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HISTORY OF CONFERENCE



The first workshop was organized by *prof. Stefan Barta* on January 22, 1996 at the Department of Physics, Faculty of Electrical Engineering and Information Technology at the Slovak University of Technology in Bratislava. The Termophysic's meetings have been established as periodical meetings of scientists working in the field of investigation of thermophysical properties of materials and the problems of heat transfer and measurement of thermophysical and other transport properties of materials.



The Thermophysics as the working group of the Slovak Physical Society was established on the meeting at the Department of Thermophysics of the Slovak Academy of Sciences in Bratislava on June 13, 1997. The aim of the constitution of the working group is to exchange actual information in the field of heat transfer phenomena.

Dr. Ludovit Kubicar acted as the coordinator of the group and organized meetings at the Institute of Physics of the Slovak Academy of Sciences in Bratislava in the years - 1997, 1998 and 1999.



Then *Dr. Libor Vozar* from Faculty of Natural Sciences at the Constantine the Philosopher University in Nitra coordinated the activities of the society for the years 2000, 2001 and 2002. The workshops were organized in Nitra, in Račková dolina and Kočovce, respectively.



Next years, the Thermophysics workshop was held in Kočovce again. *Dr. Peter Matiasovsky*, working for the Institute of Construction and Architecture at the Slovak Academy of Sciences in Bratislava, being the chairman of Thermophysical Society for the years 2003, 2004 and 2005 was taking the chair of the workshops.



Since 2006 to 2008, the Thermophysics workshop took place in Kocovce, whereas *Dr. Jozefa Lukovicova* from research group at the Department of Physics of Faculty of Civil Engineering at the Slovak University of Technology in Bratislava was taking the chair of the workshops.



Since 2009 to 2011, the Thermophysics workshop was held in Valtice. *Prof. Oldrich Zmeskal* (working at the Institute of Physical and Applied Chemistry and Centre of Material Research at the Faculty of Chemistry of the Brno University of Technology in Brno) and *prof. Robert Cerny* (working at the Department of Materials Engineering and Chemistry at the Faculty of Civil Engineering of the Czech Technical University in Prague) were taking the chairs of the workshops.



Since 2012, the Thermophysics workshop is held in Guesthouse Adam in the village of Podkylava. Guesthouse Adam is surrounded in picturesque hilly region covered with hamlets and caters to all groups' visitors and tourists. The guesthouse was built with the financial support of the European Union funds and has begun its operation in May 2006. *Dr. Vlastimil Bohac*, SAS, Bratislava, Slovak Republic in cooperation with previous organizers (*prof. Zmeskal* and *prof. Cerny*) has taken the chairmanship for the years 2012-2014.

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Numerical modelling of couplings between hygro-thermal state and chemical degradation of porous building materials

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Abstract: Chemical deterioration of porous building materials is of great practical importance when durability of structures exposed to aggressive environmental conditions is analyzed. Hygro-thermal state of a material influences to a great extent the progress of the deterioration process. The mutual couplings between the hygro-thermal state and the kinetics of chemical and mechanical processes, e.g. chemically induced damage, shrinkage, stress-strain behaviour, are discussed here both from the physicochemical and numerical viewpoint. The examples presented show that the approach allows for efficient numerical modelling the evolution of deterioration of building materials in variable hygro-thermal conditions.

Keywords: Chemical degradation, durability, hygro- thermo- chemical couplings, numerical modelling.

1. Introduction

Chemical deterioration of porous building materials is of great practical importance when durability of structures exposed to aggressive environmental conditions is analyzed. Hygro-thermal state of a material influences to a great extent the progress of the deterioration process. A general approach to modelling chemical degradation of building materials, due to combined action of variable chemical, hygro-thermal and mechanical loads, is presented in detail in [1]. Mechanics of multiphase porous media and damage mechanics are applied for this purpose. The mathematical model of the deterioration processes in variable hygro-thermal state consists of the mass-, energyand momentum balances, the evolution equations for chemical reactions, as well as several constitutive and physical relationships, [1]. In order to account for variable hygro-thermal conditions, the kinetics of chemical processes is described by means of a rate type approach, based on thermodynamics of chemical reactions. This proposed general approach can be applied for modelling such chemical deterioration processes of building materials as: calcium leaching [2], alkali-silica reaction (ASR) [3] or salt crystallization [4].

