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ANALYSIS OF GLASS FIBER REINFORCED CEMENT COMPOSITES AND THEIR THERMAL AND HYGRIC MATERIAL PARAMETERS

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Abstract

Methods of thermal analysis are employed in a study of the high-temperature properties of three different types of glass fiber reinforced cement composites together with the measurements of their thermal and hygric parameters. First, basic TG and DTG measurements are carried out to get the first insight into the high-temperature behavior of the analyzed materials. Then, mercury porosimetry and scanning electron microscopy of specimens subjected to the temperatures of 600 and 800°C are performed and compared to the reference specimens not exposed to any thermal load. Finally, measurements of thermal and hygric parameters of the studied materials are done and matched with the results of the material characterization experiments. Three main effects are found to influence the thermal and hygric properties of the analyzed materials. The first is the decomposition of the cement matrix, which is clearly a negative factor. The second is the positive effect of the presence of fibers that could partially keep the cement matrix together even after significant decomposition of cement hydration products. The third important factor affecting the thermal and hygric properties is the composition of the particular materials. The application of vermiculite aggregates instead of sand is found to be clearly positive because of its porous character leading to the bulk density decrease without worsening the other properties. Also, wollastonite aggregates are a better choice than sand because of its fibrous character that could partially magnify the effect of fiber reinforcement.

Keywords: glass fiber reinforced cement composites, hygric properties, mercury porosimetry, scanning electron microscopy, thermal analysis, thermal properties

Introduction

Cement-based materials are characterized by very good properties in compression but their brittle manner of failure under tensile or impact load was a limiting factor for their

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applicability range from the very beginnings. Fiber reinforcement is a traditional and effective method how to improve the toughness and durability of cement based products. The steel rod reinforcement became very popular during the whole last century and remains the most frequently used type of concrete reinforcement until now. However, in the second half of the 20th century, an application of uniformly dispersed short fibers strengthening the brittle cementitious matrices appeared with an increasing frequency. In the current practice, steel, glass, carbon and various polymeric fibers such as polyethylene, polypropylene, nylon, polyester, polyurethane, cellulose, etc., are commonly used in cement-based materials. The positive effect of randomly distributed fibers on the fire properties of cementitious composites may consist in their ability to keep the basic cement matrix together even after high temperature exposure. Another possibility is using fibers that burn out at relatively low temperatures and form in this way preferential paths for the removal of gaseous products of decomposition chemical reaction of cement binder. The effect of fibers is mostly combined with that of properly used fillers. Traditional aggregates can be replaced with materials having a better resistance to high temperatures that can protect fibers from melting or burning for longer time.

Thermal analysis is not often used for investigation of cementitious composites [1–6]. They are mostly supposed to be subjected to common environmental conditions as building materials [1, 2] which seems to be a logical reason for studying them mainly in the temperature range of about –20 to +50°C. However, there is a number of practical applications when cement based materials can be exposed to elevated and high temperatures. The most often mentioned situation is a fire of a structure, which was actually the main reason why the properties of cementitious composites in high temperature range began to be considered. However, there are a variety of other applications where high temperature properties of cement based materials can also be very important, for instance walls and floors exposed to high temperatures from various heat machines, pipes or chemical process vessels, envelopes or linings of special vessels such as coal gasification vessel, nuclear safety related structures in nuclear power plants, etc. In all these cases, the knowledge of high temperature properties is a necessary condition for making both performance assessment and service life assessment of the particular structure.

In this paper, thermal analysis is used in a study of the high-temperature properties of three different types of glass fiber reinforced cement composites (GFRCC) and its results are matched with the measurements of thermal and hygric parameters.

Experimental methods

Material characterization

Thermal analysis, TG and DTG were carried out using Derivatograph device – maximum temperature 1000°C, the rate of temperature increase 5°C min^{-1}. The porosimetric measurements were performed using the mercury porosimeter Micromeritics Poresizer 9310 – maximum working pressure 200 MPa, pore distribution in the range 300 to 0.006 μm. Scanning electron microscope Jeol JSM-U3 with 10 nm resolution was used for SEM measurements.

