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Effect of Moisture on the Thermal Conductivity of a Cementitious Composite[1]

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Measurements of the thermal conductivity of a cement-based composite material are performed as a function of moisture content from a dry state to a fully water-saturated state using an impulse technique. Then, the obtained data are analyzed using Brugemann and Wiener homogenization formulas. The validity of applied homogenization techniques is assessed comparing the measured and calculated results. On the basis of the experimental data and the homogenization analyses, the effects of total pore volume, pore distribution, and moisture content on the thermal conductivity are discussed.

KEY WORDS: cementitious composites; homogenization; moisture content; thermal conductivity.

1. INTRODUCTION

Cementitious composites contain a significant amount of pores of different size. As the thermal conductivity of air is $0.026\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ [1] and the thermal conductivity of cement stone is (depending on the amount and type of aggregates) in the range of $1\text{–}3\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ [2], both the

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total pore volume and the distribution of pores can affect the thermal conductivity of a cementitious material in a significant way. In usual service conditions, cementitious composites always contain a certain amount of water. The thermal conductivity of water is $0.60\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$ [1], which is more than 20 times higher than that of air. Therefore, if water is present in the pore space, its effect competes with the effect of air, and the thermal conductivity of a composite material can be considered as a result of this competition together with the effect of the cement matrix.

Cement-based composites are usually not considered good thermal insulation materials but they still possess a certain thermal insulation potential which can be utilized in supporting the function of the main thermal insulation layer. The effect of water on the thermal conductivity of cement-based composites is — similarly as for most other porous materials — always negative because it leads to an increase. Therefore, it would be useful to know how the amount of water affects the thermal conductivity. Cementitious materials can also survive severe thermal conditions. There are examples of concrete structures which were exposed to a considerably major fire, and after reconstruction they were able to be reused (for instance, the Great Exhibition Palace in Prague, Czech Republic). In this regard, not only mechanical but also thermal properties of concrete exposed to a fire can be significantly changed due to the chemical processes at elevated temperatures, and it is useful to know to the extent of charge.

The thermal conductivity, as the main heat transfer parameter, has been often the subject of measurement for various types of cement-based composites. However, mostly just one single value was determined (see, e.g., the reviews in [2–4]). The dependence of the thermal conductivity on moisture content was studied, for instance, in [5–8] where empirical relations were obtained, but such measurements can still be considered as relatively rare.

Homogenization theories working with the concept of an effective medium have been proven as useful in a variety of applications in mechanics and in the theory of electricity and magnetism where they already belong to well established treatments (see, e.g., [9] and [10]). Their utilization in heat transfer was much less frequent until recently. Within the last couple of years, some references appeared using effective media theories for estimation of thermal conductivity of refractory materials [11, 12], syntactic foams [13], and polymer-based composites [14], but not a single reference was found in common sources by the authors for cementitious composites.

In this paper, the effects of the amount and size of the pores on the thermal conductivity of cement-based composites are studied in conditions when these are either empty or partially or fully filled with water.

The analysis is performed using both experiments and effective medium theories for a carbon fiber reinforced cement composite exposed to different external conditions before the measurement.

2. EXPERIMENTAL METHODS

The thermal conductivity was determined using the commercial device, ISOMET 2104 (Applied Precision, Ltd.). ISOMET 2104 is a multifunctional instrument for measuring the thermal conductivity, thermal diffusivity, and volumetric 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 the analysis of temperature response of the analyzed material to heat flow impulses. The heat flow is induced by electrical heating using a resistor heater having direct thermal contact with the surface of the sample. The measurements in this paper were carried out as a function of moisture content.

The reason why an impulse method was chosen for measurements in this paper was that standard steady-state methods such as the guarded hot-plate method according to ISO 8302 require significantly longer time. For partially water-saturated materials, long measuring times may present a potential source of errors due to water transport in the measured specimens during the experiment. This is not likely to occur when using impulse techniques where data acquisition takes just tens of seconds, thus also decreasing the risk of water evaporation from the heated surface during the measurement.