In this paper the mutual couplings between the hygro-thermal state and the kinetics of chemical and mechanical processes, e.g. chemically induced damage, shrinkage, stress-strain behaviour, are discussed both from the physicochemical and numerical viewpoint.

2. Mathematical model

The mathematical model describing chemical deterioration of building materials and development of its equations, starting from the local, microscopic balance equations with successive volume averaging, is presented in [1]. The final forms of the model governing

equations, written in terms of chosen *primary variables*: gas pressure, $p^{g}(\mathbf{x},t)$, capillary pressure, $p^{c}(\mathbf{x},t)$ ($p^{c}=p^{g}-p^{w}$, where $p^{w}(\mathbf{x},t)$ means water pressure in point \mathbf{x} at time instant t), temperature, $T(\mathbf{x},t)$, mass concentration of chemical species x in water, $c_{x}(\mathbf{x},t)$, and displacement vector, $\mathbf{u}(\mathbf{x},t)$, are given in detail in [1], [5]. The mathematical model consists of the *macroscopic mass conservation equations* (obtained from their integration within the *Representative Volume Element*, *RVE*) of dry air, water and chemical species, *macroscopic enthalpy conservation equation* for the multiphase medium and the *macroscopic linear momentum conservation equation* for the medium, [5], which can be written in the following concise matrix form,

$$\begin{bmatrix} C_{gg} & C_{gc} & C_{gt} & C_{gs} & C_{gu} \\ 0 & C_{cc} & C_{ct} & C_{cs} & C_{cu} \\ 0 & C_{tc} & C_{tt} & C_{ts} & C_{tu} \\ 0 & C_{sc} & C_{st} & C_{ss} & C_{su} \\ C_{ug} & C_{uc} & C_{uc} & C_{us} & C_{uu} \end{bmatrix} \stackrel{\partial}{\partial t} \begin{bmatrix} p^{g} \\ p^{c} \\ T \\ c_{x} \\ u \end{bmatrix} + \begin{bmatrix} K_{gg} & K_{gc} & K_{gt} & K_{gs} & 0 \\ K_{cg} & K_{cc} & K_{ct} & K_{cs} & 0 \\ K_{tg} & K_{tc} & K_{tu} & 0 & 0 \\ K_{sg} & K_{sc} & K_{st} & K_{ss} & 0 \\ 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} p^{g} \\ p^{c} \\ T \\ c_{x} \\ u \end{bmatrix} = \begin{bmatrix} f_{g} \\ f_{c} \\ f_{t} \\ f_{s} \\ f_{u} \end{bmatrix},$$
(1)

where C_{ij} and K_{ij} (*i*, *j*= *g*, *c*, *t*, *s*, *u*) are the coefficients describing mutual couplings between transport of gas, water, heat, chemical species and material strains. From the above equations it is evident that the progress of chemical deterioration and strains caused by the process are dependent on the hygro-thermal state of porous building materials.

Then, the model consists of the appropriate evolution equations describing progress of the chemical and mechanical deterioration processes, which are discussed in Section 2.1, where effect of the hygro-thermal state on their progress is addressed.

2.1 Modelling evolution of chemical deterioration processes

For sake of brevity only two specific chemical deterioration processes, i.e. calcium leaching from the material skeleton and salt precipitation/crystallization in the pore solution are described in detail in this subsection. The progress of these chemical processes is given by the evolution equations written in terms of the appropriate internal variable, the calcium degree of leaching or the saturation degree with precipitated salt.