Thermal and hygric parameters

Among the thermal properties, room temperature thermal conductivity and specific heat capacity were determined using the microprocessor controlled portable device Isomet 104 (Applied Precision, Ltd). The measurements of high-temperature thermal diffusivity were carried out using the method of Černý and Toman [7] based on the measurement of temperature field in the sample during one-sided heating and a subsequent solution of an inverse problem of heat conduction. The measurements of high-temperature linear thermal expansion were performed using the device of Toman *et al*. [8] based on the application of a comparative technique.

The term ‘hygric parameters’ is common in building physics and the readers in the field of thermal analysis and calorimetry may not be very familiar with it. Therefore, we note that this term usually means water and water vapor transport and storage parameters in general. In this work, we used liquid moisture diffusivity as a typical hygric parameter characterizing the behavior of cementitious composites after subjecting them to high temperatures. The moisture diffusivity was determined by the simple gravimetric method of Drchalová and Černý [9] based on a one-sided water suction experiment.

Materials

The measurements were conducted on three types of glass fiber reinforced cement composites, denoted as SC-I, II, III in what follows. The samples were plate materials with Portland cement matrix, which was reinforced by alkali-proof glass fibers, the materials SC-II and III contained vermiculite and wollastonite. The basic composition of SC-I, II, III is shown in Table 1 where the percentage is calculated among the dry substances only. Cement CEM I 52.5 Mokrá was used in all materials. Glass fibers Nippon Electric Glass with the length of 35 mm and 14 mm diameter were used for SC I, CEM-FIL 70/30 with the length of 6 mm and 20 mm diameter for SC II and SC III. The water to cement ratio was for SC I 0.36, for SC II 1.46 and for SC III 1.40. The bulk density in dry state was 1957 kg m^{-3} for SC-I, 1016 kg m^{-3} for SC-II, and 763 kg m^{-3} for SC-III.

The samples for the material characterization experiments and those for determination of thermal conductivity, specific heat capacity and moisture diffusivity were exposed to thermal load prior to the measurements. The chosen temperatures were 600 and 800°C, the time of subjecting the samples to high temperatures was 2 h in all cases. For the sake of comparison, also the measurements with unloaded samples were done.

The samples for thermal analysis had the mass of approximately 1.5 g, for mercury porosimetry about 1–3 g, for scanning electron microscopy the sample dimension was 10×10 mm.

The samples for determination of thermal conductivity, specific heat capacity and moisture diffusivity had prismatic shape, for SC I 60×70×10 mm, for SC-II and SC-III 60×60×13 mm. The specimens for moisture diffusivity measurements were water and vapor-proof insulated on four sides by two-component epoxy resin Chs Epoxy 1200.

Table 1 Composition of glass fiber reinforced cement composites in % of dry substances

Specimen	Cement	Sand	Plasticizer	Alkali-proof fiber	Wollastonite	Vermiculite	Microsilica
SC-I	47.99	47.99	0.62	3.40	–	–	–
SC-II	47.60	–	0.45	3.84	38.50	9.61	–
SC-III	56.88	–	0.92	7.66	8.68	21.51	4.35

Table 2 Global characteristics of the porous space

Specimen	V_p/cm^3 g^{-1}	A_p/m^2 g^{-1}	d_v/μm
SC-I, 20°C	0.0731	11.62	0.07
SC-I, 600°C	0.1234	7.17	0.18
SC-I, 800°C	0.1755	3.72	0.28
SC-II, 20°C	0.5180	27.37	0.84
SC-II, 600°C	0.4844	19.12	1.03
SC-II, 800°C	0.5840	16.08	1.24
SC-III, 20°C	0.6999	45.79	0.67

The samples for measuring high temperature thermal expansion had the dimension 100×40×40 mm, those for measuring the high temperature thermal diffusivity were cubic, 71×71×71 mm.