Measuring errors in the determination of thermal conductivity using the impulse method described above can be determined only indirectly because a commercial device was used, which is in fact a "black box" from the point of view of data evaluation. The calibration error can be estimated on the basis of a comparison of measured values with the declared values of the etalons provided by the producer. For the particular case of measurements in this paper, the differences in the declared values were less than 3.5%. Naturally, there were also random errors due to the inhomogeneity of the samples that had to be added to this error. These were estimated to be less than 5%, based on the differences within a set of measurements on different specimens.

3. HOMOGENIZATION TECHNIQUES

In terms of a homogenization procedure, a porous material can be considered basically as a mixture of three phases, namely solid, liquid, and gaseous phases. In the cement-based material studied in this work, the solid phase is represented by cement, microdorsilite, carbon fibers, and wollastonite; the liquid phase by water; and the gaseous phase by air. Therefore, the homogenization should be performed in three steps. The first task is the determination of thermal conductivity of the cement matrix. This can be done on the basis of known thermal conductivities and amounts, of its constituents. The second step should be the determination of thermal conductivity of the dry material where only the solid and gaseous phases are to be considered. This can be realized using the volumetric fraction of the air obtained in porosimetric measurements and the known thermal conductivities of the matrix and the air. For the evaluation of the thermal conductivity of the whole material, which is the third and last step of the homogenization procedure, cement matrix, air, and water were mixed.

In this work, three Bruggeman-type homogenization formulas (see [15]) were employed for calculation of thermal conductivity of the cement matrix–air–water system. The first of them, the original one, was proposed for spherical inclusions, the second assumes acicular orientation of inclusions, and the third was derived for their board-like (disk) orientation. The applied mixing formulas are described, respectively, as

$$\lambda_{\mathrm{eff}} = \lambda_{\mathrm{M}} + \sum f_{\mathrm{j}}(\lambda_{\mathrm{j}} - \lambda_{\mathrm{M}}) \frac{3\lambda_{\mathrm{eff}}}{2\lambda_{\mathrm{eff}} + \lambda_{\mathrm{j}}}, \tag{1}$$

$$\lambda_{\mathrm{eff}} = \lambda_{\mathrm{M}} + \sum f_{\mathrm{j}}(\lambda_{\mathrm{j}} - \lambda_{\mathrm{M}}) \frac{5\lambda_{\mathrm{eff}} + \lambda_{\mathrm{j}}}{3\lambda_{\mathrm{eff}} + 3\lambda_{\mathrm{j}}}, \tag{2}$$

$$\lambda_{\mathrm{eff}} = \lambda_{\mathrm{M}} + \sum f_{\mathrm{j}}(\lambda_{\mathrm{j}} - \lambda_{\mathrm{M}}) \frac{2\lambda_{\mathrm{j}} + \lambda_{\mathrm{eff}}}{3\lambda_{\mathrm{j}}}, \tag{3}$$

where λ_{eff} is the thermal conductivity of the studied material, λ_M is the thermal conductivity of the cement matrix ($1.6\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$), which was determined using the Rayleigh [16] mixing rule,

$$\frac{\lambda_{\mathrm{M}} - 1}{\lambda_{\mathrm{M}} + 2} = f_{\mathrm{c}} \left(\frac{\lambda_{\mathrm{c}} - 1}{\lambda_{\mathrm{c}} + 2} \right) + f_{\mathrm{m}} \left(\frac{\lambda_{\mathrm{m}} - 1}{\lambda_{\mathrm{m}} + 2} \right) + f_{\mathrm{cf}} \left(\frac{\lambda_{\mathrm{cf}} - 1}{\lambda_{\mathrm{cf}} + 2} \right) + f_{\mathrm{w}} \left(\frac{\lambda_{\mathrm{w}} - 1}{\lambda_{\mathrm{w}} + 2} \right), \tag{4}$$

from the known thermal conductivities of cement, microdorsilite, carbon fibers, and wollastonite [1], f_j is the volumetric fraction of air or water, and λ_j is the thermal conductivity of air ($0.026\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$) or water ($0.6\,\mathrm{W{\cdot}m^{-1}{\cdot}K^{-1}}$).

In Eq. (4), $f_c$is the volumetric fraction of cement, $f_m$is the volumetric fraction of microdorsilite, $f_{cf}$is the volumetric fraction of carbon fibers,f_w is the volumetric fraction of wollastonite, λ_c is the thermal conductivity of cement, λ_m is the thermal conductivity microdorsilite, λ_{cf} is the thermal conductivity of carbon fibers, and λ_w is the thermal conductivity of wollastonite.