The calcium leaching degree, $\Gamma_{leach}^{Ca}(\mathbf{x},t)$, is defined in terms of the initial (i.e. for chemically not deteriorated material) and the actual values of solid calcium content, which might be leached from the skeleton, s_{Ca}^0 and $s_{Ca}(\mathbf{x},t)$, as follows,

$$\Gamma_{leach}^{Ca}\left(\mathbf{x},t\right) = \frac{s_{Ca}^{0} - s_{Ca}\left(\mathbf{x},t\right)}{s_{Ca}^{0}}$$
(2)

Hence its value might increase from 0 to 1.0 during progressing calcium leaching process. The evolution equation for non-isothermal calcium leaching has the following form [2],

$$\dot{\Gamma}_{leach}^{Ca} = \frac{d\Gamma_{leach}^{Ca}}{dt} = -\frac{A_{leach}^{Ca}}{s_{Ca}^{0}RT_{ref}\tau_{leach}^{Ca,\kappa}}$$
(3)

where chemical affinity of the calcium leaching process is defined as follows,

$$A_{leach}^{Ca} = \int_{s_{Ca}^{0}}^{s_{Ca}} \xi\left(\overline{s}, T_{ref}\right) d\overline{s} - \int_{s_{Ca}^{0}}^{s_{Ca}} \xi\left(\overline{s}, T_{ref}\right) d\overline{s} .$$

$$\tag{4}$$

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 $\tau_{leach}^{Ca} = f(s_{Ca}, T)$ is the characteristic time of the process, T_{ref} the reference temperature, ξ the equilibrium function. The characteristic time $\tau_{leach}^{Ca,\kappa}$ for different phases of solid calcium can be expressed by the following approximate relationships [2]:

$$\tau_{leach}^{Ca,\kappa}\left(T\right) \cong \tau_{leach}^{Ca,\kappa}\left(T_{ref}\right) \times \exp\left[B_{\tau}\left(T-T_{ref}\right)\right],\tag{5}$$

where T_{ref} = 298.15 K, B_T = -0.0239 K⁻¹, and superscript = *por*, *etr*, *CSH* means the portlandite, ettringite or CSH phases, depending which calcium phase dissolution is dominating in a given range of liquid calcium concentration. Equation (3) determines the rate of calcium leaching process. In order to calculate the degree of process advancement, one has to integrate eq. (3) over the considered period of time [*to*,*t*], as follows:

$$\Gamma_{leach}^{Ca}\left(\mathbf{x},t\right) = \Gamma_{leach}^{Ca}\left(\mathbf{x},t_{0}\right) + \int_{t_{0}}^{t} \dot{\Gamma}_{leach}^{Ca}\left(\mathbf{x},t\right) dt .$$

$$\tag{6}$$

One should underline that calcium leaching is an irreversible chemical process and it is described here by a non-equilibrium model, what allows to take into account the effect of variable temperature, moisture content and calcium ions concentration upon the process progress rate. More details about this model can be found in [2].

The progress of salt crystallization/dissolution is described in terms of the pore saturation degree with precipitated salt, $S_p(\mathbf{x},t) = V_p(\mathbf{x},t) / V_{pore}(\mathbf{x},t)$, which during the process might increase from zero up to one, when the whole pore volume is occupied by crystals of salt. Liquid water is assumed incompressible here and the model can be applied only below the limit value of $S_{p,max}(\mathbf{x},t) < 1 - S_w(\mathbf{x},t)$, when serious numerical problems arise. The liquid water saturation degree is defined as, $S_w(\mathbf{x},t) = V_w(\mathbf{x},t) / V_{pore}(\mathbf{x},t)$.