Results

Material characterization

The results of material characterization experiments are summarized in Figs 1–6. Figures 1–3 show the results of thermal analysis (TG and DTG) of the studied GFRCC. The total mass loss of SC-I sample was 13.37%. From this amount, 4.22% can be attributed to the loss of water from CSH gels and sulfoaluminates in the temperature range up to 182°C. The loss of water due to decomposition of $Ca(OH)_2$ at 500°C presents 1.41%, which corresponds to 5.78% of $Ca(OH)_2$ in the sample. SC-I also exhibits a mass loss of 0.77% in the temperature range of 770 to 815°C. This corresponds to the loss of carbon dioxide released from $CaCO_3$ that originated from carbonation of $Ca(OH)_2$. The remaining 6.97% of mass loss can be attributed to the loss of water released from other hydrated clinker minerals.

SC-II sample exhibited the total mass loss of 30.56%. For temperatures up to 160°C, there was released water from CSH gels and sulfoaluminates in the amount corresponding to 5.49% of the total mass of the sample. From the loss of mass corresponding to calcium hydroxide decomposition between 480 and 500°C the original amount of $Ca(OH)_2$ was 7.68%. The mass loss between 742 and 818°C can be attributed to the decomposition of $CaCO_3$ when CO_2 is released. The calculated amount of $CaCO_3$ was 16.15%. The remaining mass loss of 16.10% was due to the decomposition of other products of cement hydration and products of chemical reactions of microfillers with calcium hydroxide.

SC-III sample had the total mass loss of 25.66%. The CSH gels decomposition up to 160°C accompanied by water removal corresponded to the mass loss of 5.85%.

