a particular material since heat can be produced or absorbed depending on the type of reaction. These processes are accentuated with the increasing temperature when the reactions are faster, and for some material components increasing risk of burning arises.

A representative mathematical description of transport phenomena in building materials at higher temperatures, which is particularly important for instance in the solution of fireprotection tasks, includes formulation of a relatively complicated problem of continuum mechanics and thermodynamics. Generally, it can be solved using the theory of chemically reacting mixtures [1], and formulating a set of balance equations for both the mixture and the particular components, which has to be closed with the help of material relations derived by means of nonequilibrium thermodynamics. Solution of large sets of differential equations obtained by this way was not very frequent in practical applications until now for several reasons: analytical solutions are mostly not available, numerical solutions can face problems with computer memory and reasonable CPU time, and in addition, many material parameters entering the equations after applying the laws of nonequilibrium thermodynamics are very difficult to measure. Therefore, simplifications making the solutions easier while keeping characteristic features of the process are desirable.

In [1], a concept of effective specific heat capacity of building materials was introduced which included also thermal effects due to the chemical reactions and/or phase change processes. In this paper, we present an example of application of the effective specific heat capacity concept from [1] for several typical building materials.

2. 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 batch): Portland cement ENV 197 - 1 CEM I 42.5 R (Králův 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 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 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 remoteed cement composites in 76.												
	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					

Table 1 Composition of glass fiber reinforced cement composites in %

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 Mokrá 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.

	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	-

Table 2 Composition of carbon fiber reinforced cement composites in %

The dimensions of the specimens were 71x71x71 mm.

3. Experimental Methods

Using the classical adiabatic-calorimetry methods in measuring the specific heat capacity of building materials can lead to certain difficulties because the samples of mostly inhomogeneous building materials have to be relatively large. In combination with their low thermal conductivity this results in relatively long times necessary to reach temperature equilibration, thus in significant heat loss. Therefore, a nonadiabatic method [2] was employed for the determination of temperature-dependent specific heat capacity.

4. Experimental Results and Discussion

The results of specific heat capacity measurements carried out using the nonadiabatic method from [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^oC can be attributed probably to the effect of siliceous aggregates. Silicon dioxide has at 25^oC the specific heat capacity of 730 J/kgK while at 575^oC it is 1380 J/kgK [3]. 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^oC. Silicon dioxide undergoes at 573^oC the $\alpha \rightarrow \beta$ transition [3], and the newly formed β form has the specific heat capacity of only 1125 J/kgK [3].

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 binder 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., [3]) 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 complexity of the studied systems where quite a few chemical reactions and phase transitions occur after the temperature increase.

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References

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MĚRNÁ TEPELNÁ KAPACITA STAVEBNÍCH MATERIÁLŮ ZA VYSOKÝCH TEPLOT

Anotace

V článku je prezentována koncepce efektivní měrné tepelné kapacity, která pro stavební materiály za vysokých teplot představuje značné zjednodušení v porovnání s klasickou analýzou v rámci termomechaniky kontinua. Praktické aplikace této koncepce je ilustrována na příkladu několika typických stavebních materiálů vystavených působení vysokých teplot do 1000^{0} C.