The progress of precipitation/dissolution process of salt X depends on the solution supersaturation ratio, S_x , and it might be described by the equation based on the non-equilibrium Freundlich isotherms [3],

$$\dot{S}_{p} = \frac{dS_{p}}{dt} = \begin{cases} S_{w}\left(\mathbf{x},t\right)H^{X}\left[S^{X}\left(\mathbf{x},t\right)-A^{'}\right]^{p}, & S^{X} \ge A^{'} \land S_{p} < 1; \\ -S_{w}\left(\mathbf{x},t\right)H^{X} \mid S^{X}\left(\mathbf{x},t\right)-1 \mid^{p}, & S^{X} < 1 \land 0 < S_{p} < 1; \end{cases}$$

$$(7)$$

where p is the process order, H^x the reaction constant depending on the kind of salt and the properties of porous material. The first line of eq. (7) concerns the salt crystallization from the supersaturated solution, while the second line describes the salt crystals dissolution, which proceeds when the solution supersaturation ratio is lower than one. A' means the primary crystallization coefficient, the value of which might vary from 1.7 up to 10, depending on the kind of salt, pores structure and the solid composition [3]. Equation (7) describes the evolution of salt crystals volume (i.e. the advancement of salt precipitation process). It is assumed that there is no salt in the solid phase until the solution becomes supersaturated. Most salt solutions are the electrolytes, so they decompose into ions (cations and anions), therefore the ion interaction must be considered while modelling their transport and crystallization.

The salt crystallization is induced by the existence of non-equilibrium of the chemical potentials of salt X in the solid- and liquid phase. Quantitatively this driving potential is described by the solution supersaturation ratio, S^x ,

$$S^{X}(\mathbf{x},t) = a_{X}(\mathbf{x},t) / K_{X}$$
(8)

where $a_X(\mathbf{x}, t)$ means the ion activity product and K_X the equilibrium constant for salt *X*. The ion activity product for hydrated salt *X* is calculated according to equation [3]:

$$\ln a_{X} = v_{C} \ln \left(m_{C} \right) + v_{A} \ln \left(m_{A} \right) + v_{C} \ln \left(\gamma_{C} \right) + v_{A} \ln \left(\gamma_{A} \right) + v_{0} \ln \left(a_{w} \right)$$
(9)

where $m_C(\mathbf{x},t)$ and $m_A(\mathbf{x},t)$ are the molalities of cations (described with subscript *C*) and anions (*A*), respectively, γ_C , γ_A the activity coefficients of the ions, v_C , v_A , v_0 the stoichiometric coefficients, and $a_w(\mathbf{x},t)$ the water activity (relative humidity). In order to calculate the ion activity coefficients, the Pitzer ion interaction model is employed [6].

2.2 Modelling strain of a chemically deteriorated, moist porous material

Moist porous building materials are multi-phase porous media, hence analyzing the stress state and the deformation of the material it is necessary to consider not only the action of an external load, but also the pressure exerted on the skeleton by fluids and crystals present in its voids. The total stress tensor acting in a point of the porous medium may be split into the effective stress $t^{ef}(\mathbf{x},t)$, which accounts for stress effects due to changes in porosity, spatial variation of porosity and the deformations of the solid matrix, and a part accounting for the solid phase pressure exerted by the fluids and crystals present in pore volume, $p^{s}(\mathbf{x},t)$, [7],

$$\mathbf{t}^{tot} = \mathbf{t}^{ef} - p^{s}\mathbf{I} = \mathbf{t}^{ef} - \left(p^{g} - \chi^{ws}_{s}p^{c} - \chi^{cs}_{s}p^{cryst}\right)\mathbf{I},$$
(10)

where **I** is the second order unit tensor, $p^{cryst}(\mathbf{x},t)$ the crystallization pressure, while χ_s^{ws} and χ_s^{cs} , the fractions of skeleton area in contact with liquid water and salt crystals, respectively.

The precipitated salt crystals are considered as an additional (with respect to the skeleton) solid phase, which does not participate in the transmission of external load. The growing salt crystals exert an additional crystallization pressure, p^{cryst} , on the solid skeleton which acts as an obstacle confining crystals between the pore walls. The crystals exert the pressure on the material skeleton only if a thin solution film is situated between the growing crystal and the skeleton. In order to describe the crystallization pressure, the chemical potentials on the loaded and unloaded faces of the crystal and the chemical potential of the solute are compared. The crystallization pressure p^{cryst} is given by the following formula [7],

$$p^{cryst} = \frac{RT}{V_m^X} \ln\left(\frac{a_X}{K_X}\right),\tag{11}$$

where *R* is the universal gas constant and V_m^X is the molar volume of salt *X*.