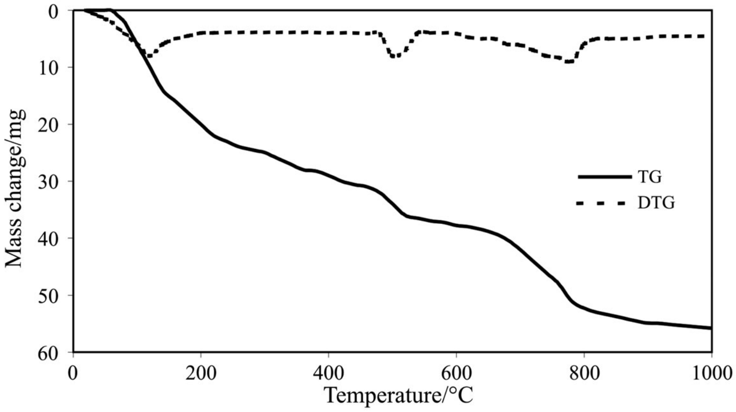

Fig. 1 DTG and TG of SC-I sample

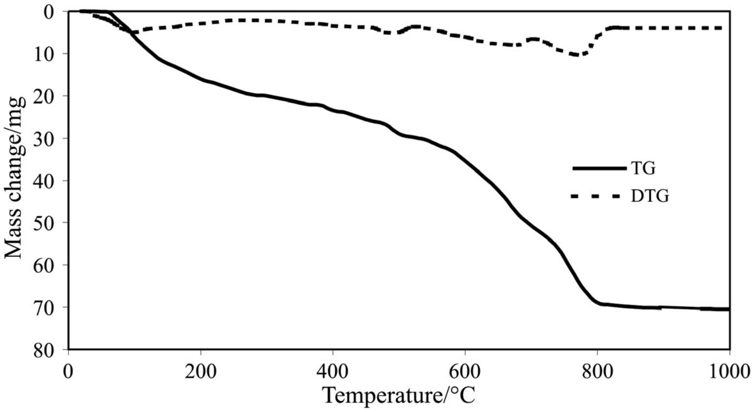

Fig. 2 DTG and TG of SC-II sample

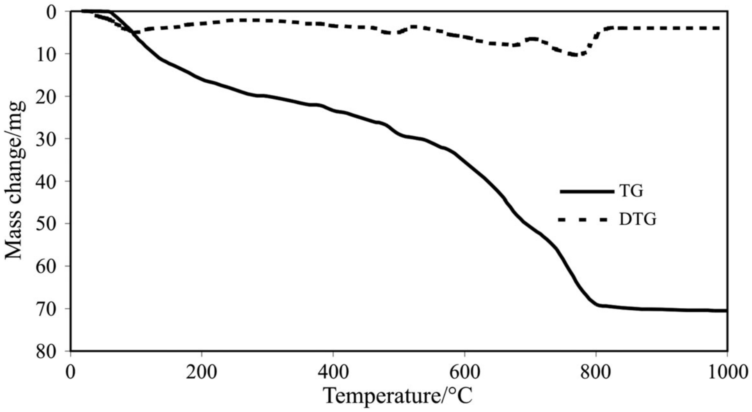

Fig. 3 DTG and TG of SC-III sample

Calcium hydroxide was decomposed at 490°C and from the mass loss its amount of 6.27% in the sample was calculated. In the temperature range of 746 to 810°C, CO_2 was released at $CaCO_3$ decomposition. The amount of $CaCO_3$ was calculated as 12.10%. The remaining mass loss of 12.94% was due to the decomposition of other products of cement hydration and products of chemical reactions of fine grain filler with calcium hydroxide.

The results of mercury porosimetry measurements are presented in Table 5, where V_p is the total intrusion volume, A_p the total pore area, and d_v the median pore diameter by volume. In general, it can be observed that the addition of wollastonite and vermiculite (SC-II and SC-III) leads to a significant increase of initial porosity. This increase was due to the fact that the volumetric amount of binder (cement) decreased relatively and the void fraction increased not primarily due to the fillers themselves but because of the appearance of voids in the material. The changes in porosity during heating were due to the decomposition of the binder (cement).

The experimental results give a clear evidence that the effect of temperature on the porosity of SC-I sample was very significant. While the initial volume of pores at 20°C was 0.07 $cm^3\ g^{-1}$, after heating to 800°C it increased to 0.17 $cm^3\ g^{-1}$. In the material, there are no fillers reacting either in pozzolanic or hydraulic way. Therefore, the increase in porosity is probably due to successive changes in the binder, particularly dehydration of hydrated calcium silicates and calcium aluminates.

The SC-II sample containing wollastonite and vermiculite had the initial pore volume much higher than SC-I, 0.52 $cm^3\ g^{-1}$. However, after heating to 800°C it increased only to 0.58 $cm^3\ g^{-1}$. This lower increase it probably due to the fact that the sample contains a lower volumetric amount of binder, so that lower amount of hydration products is decomposed and the resulting volume of the pores is lower.

The SC-III sample containing besides of wollastonite and vermiculite also fine grain filler in the form of silica fume that requires higher amount of mixing water exhibited higher initial pore volume than both SC-I and SC-II, namely 0.69 $cm^3\ g^{-1}$. Heating to 800°C has lead to an increase to only 0.75 $cm^3\ g^{-1}$. The low changes in porosity due to heating had the same cause as in the case of SC-II.

SEM images in Fig. 4 show that heating of SC-I sample to 600°C leads to decomposition of CSH gels and melting of fibers. At the temperature of 800°C, sintering of fiber bundles becomes apparent, as well as their deformation. Figure 5 shows that for SC-II material heating to 600°C leads to decomposition of cement hydration products, particularly CSH gels and hydrated aluminates. Melting of fibers appears at 800°C and deformation of fibers is not so noticeable as at SC-I. SC-III material in Fig. 6 seems to be the most stable among the studied GFRCC. Decomposition of CSH gels appears here as well but melting of fibers is not very distinctive even at 800°C.