For verification of the obtained results, Wiener's bounds [17] for parallel (Eq. (5)) and serial models (Eq. (6)) were used. These bounds represent upper and lower limits of the thermal conductivity vs. water content function. Wiener's bounds are given in the following relations:

$$\lambda_{\text{eff}} = \frac{1}{\frac{f_1}{\lambda_1} + \frac{f_2}{\lambda_2} + \frac{f_3}{\lambda_3}}, \tag{5}$$

$$\lambda_{\text{eff}} = f_1\lambda_1 + f_2\lambda_2 + f_3\lambda_3, \tag{6}$$

where λ_{eff} is the thermal conductivity of the studied material, f_1 to f_3 are the volumetric fractions of the particular constituents of the porous body, and λ_1 to λ_3 are the thermal conductivities of the constituents.

4. MATERIALS AND SAMPLES

The measurements were done on carbon fiber reinforced cement (CFRC) produced in the laboratories of VUSH Brno (Czech Republic). The composition of the CFRC material (calculated among the dry substances only) is presented in Table I. Portland cement used was CEM I 52.5 produced in the cement factory Mokrá (Czech Republic), and carbon fiber was PAN-type. The water/cement ratio corresponding to the amount of water added the mixture was 0.9.

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

Table I. Composition of the Carbon Fiber Reinforced Cement Composite (in Mass%) of Dry Substances

Cement	Microdorsilite	Plasticizer	Carbon fiber	Wollastonite	Methyl-cellulose	Defoamer	Microsilica
39.71	16.50	0.98	0.98	39.60	0.11	0.16	1.96

was thoroughly mixed with water, defoamer, and plasticizer. Then, the carbon fibers were added and the mixture shortly mixed again. Finally, the prepared mixture was vacuum-treated in special molds with a perforated bottom. The material was autoclaved at 180°C and then dried at 105°C. After a time period of 28 days after mixing, the samples were prepared for testing.

In the experimental measurements, five 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°C during 2 h, then left for another 2 h at the final temperature and slowly cooled.
- Specimen exposed to tensile load till breaking.

The measured samples were cut from plates of 10 mm thickness. Five specimens (60 mm × 60 mm × 10 mm) for each pre-treatment were used in the thermal conductivity measurements. Average values from measurements on five specimens were taken for data presentation.

Before the measurements, all specimens were dried in an oven at 110°C. The measurements on both reference and pre-treated specimens were performed in laboratory conditions at 24 ± 1°C and 30–35% relative humidity.

5. RESULTS AND DISCUSSION

Tables II and III show the bulk density and thermal conductivity of the studied cementitious composite in a dry state. The tensile load was not found to affect the thermal conductivity in a dry state in a significant way. We observed a 10% increase (see Table III) compared to the reference specimens. Also, the moisture dependence of the thermal conductivity of the samples subjected to tensile load did not exhibit any remarkable changes compared to the reference state, as illustrated in Fig. 1. The only exception was in the range of the highest moisture content where the tensile load resulted in a 30% increase in thermal conductivity. This may be related to the appearance of tensile cracks that increased the effective porosity in a certain range, but the effect of nonhomogeneities in the material specimens cannot be excluded as well. Mercury intrusion porosimetry (MIP) results in Fig. 2 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

Table II. Bulk Density of the Carbon Fiber Reinforced Cement Composite

Specimen type	reference	600°C	800°C	1000°C	tension
Bulk density [kg·m^{-3}]	1468	1378	1344	1352	1430

Table III. Thermal Conductivity of the Carbon Fiber Reinforced Cement Composite in Dry State

Specimen type	reference	600°C	800°C	1000°C	tension
Thermal conductivity [W·m^{-1}·K^{-1}]	0.318	0.265	0.303	0.337	0.350

measurements does not allow for the discovery of the majority of cracks that mostly have larger dimensions.

