# THE EFFECT OF HIGH TEMPERATURES ON POROSITY AND THERMAL CONDUCTIVITY OF COMPOSITE MATERIALS

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**Abstract**

The effect of high temperatures on porosity and thermal conductivity of composite materials is analyzed for the particular case of two carbon fiber reinforced cement composites. The thermal conductivity is measured for the specimens exposed to the pre-heating temperatures of $600^0$C, $800^0$C and $1000^0$C. Also, the effect of the tensile load and of the combinations of thermal load and tensile load is analyzed. It is found that thermal load results in the significant changes of both the porosity and the thermal conductivity of the studied materials. In a comparison of the results of porosity and thermal conductivity measurements, it is realized that a more homogeneous pore structure results in a relative increase of the effect of air voids in the material on its heat transport properties and a decrease in thermal conductivity while a presence of significantly bigger pores can lead to the formation of thermal bridges in the pore structure accompanied by an increase in thermal conductivity.

**Key words:** porosity, thermal conductivity, high temperatures

## 1 Introduction

Cementitious composites contain a significant amount of pores of different size that can be filled either by air or water. Therefore, both the total pore volume and the distribution of pores can affect their thermal conductivity in a very significant way. In this paper, the effect of the amount and the size of the pores on the thermal conductivity is studied for two carbon fiber reinforced cement composites. The changes in their porosity are induced by the thermal load, tensile load and their combinations.

## 2 Materials and samples

The measurements were done on two different types of carbon fiber reinforced cement composites (CFRC) produced in the laboratories of VUSH Brno that will be denoted as UC II, UC III in what follows. The composition of CFRC materials (calculated among the dry substances only) is presented in Table 1. Portland cement CEM I 52.5 Mokrá was used for UC II, high alumina cement Alcoa CA-14M for UC III. Carbon fiber was PAN for UC II, pitch based for UC III, both with 10 mm length. Water in the amount corresponding to the w/c ratio of 0.9 was added to the mixture for UC II, 0.73 for UC III.

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

| | Cement | Microdorsilite | Plasticizer | Carbon fiber | Wollastonite | Methylcellulose | Defoamer | Microsilica |
|---|---|---|---|---|---|---|---|---|
| UC II | 39.71 | 16.50 | 0.98 | 0.98 | 39.60 | 0.11 | 0.16 | 1.96 |
| UC III | 40.00 | 28.40 | 0.80 | 1.00 | 29.50 | 0.10 | 0.20 | - |

The samples were produced using a successive homogenization procedure. First, wollastonite, microdorsilite and microsilica were homogenized in a mixing device, then cement and methylcellulose were added and the dry mixture was homogenized again. The dry well homogenized mixture was thoroughly mixed with water, defoamer and plasticizer. Finally, the carbon fibers were added and the mixture shortly mixed again. The prepared mixture was cast into the molds and vibrated. The material UC II was autoclaved at $180^0$C and then dried at $105^0$C, the material UC III was cured in common way. After the time period of 28 days after mixing, the samples were prepared for testing.

In the experimental measurements, eleven various specimen pre-treatment conditions were tested:

- Reference specimen not exposed to any load.
- Specimen exposed to a gradual temperature increase up to 600, 800 and $1000^o$C during two hours, then left for another 2 hours at the final temperature and slowly cooled.
- Specimen exposed to tensile load up to breaking.
- Specimen exposed first to tensile load up to breaking, then to a gradual temperature increase up to 600, 800 and $1000^o$C during two hours, after that left for another 2 hours at the final temperature and slowly cooled.
- Specimen exposed to a gradual temperature increase up to 600, 800 and $1000^o$C during two hours, then left for another 2 hours at the final temperature, slowly cooled and finally exposed to tensile load up to breaking.

The measured samples were cut from the plates of 10 mm thickness. For every pre-treatment, 5 specimens 60 x 60 x 10 mm were used. Before the measurements of thermal conductivity, all specimens were dried in an oven at 110 °C. The measurements on both reference and pre-treated specimens were performed in the laboratory conditions at 24±1 °C and 30-35% relative humidity.