Thermal and hygric parameters

The measurements of room temperature values of thermal conductivity λ, specific heat capacity C, maximum moisture content by mass achieved by capillary saturation

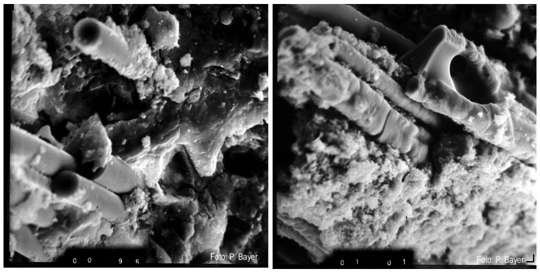

Fig. 4 Scanning micrographs of SC-I sample after heating to 600 and 800°C

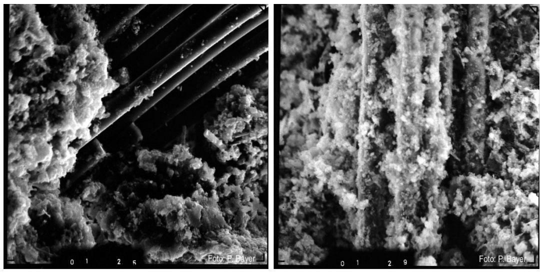

Fig. 5 Scanning micrographs of SC-II sample after heating to 600 and 800°C

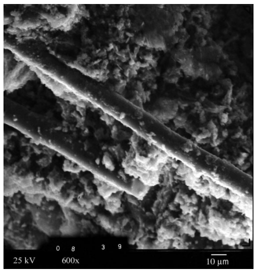

Fig. 6 Scanning micrograph of SC-III sample after heating to 800°C

$u_{\max}$ and moisture diffusivity κ after thermal load are summarized in Tables 3–5. Always an average value from the measurements on five samples is given.

The maximum moisture content of SC-II and SC-III is significantly higher than of SC-I. This is in accordance with the fact that bulk density of SC-II and SC-III materials is about two times lower than of SC-I as an apparent consequence of using wollastonite and vermiculite instead of sand. The effect of temperature on maximum moisture content is relatively more important for SC-I (50–60% increase) than for SC-II and SC-III (15–20% increase).

Both thermal conductivity and specific heat capacity are found to decrease with increasing loading temperature, and the decrease of thermal conductivity is very remarkable, almost 50% compared to the room temperature data. The moisture diffusivity exhibits an opposite behavior. A two-order of magnitude increase for SC-I and one order of magnitude increase for SC-II and SC-III are observed comparing the room temperature data with the data for high temperature exposure to 800°C. It should be noted that the changes of thermal and hygric parameters are more remarkable between 25 and 600°C than between 600 and 800°C.

Table 3 Thermal and hygric parameters of SC-I

Temperature exposure/ °C	C/ J m^{-3} K^{-1}	λ/ W m^{-1} K^{-1}	$u_{\max}$/ kg kg^{-1}	κ/ m^2 s^{-1}
25	$1.80\cdot10^{6}$	1.124	0.106	$1.28\cdot10^{-9}$
600	$1.72\cdot10^{6}$	0.706	0.156	$9.57\cdot10^{-8}$
800	$1.64\cdot10^{6}$	0.666	0.162	$1.79\cdot10^{-7}$

Table 4 Thermal and hygric parameters of SC-II

Temperature exposure/ °C	C/ J m^{-3} K^{-1}	λ/ W m^{-1} K^{-1}	$u_{\max}$/ kg kg^{-1}	κ/ m^2 s^{-1}
25	$1.19\cdot10^{6}$	0.275	0.475	$2.52\cdot10^{-8}$
600	$1.08\cdot10^{6}$	0.198	0.568	$1.27\cdot10^{-7}$
800	$0.95\cdot10^{6}$	0.160	0.568	$3.18\cdot10^{-7}$

Table 5 Thermal and hygric parameters of SC-III

Temperature exposure/ °C	C/ J m^{-3} K^{-1}	λ/ W m^{-1} K^{-1}	$u_{\max}$/ kg kg^{-1}	κ/ m^2 s^{-1}
25	$1.25\cdot10^{6}$	0.274	0.581	$3.36\cdot10^{-8}$
600	$0.85\cdot10^{6}$	0.198	0.684	$1.92\cdot10^{-7}$
800	$0.75\cdot10^{6}$	0.159	0.684	$3.36\cdot10^{-7}$

The high temperature data of linear thermal expansion are shown in Fig. 7. Clearly, the SC-I specimens exhibit a similar high temperature behavior as cement mortar and concrete ([10] for data survey), the linear thermal expansion coefficient α remains almost constant to about 400°C, then it increases to about 600°C, and finally decreases even under the room temperature value at approximately 800°C. On the other hand, the linear thermal expansion coefficients of SC-II and SC-III specimens decrease in the whole temperature range from 20 to 800°C, which is a positive feature for a material designed as fire protection because it results in lower thermal strains.