The results in Table III show that the studied material did not seem to be significantly affected by the thermal pre-treatment. Its thermal conductivity after 600°C pre-heating decreased by about 15% compared to the reference specimens; for 800°C the decrease was only 5%, and for 1000°C,

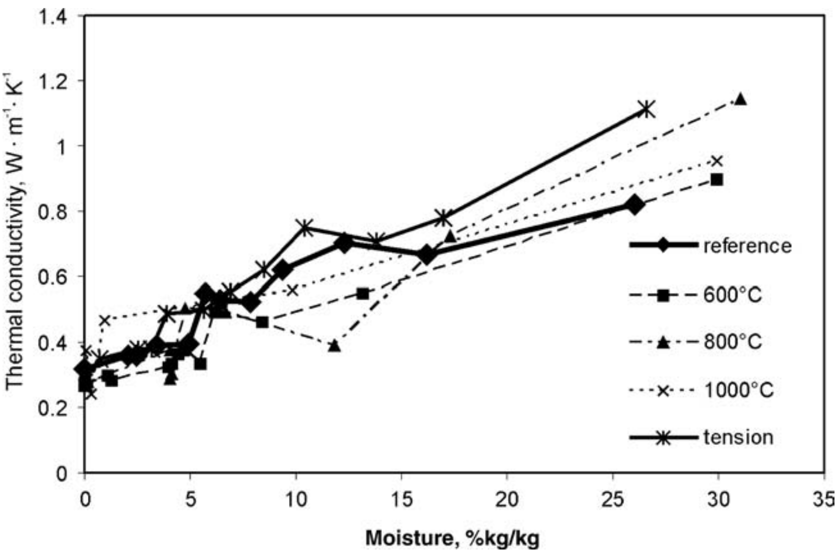

Fig. 1. Experimentally determined thermal conductivity of the studied material as a function of moisture content.

Table IV. Global Characteristics of the Pore Space of the Carbon Fiber Reinforced Cement Composite

Material sample	Total intrusion volume ($cm^3 \cdot g^{-1}$)	Total pore area ($m^2 \cdot g^{-1}$)	Median pore diameter (μm)
reference	0.216	42.97	0.0236
600°C	0.199	31.76	0.0335
800°C	0.264	6.65	0.978
1000°C	0.310	9.57	0.558

the thermal conductivity increased by 6% in comparison with the reference material. Similar features were observed in the thermal conductivity vs. moisture functions in Fig. 1.

In looking for a correlation of the thermal conductivity of thermally pre-treated samples with the changes in porosity and pore distribution, the results of an analysis of the data are shown in Table IV and Fig. 2. Table IV shows that compared to the reference specimen, the porosity of the material 600°C pre-heating decreased by 8%, at 800°C it increased by 22%, and at 1000°C it increased by 44%. The changes in the pore distribution were more remarkable. At 600°C pre-heating, the most distinct peak of the incremental volume curve at 20 nm decreased to about one-half and the amount of bigger pores increased over practically the whole range. The 800°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 3μm became dominant. Pre-heating to 1000°C resulted in a remarkable increase of the amount of bigger pores at a relatively wide range of 200 nm to 10μm.

In Figs. 3–7 are presented the thermal conductivity vs. moisture content functions calculated using three different Bruggeman-type mixing formulas and Wiener's formulas. From the point of view of Wiener's bounds, we can see that the calculated results as well as the experimentally measured data lie between the serial and parallel models, which basically justifies the reasonable accuracy of both experiment and calculations.

Looking at the data from the point of view of accuracy of the analyzed Bruggeman-type mixing formulas, we can see large differences between the particular types of inclusions. Systematically, the highest values of thermal conductivity were obtained for spherical and needle models, and the lowest values were reached using the board model. This is a logical result because the board-shaped inclusions should lead to results closer to the parallel model than to the serial model (taken from the point of view of mixing thermal conductivities in Eqs. (5) and (6); for the