The tensile loading was done in Klokner Institute of the Czech Technical University in Prague using the MTS 500 kN testing device. The thermal loading was carried out in the laboratory oven at the Department of Structural Mechanics. The thermal-loading temperatures were chosen with respect to the main decomposition processes taking place in Portland cement. According to [1], in Portland cement the decomposition of $Ca(OH)_2$ appears at about 460-480 °C and decomposition of $CaCO_3$ at about 700 °C. Each of the loading temperatures of 600°C and 800 °C is safely above one of these decomposition temperatures. The temperature of 1000 °C was chosen to simulate a characteristic fire load.

## 3 Experimental results and discussion

The thermal conductivity was measured using the commercial device ISOMET 2104 (Applied Precision, Ltd., SK). It is equipped with various types of optional probes, where 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.

Fig. 1 shows that for the reference specimens, the thermal conductivity of the material UC II in dry state is more than two times lower compared to UC III although its bulk density is only by about 6% lower. The reason for this unusual combination of properties might be the more homogeneous pore structure of UC II achieved by autoclaving. Therefore, characterization experiments by mercury intrusion porosimetry (MIP) were performed on both materials.

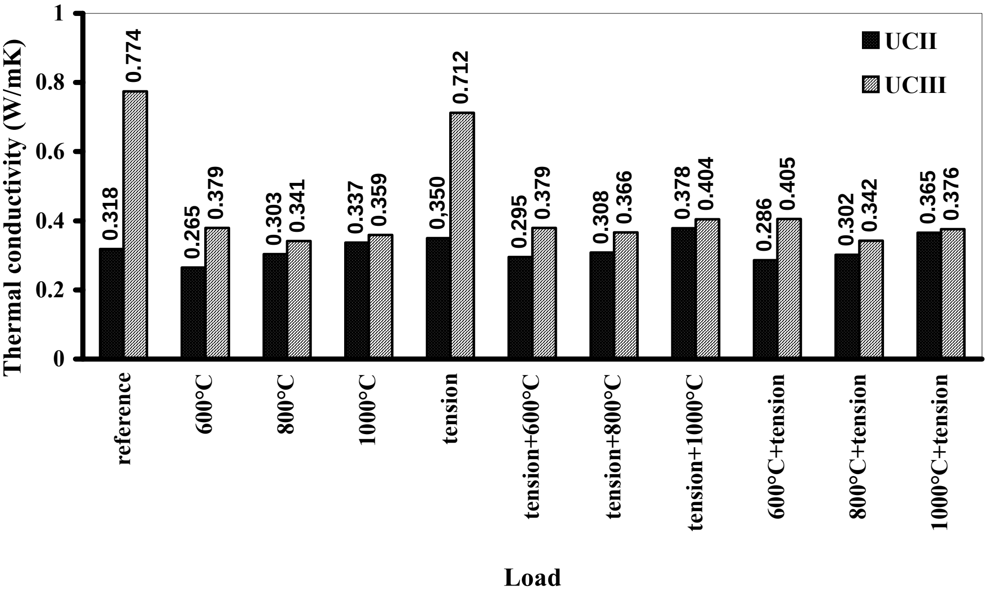

Fig. 1 Thermal conductivity of the analyzed CFRC.

The results of MIP measurements in Figs. 2a,b show that the distribution of pores of both materials is for the reference specimens very different. The material UC II clearly has the majority of pores between 10 nm and 100 nm, contrary to UC III where the majority of pores is at 1 µm. The global characteristics of the pore space in Table 2 reveal that while the total intrusion volume of both materials is almost the same, the total pore area of the material UC II is about nine times higher than of UC III and the median pore diameter by volume of UC II is about 40 times lower compared to UC III. Therefore, there is a clear evidence that the pore structure of UC II is much finer and the pore distribution much more homogeneous compared to UC III. The more homogeneous pore structure in UC II probably results in the relative increase of the effect of air voids in the material on its heat transport related macroscopic properties while in UC III the presence of significantly bigger pores can lead to the formation of thermal bridges in the pore structure accompanied by an increase in thermal conductivity.