The high temperature thermal diffusivity is presented in Fig. 8. We can see that thermal diffusivity of all samples depends very dramatically on temperature. The qualitative character of all $a(T)$ curves is very similar. First, there is a decrease to about 200°C, then a sudden increase to about 400°C, and finally a decrease to almost 800°C where the character of the curves begins to change again to an increase. This is not very typical course of thermal diffusivity dependence on temperature, and it is quite apparent that chemical reactions in the higher temperature range in Portland cement played here a substantial role. Comparing the particular types of GFRCC studied we can observe that SC-I had the highest thermal diffusivity in lower temperature range, up to about 450°C but then its thermal diffusivity was lowest among the three GFRCC. SC-III exhibited quite an opposite behavior, its thermal diffusivity was lowest among the studied GFRCC up to about 350°C but then it was the highest.

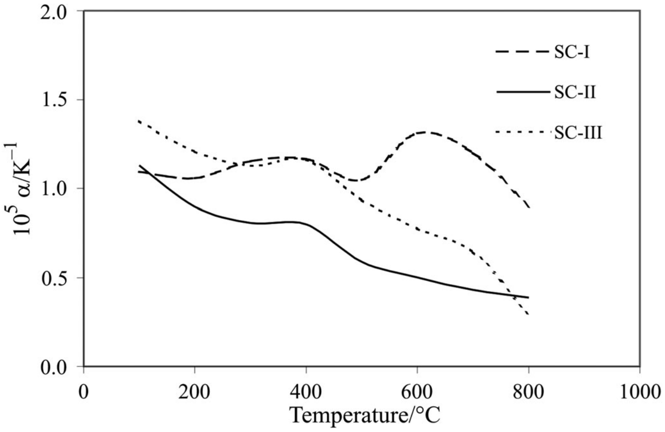

Fig. 7 Linear thermal expansion coefficient of glass fiber reinforced cement composites SC-I, SC-II, SC-III

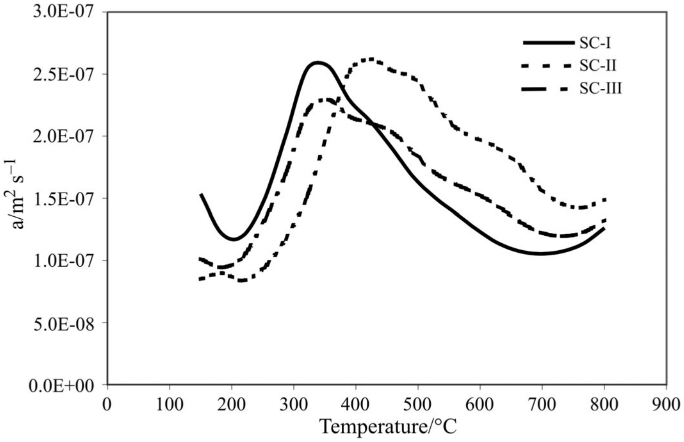

Fig. 8 Thermal diffusivity of glass fiber reinforced cement composites SC-I, SC-II, SC-III

Discussion

Thermal analysis experiments gave a clear evidence that the primary reason for the observed changes in hygric and thermal properties of analyzed GFRCC were two chemical reactions affecting the cement binder in the high temperature range, namely the decomposition of $Ca(OH)_2$ at 480–500°C and decomposition of $CaCO_3$ between 740 and 810°C. The magnitude of these changes was, however, significantly influenced by the composition of the particular GFRCC.