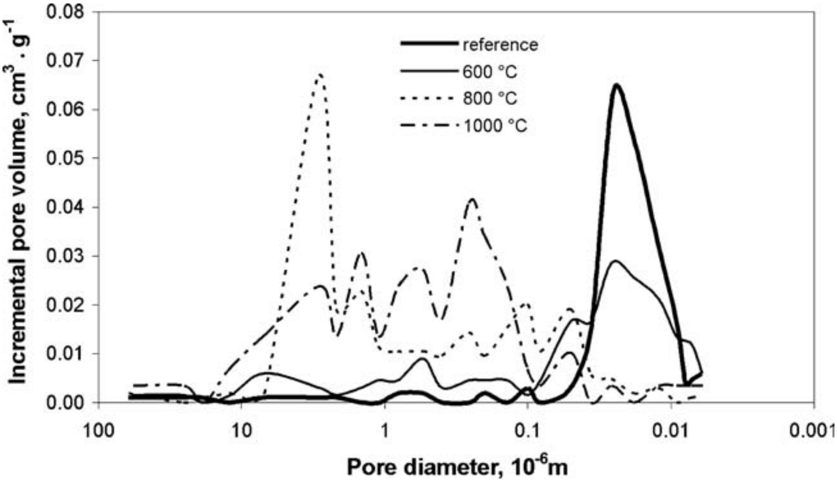

Fig. 2. Mercury intrusion porosimetry of the studied material.

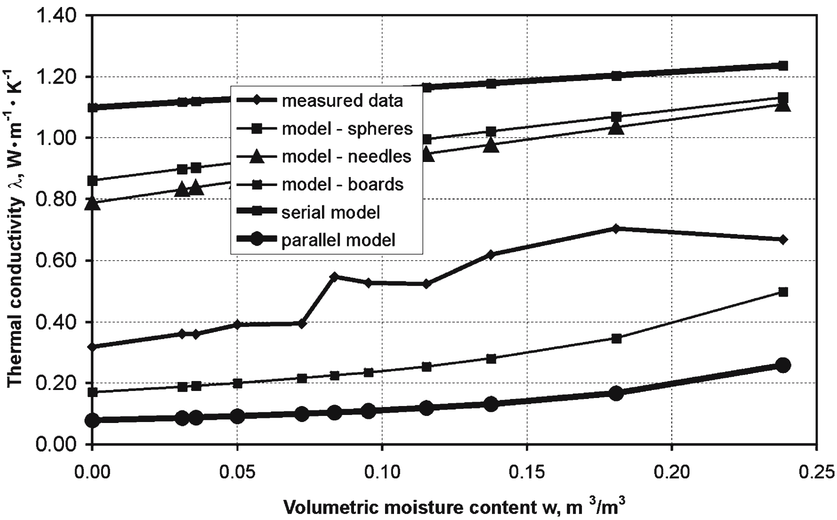

Fig. 3. Measured and calculated thermal conductivity of the reference sample in dependence on moisture content.

thermal resistances the serial–parallel orientation is naturally quite the opposite, i.e., the serial model should be closer to the board-type inclusions).

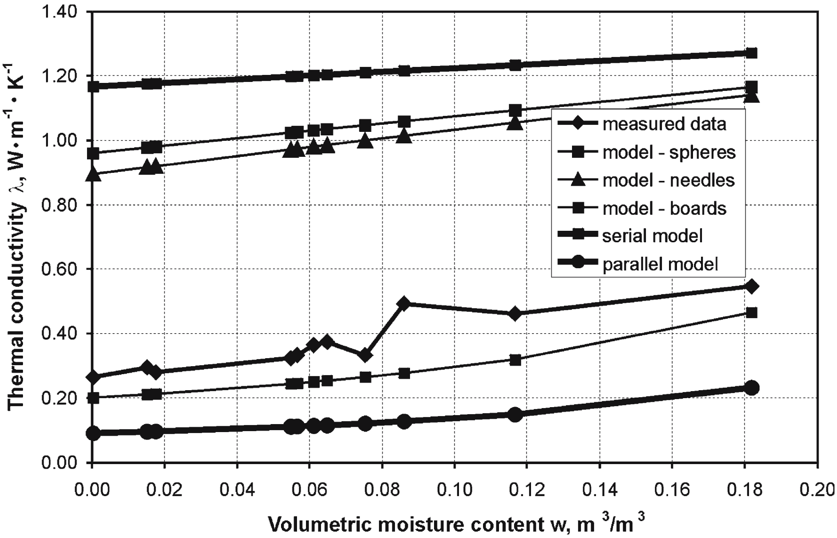

Fig. 4. Measured and calculated thermal conductivity of the sample exposed to 600°C.