In order to take into account the effects of micro-cracking processes due to chemical degradation of the material strength properties, caused by the leaching process or the salt crystallization, a scalar damage model has been adopted here. The use of a separate measure of

damage for the chemical deterioration process, $V(\mathbf{x},t)$, allows for a clear distinction between such a process and the evolution of damage of different nature (e.g. cracking).

The chemical damage variable $V(\mathbf{x},t)$ for the leaching of calcium species is defined as [12],

$$V(\mathbf{x},t) = 1 - \frac{E\left(\Gamma_{leach,\max}^{Ca}\left(\mathbf{x},t\right)\right)}{E_{0}},$$
(12)

and for the salt crystallization as,

$$V(\mathbf{x},t) = 1 - \frac{E(S_p(\mathbf{x},t))}{E_0},$$
(12)

where E_0 and E are the Young moduli of a sound and chemically deteriorated material, respectively, and $\Gamma_{leach,max}^{Ca}(\mathbf{x},t)$ is the highest value of calcium leaching degree, reached in point **x** until time instant t. This means that the chemical degradation of building materials is irreversible, though the salt precipitation itself is reversible.

Building materials are treated as multiphase porous media, thus also for the chemical deterioration processes the effective stress tensor has been used in the constitutive relationship [12],

$$\mathbf{t}^{ef} = (1 - V) \mathbf{D}_0 \left(\mathbf{\varepsilon}_{tot} - \mathbf{\varepsilon}_c - \mathbf{\varepsilon}_{ch} - \mathbf{\varepsilon}_t \right), \tag{13}$$

where $\boldsymbol{\varepsilon}_{tot}$, $\boldsymbol{\varepsilon}_{c}$, $\boldsymbol{\varepsilon}_{ch}$ and $\boldsymbol{\varepsilon}_{t}$ are the total-, creep-, chemical- and thermal strain tensors, and $\mathbf{D}_{0}(\mathbf{x},t)$ is the tangent matrix for the material which is not chemically deteriorated. Shrinkage and creep strains are modelled by means of the effective stresses [8].

3. Numerical solution

The conservation equations are discretized in space by means of the finite element method. The unknown variables are expressed in terms of their nodal values (denoted by upper bars) and shape functions **N** (= p, t, X, u) as,

$$p^{g}(\mathbf{x},t) \cong \mathbf{N}_{p}(\mathbf{x})\overline{\mathbf{p}}^{g}(t), \qquad p^{c}(\mathbf{x},t) \cong \mathbf{N}_{p}(\mathbf{x})\overline{\mathbf{p}}^{c}(t), \qquad T(\mathbf{x},t) \cong \mathbf{N}_{t}(\mathbf{x})\overline{\mathbf{T}}(t),$$

$$C_{x}(\mathbf{x},t) \cong \mathbf{N}_{x}(\mathbf{x})\overline{\mathbf{C}}_{x}(t), \qquad \mathbf{u}(\mathbf{x},t) \cong \mathbf{N}_{u}(\mathbf{x})\overline{\mathbf{u}}(t).$$
(14)

The discretized form of the model equations was obtained in [1] by means of Galerkin's method and can be written in the following concise matrix form:

$$\mathbf{C}_{ij}\left(\overline{\mathbf{Y}}\right)\frac{\partial\overline{\mathbf{Y}}}{\partial t} + \mathbf{K}_{ij}\left(\overline{\mathbf{Y}}\right)\overline{\mathbf{Y}} = \mathbf{f}_{i}\left(\overline{\mathbf{Y}}\right), \qquad \overline{\mathbf{Y}} = \left\{\overline{\mathbf{p}}^{g}, \, \overline{\mathbf{p}}^{c}, \, \overline{\mathbf{T}}, \, \overline{\mathbf{C}}_{X}, \, \overline{\mathbf{u}}\right\}^{T},$$
(15)