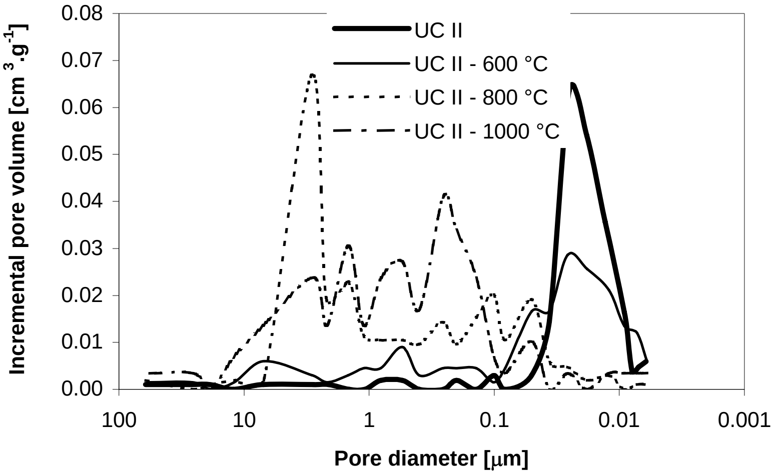

Fig. 2a Mercury intrusion porosimetry of the material UC II

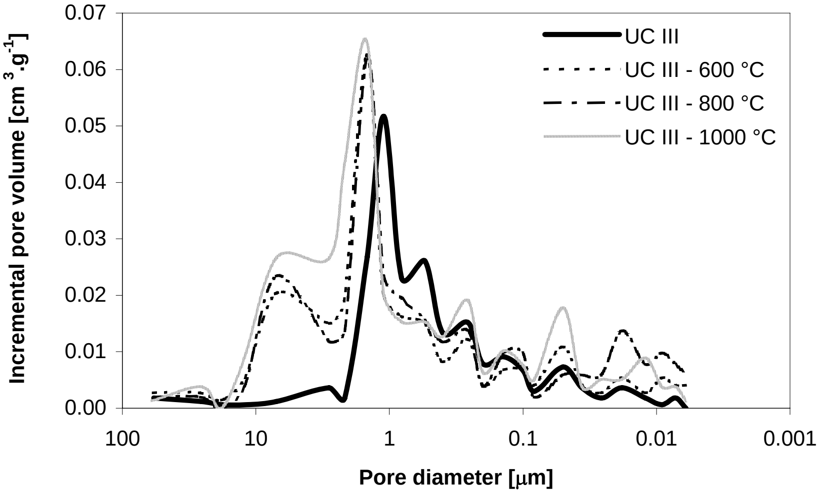

Fig. 2b Mercury intrusion porosimetry of the material UC III

Table 2 Global characteristics of the pore space of CFRC

| material sample | total intrusion volume (cm$^3$/g) | total pore area (m$^2$/g) | median pore diameter (μm) |
|---|---|---|---|
| UC II | 0.216 | 42.97 | 0.0236 |
| UC III | 0.215 | 4.78 | 0.877 |
| UC II - 600$^0$C | 0.199 | 31.76 | 0.0335 |
| UC II - 800$^0$C | 0.264 | 6.65 | 0.978 |
| UC II – 1000$^0$C | 0.310 | 9.57 | 0.558 |
| UC III – 600$^0$C | 0.263 | 10.88 | 1.438 |
| UC III – 800$^0$C | 0.291 | 18.67 | 1.055 |
| UC III – 1000$^0$C | 0.337 | 11.09 | 1.550 |

The tensile load was not found to affect the thermal conductivity in dry state of both materials in a very significant way. For UC II we observed a 10% increase (see Fig. 1), for UC III an 8% decrease compared to the reference specimens. MIP did not show any variations of the pore distribution in comparison with the reference specimen. This is, however, quite logical because the small size of the specimens for MIP measurements does not allow to discover the majority of cracks that mostly have larger dimensions.

The thermal load appeared as a very important factor affecting the thermal conductivity of the material UC III in dry state, as presented in Fig. 1. The $600^0$C pre-heating has led to a decrease in thermal conductivity of UC III to about one half of the reference value. Pre-heating to higher temperatures, however, did not result in any further significant decrease. This is certainly related to the stabilization of the structure of high alumina cement based composites in the high temperature range (see, e.g., [1]).