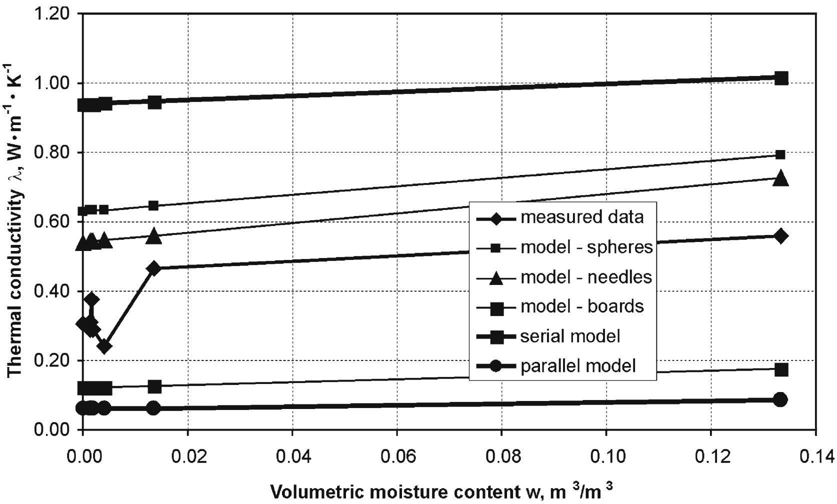

Fig. 5. Measured and calculated thermal conductivity of the sample exposed to 800°C.

The measured data were found in all cases between the spherical and board-shaped inclusion variants of the Bruggeman model. For the reference specimen and tensile load-exposed specimens, they were closer to the board inclusion model; for the thermal load-exposed samples, they were closer to the spherical inclusions model. This is in good qualitative

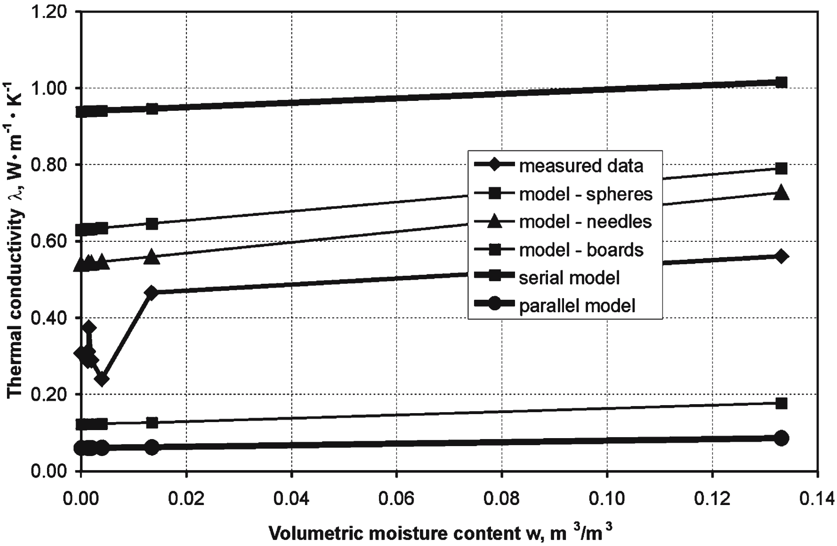

Fig. 6. Measured and calculated thermal conductivity of the sample exposed to 1000°C.