where the non-linear matrix coefficients $C_{ij}(\overline{\mathbf{Y}})$, $K_{ij}(\overline{\mathbf{Y}})$ and $f_i(\overline{\mathbf{Y}})$ (*i*,*j*= *g*, *c*, *t*, *X*, *u*) for different deterioration processes are defined in [2], [3], [4]. The time discretization is accomplished through a fully implicit finite difference scheme,

$$\Psi^{i}\left(\overline{\mathbf{Y}}_{n+1}\right) = \mathbf{C}_{ij}\left(\overline{\mathbf{Y}}_{n+1}\right)\frac{\overline{\mathbf{Y}}_{n+1} - \overline{\mathbf{Y}}_{n}}{\Delta t} + \mathbf{K}_{ij}\left(\overline{\mathbf{Y}}_{n+1}\right)\overline{\mathbf{Y}}_{n+1} - \mathbf{f}_{i}\left(\overline{\mathbf{Y}}_{n+1}\right) = \mathbf{0},\tag{16}$$

where superscript i (i= g, c, t, X, u) denotes the state variable, subscript n is the time step number and t is the time step length. The equation set (16) is solved by means of a monolithic Newton-Raphson type iterative procedure using a frontal solver, see e.g. [2].

3.1 Numerical example

Two examples of the model application for analyzing non-isothermal leaching of a 16-cm cement mortar wall and salt precipitation in a drying wall made of cement mortar, initially saturated with the NaCl salt solution, were presented in [5]. Here an example showing evolution of crystallization pressure in a drying wall made of ceramic brick is analyzed.

The two-side drying of a brick wall, initially saturated with the NaCl solution, was simulated using the HMTRA_SALT software [4]. The following material properties were assumed during the simulation: intrinsic permeability coefficient k= $3\cdot10^{-17}$ m², porosity *n*=0.293, skeleton density ρ^{σ} =1834 kg/m³. The process order constant in eq. (7) was assumed as *p*=7.5 [1]. The sorption isotherm of the brick was measured by means of the saturated salt solution method, was described by the following equation, proposed by Baroquel-Bouny et al. [9],

$$p^{c} = a \left(S_{w}^{-b} - 1 \right)^{1 - 1/b}, \tag{17}$$

with *a*= 5.63 and *b*= 1.5.

On the both surfaces of the wall the external conditions were the same. Due to this symmetry, only one half of the wall was modelled with 100 isoparametric eight-noded finite elements of equal size. The wall drying was induced by a rapid decrease of relative humidity of the surrounding air from RH₀=100% to RH₀=85%, while the air temperature was equal to 20°C. Convective heat and moisture exchange was assumed at the surface with heat and mass surface coefficients: $\alpha = 8 \text{ W/m}^2\text{K}$ and $\beta = 0.008 \text{ m/s}$. The simulations were performed for the time period of 500 h.



Figure 1: The simulation results for drying of a brick contaminated with NaCl - *profiles at different time stations: t= 100, 200, 300, 400 and 500 h: a) salt supersaturation ratio, b) relative volume of salt crystals.*



Figure 2: The simulation results for drying of a brick contaminated with NaCl - profiles at different time stations: t= 100, 200, 300, 400 and 500 h: a) crystallization pressure in the surface zone, b) distribution of stresses in the surface zone.