The effect of different composition of the particular GFRCC was very clear and remarkable already in room temperature conditions. Application of wollastonite (fibrous character) and vermiculite (light aggregates in expanded form with porous character) in SC-II and SC-III instead of sand aggregates in SC-I led to a remarkable decrease of thermal conductivity. Moisture diffusivity of GFRCC with wollastonite and vermiculite was at room temperature about one order of magnitude higher compared to SC-I with sand aggregates, which is again a clear consequence of density decrease to about one half and corresponding increase of porosity.

On the other hand, the changes of hygric and thermal properties during and after subjecting to higher temperatures were not so unambiguous.

The only measured parameter that was changed in quite a clear way was the linear thermal expansion coefficient. One of the reasons for more favorable high temperature behavior of linear thermal expansion coefficient of SC-II and SC-III compared to SC-I was better adhesion of glass fibers in SC-II and SC-III to the cement matrix as it was documented by SEM measurements. The higher porosity of SC-II and SC-III accompanied by lower thermal conductivity made heat transport through the cement gel to the fibers slower, so that melting of fiber bundles was delayed for some time. Another positive effect for the delayed heat transport to the glass fibers was pulping of fiber bundles during the preparation of the mixture caused by the additives of wollastonite, vermiculite and microsilica. Also, the presence of fibers of wollastonite could be a positive factor. Wollastonite is more stable at high temperatures than glass fibers, so that its fibers can maintain a relatively rigid structure of cement paste even after partial loss of its mass.

The very fast increase of moisture diffusivity of all three materials with the heating temperature corresponds to the theoretical predictions of the effects of high temperatures on concrete in general. During the decomposition processes in cement binder mentioned earlier gaseous substances are released, mainly water vapor and carbon dioxide. Therefore, the amount of bigger pores increases which makes the liquid water transport easier and faster. In addition, because the gaseous substances are generated relatively fast and in a substantial amount, the local overpressure in some parts of the porous system may lead to crack appearance, and consequently to the opening of preferential paths for pore water flow. The much faster increase in moisture diffusivity of SC-I between 25 and 600°C compared to SC-II and SC-III was most probably a consequence of opening wider preferential paths compared to SC-II and SC-III after the high temperature exposure because in normal conditions SC-I has more than one order of magnitude lower moisture diffusivity than SC-II and SC-III.

The highest value of thermal diffusivity of SC-I in lower temperature range up to 450°C is a consequence of its more compact structure and corresponds to its highest value among the studied GFRCC at room temperature. The maxima on all three $a(T)$ curves between 300 and 400°C should be related to decomposition in cement binder but there is not any clear link to a particular process. It can only be stated that in the temperature range above the decomposition temperature of $Ca(OH)_2$ the thermal diffusivity was decreasing function with temperature for all three GFRCC. The higher thermal diffusivity of SC-II and SC-III than SC-I in the higher temperature range above 450°C can be attributed to their porosity that remains several times higher compared to SC-I also after subjecting to high temperatures as it was evidenced by porosimetric measurements. The higher amount of relatively large pores in SC-II and SC-III that was shown by mercury porosimetry generally leads to an increasing role of convection and radiation modes of heat transfer. As the thermal diffusivity was determined during a one-side heating experiment where the effects of conduction are combined with convection and radiation, so that in fact an 'apparent value' of thermal diffusivity was measured, the effects of convection and radiation could be distinct.

Conclusions

Thermal analysis methods were used in a study of the high-temperature properties of three different types of glass fiber reinforced cement composites. In this analysis, two chemical reactions affecting the cement binder in the high temperature range, namely the decomposition of $Ca(OH)_2$ at 480–500°C and decomposition of $CaCO_3$ between 740 and 810°C were identified as the most important parameters affecting the thermal and hygric properties. A decrease of thermal conductivity as high as 50%, and an increase of moisture diffusivity in the range of one to two orders of magnitude were observed for all types of the studied materials after heating to 800°C. On the other hand, specific heat capacity in the same situation decreased by only about 10%. The positive effects of using wollastonite and vermiculite instead of sand aggregates were observed particularly in the values of the linear thermal expansion coefficient α, where a significant decrease of α in the high temperature range was found. This leads to lower thermal stress after high temperature exposure, and also to the better fire resistance of the material.

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