The remarkable decrease in thermal conductivity of UC III after the $600^0$C pre-heating was clearly a consequence of a significant increase of porosity after heating. The global pore characteristics in Table 2 show that the samples of UC III preheated to $600^0$C exhibited an about 20% increase in porosity compared to the reference specimens. Comparison of the respective pore distribution curves in Fig. 2b shows for the $600^0$C preheated UC III samples a shift of the most distinct peak from 1 μm to 1.5 μm and its increase by about 25%. This peak remained at the same position also for the specimens pre-heated to $800^0$C and $1000^0$C which is in a good accordance with the thermal conductivity measurements.

On the other hand, Fig. 1 shows that the material UC II did not seem to be affected by the thermal pre-treatment very much. Its thermal conductivity after the $600^0$C pre-heating decreased by about 15% compared to the reference specimens, for $800^0$C the decrease was only 5% and for $1000^0$C the thermal conductivity of UC II increased by 6% in comparison with the reference material.

In looking for the correlation of thermal conductivity of thermally pre-treated UC II samples with the changes in porosity and in the pore distribution we will analyze the data in Table 2 and Fig. 2a. Table 2 shows that compared to the reference specimen, the porosity of UC II for the $600^0$C pre-heating decreased by 8%, for $800^0$C it increased by 22% and for $1000^0$C by 44%. The changes in the pore distribution were more remarkable. For the $600^0$C pre-heating the most distinct peak of the incremental volume curve of UC II at 20 nm decreased to about one half and the amount of bigger pores increased in practically the whole range. The $800^0$C pre-heating then led to an almost complete reversal of the pore distribution curve. The 20 nm peak completely disappeared and a new peak at about 3 μm became dominant. The pre-heating to $1000^0$C resulted in a remarkable increase of the amount of bigger pores in a relatively wide range of 200 nm to 10 μm.

The relatively low effect of the pre-heating of the material UC II to $600^0$C on its pore structure indicates that the decomposition of $Ca(OH)_2$ supposed to take place in Portland cement based composites at about 460-480 °C was of much lower importance in our particular case which was probably due to the autoclaving procedure applied in the specimen production.

It seems surprising that the very significant difference in the pore distribution curves of the samples pre-heated to $600^0$C and $800^0$C resulted in only relatively small difference in thermal conductivity. However, the overall character of the correlation of changes in thermal conductivity with the changes in the porosity and in the pore distribution looks similar as in the case of the above analyzed differences between the room temperature values of thermal conductivity and porosity of UC II and UC III. It can be summarized that for the measurements throughout this paper, the higher porosity has led in all cases to lower thermal conductivity but the presence of bigger pores resulted in an increase of thermal conductivity, probably due to the appearance of thermal bridges.

In the combinations of thermal and mechanical load the effect of thermal load on thermal conductivity of both studied materials was clearly the dominant one.

## 4 Conclusions

The thermal load up to $1000^0$C, tensile load up to breaking and their combinations were found to have very different effects on the thermal conductivity of the two investigated types of CFRC. Generally it can be concluded that the effect of thermal load was much more remarkable than that of tensile load. The thermal decomposition processes also dominated the changes of thermal conductivity for all the analyzed combinations of thermal and tensile load.

The effect of high alumina cement on the thermal conductivity of samples subjected to elevated temperatures was not found to be so distinct as it might be anticipated from the expected stabilization of the aluminate structure after the conversion occuring at relatively low temperatures. After the pre-heating procedures, the thermal conductivity of the CFRC material UC III containing high alumina cement were very similar to the properties of the material UC II containing common Portland cement. The reason for this could be the autoclaving of UC II applied at its production.

It should be pointed out that except for the decrease of thermal conductivity of the material UC III after pre-heating to $600^0$C the changes were mostly within the range of 10-20%. The possible reason could be the competition of the effects of the total pore volume and the pore distribution on the thermal conductivity. The more homogeneous pore structure of a material probably resulted in the relative increase of the effect of air voids on the heat transport related macroscopic properties while the presence of significantly bigger pores could lead to the formation of thermal bridges in the pore structure accompanied by an increase in thermal conductivity.

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## References

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