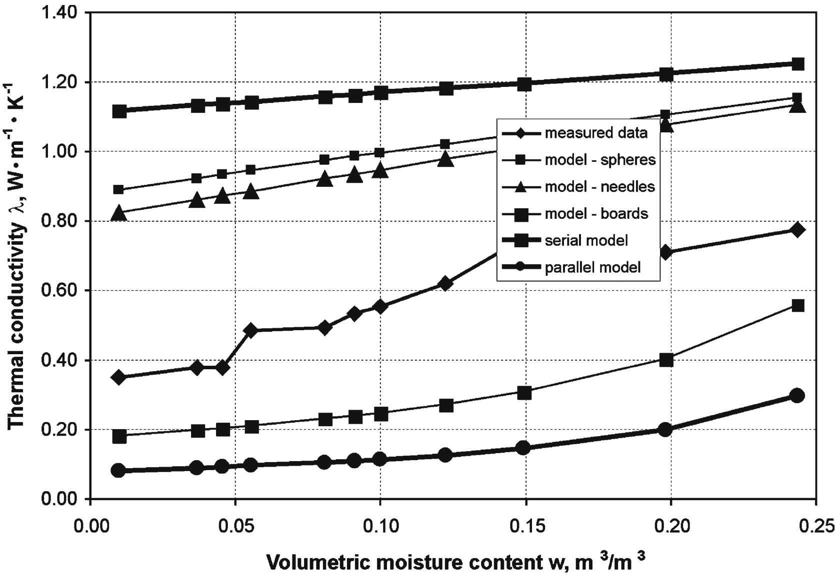

Fig. 7. Measured and calculated thermal conductivity of the sample exposed to tensile load.

agreement with the change in the porous structure after thermal load found by mercury intrusion porosimetry measurements which were characterized by the appearance of larger pores.

The analysis of the obtained results from the point of view of the effect of moisture content on the agreement between experimental and calculated data showed that all applied mixing formulas were sensitive to the moisture content in a similar manner so that the slopes of the thermal conductivity vs. moisture content functions were similar.

6. CONCLUSIONS

Summarizing the measurements of thermal conductivity vs. moisture content functions of the carbon fiber reinforced cement composite in this paper, it seems surprising that the significant difference in the pore distribution curves of the samples pre-heated at 600°C and 800°C resulted in only relatively small differences in thermal conductivity. However, the changes in the volumetric amount of pores and in the pore distribution were probably partially compensating each other. In the measurements throughout this paper, the higher porosity has led in all cases to a lower thermal conductivity but the presence of larger pores resulted in an increase of the thermal conductivity, probably due to the appearance of thermal bridges.

The application of Bruggeman-type mixing formulas for the calculation of the thermal conductivity and its dependence on moisture content were found to provide useful estimates of measured data. However, a unified formula could not be found for all the material pre-treatment cases which were studied. This was probably due to the changes in pore distribution, particularly after thermal loading of the samples.

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REFERENCES

1. D. R. Lide, ed., In *CRC Handbook of Chemistry and Physics*, 79^{th} Ed. (CRC Press, Boca Raton, Florida, 1998).
2. R.Černý and P. Rovnaníková, *Transport Processes in Concrete* (Spon Press, London, 2002).
3. A .M. Neville, *Properties of Concrete* (Pitman, London, 1973).

4. Z. P. Bažant and M. F. Kaplan, *Concrete at High Temperatures: Material Properties and Mathematical Models* (Longman, Harlow, 1996).
5. IEA-Annex XIV, *Condensation and Energy*, Vol. 3, *Material Properties* (International Energy Agency, Leuven, 1991).
6. R. Černý, J. Maděra, J. Poděbradská, J. Toman, J. Drchalová, T. KleČka, K. Jurek, and P. Rovnaníková, *Cem. Concr. Res.* **30**:1267 (2000).
7. J. Toman and R. Černý, *Acta Polytechnica* **41**:8 (2001).
8. J. Grunewald, *DELPHIN 4.1 – Documentation, Theoretical Fundamentals* (TU Dresden, Dresden 2000).
9. R. M. Christensen, *Mechanics of Composite Materials* (Wiley, New York, 1979).
10. A. Sihvola, *Electromagnetic Mixing Formulas and Applications* (The Institution of Electrical Engineers, London, 1999).
11. A. A. Ogacho, B. O. Aduda, and F. W. Nyongesa, *J. Mater. Sci.* **38**:2293 (2003).
12. D. S. Smith, S. Fayette, S. Grandjean, and C. Martin, *J. Am. Ceram. Soc.* **86**:105 (2003).
13. J. D. Felske, *Int. J. Heat Mass Transfer* **47**:3453 (2004).
14. F. Macedo and J. A. Ferreira, *Rev. Sci. Instrum.* **74**:828 (2003).
15. D. Polder and J. H. Van Santen, *Physica* **12**:257 (1946).
16. Lord Rayleigh, *Phil. Mag*. **34**:481 (1892).
17. O. Wiener, *Abh. D. Leipz. Akad.* **32**:509 (1912).