The decrease of ambient air relative humidity causes the evaporation of water and the transport of the liquid phase from the interior of the wall toward its surface. Salt, migrating with water toward the surface, cannot evaporate, therefore its concentration gradually increases in the vicinity of the wall surface, where the solution often becomes supersaturated. Significant gradients of the supersaturation ratio are observed in the vicinity of the wall surface, Figure 1a. It causes the salt diffusion in the opposite direction to the capillary flow. The diffusive flow tends to diminish the supersaturation gradient. When the solution is supersaturated, the salt crystallization proceeds. According to the simulation results, after 500 h of drying, 26% of the pore volume in the surface zone is occupied by the salt crystals, Figure 1b. The growing crystals exert an additional pressure on the solid skeleton, which acts as an obstacle opposing the crystals formation, Figure 2a. The crystallization pressure depends on the solution supersaturation ratio, see eq. (11). Only a part of the solid internal surface is covered by the solidcrystal interface, which transmits the crystallization pressure. The crystallization pressure causes an additional tensile stresses in the solid skeleton. One can observe that during the salt crystallization positive tensile stresses are induced in the zone close to the surface, Figure 2b. The tensile strength of the brick equals approximately 1MPa. The results of simulation show that such value can be reached during the drying of brick contaminated with a salt. As a consequence, the brick can be destroyed due to the crystallization pressure, giving, as a brittle material, no signal of damage until the scaling appears.

Conclusions

A mathematical model of hygro- thermo- chemo- mechanical behaviour of porous building materials, considering their multiphase nature and several mutual couplings of different physicochemical phenomena, has been briefly presented and numerically solved. Mechanics of multiphase porous media and damage mechanics are applied for this purpose, and kinetics of

deterioration processes is described with evolution equations based on thermodynamics of chemical reactions, what allows for analyzing degradation of porous building materials in variable hygro-thermal conditions. The results presented here and elsewhere [2 - 5] show that progress of chemical degradation of the materials is strongly coupled with their hygro-thermal state.

Acknowledgments

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A Proposal to Reduce GUM's Recommendations to Practice in Flash Methods

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Abstract: Since the first formulation of the principles of flash techniques, given by parker et al. in the 60ies of the last century, lots of models were developed to examine diffusivity from the thermal response of a sample. Current models mainly consider both, the interaction of a sample with its environment and the finite pulse length of the thermal impact. They do not consider any thermal effect coming from the sample itself. Till today the basic idea in flash techniques traces back to the thermal balance of a thermally inert sample without any consumption or release of heat during the measurement process. This basic assumption more and more is not fulfilled for complex materials or processing materials. Thus, current models often do not describe the thermal response of a sample in a sufficient way. This causes non negligible contributions to the uncertainty of the measurement result – mainly the so called Model Specific Uncertainty MSU. Currently it cannot be estimated sufficiently, because models operate numerically and are like a black box for the user. Therefor this paper cannot give a method how to formulate the MSU sufficiently. But it tries to propose a concept to formulate the uncertainty of diffusivity results using three fundamental sources of uncertainty: the Model Specific Uncertainty MSU, the Sample Specific Uncertainty SSU and the Equipment Specific Uncertainty ESU.

Keywords: Flash Techniques, Thermal Diffusivity, Uncertainty

1. Requirements & motivation

The first statement in the introduction of the "GUIDE TO EXPRESS UNCERTAINTY IN MEASUREMENT" (GUM) is: "When reporting the result of a measurement of a physical quantity, it is obligatory that some quantitative indication of the quality of the result be given so that those who use it can assess its reliability" /1/. And in its basic concepts the GUM points out that "The result of a measurement after correction for recognized systematic effects is still only an estimate of the value of the measurands because of the uncertainty arising from random effects and from imperfect correction of the result for systematic effects". The recognition of systematic effects requires the profound understanding of the applied measuring techniques including a sufficient mathematical description of all significant effects involved, and the perpetual improvement of corrections necessary to consider systematic effects as mentioned. Unfortunately till now the recommendations of the GUM are not implemented all-over. Here it is attempted to give a proposal to reduce GUM's recommendations to practice for flash techniques.

2. Basic assumptions in flash methods – heat balance

Only under the assumption of a conservative system, of homogeneity of the thermally conducting medium (no spatial dependence of the material properties: thermal conductivity λ , specific heat c_p , and the density ρ) and of the neglect of any non-linearity, the thermal balance of a body leads to the applied version of Fourier's thermal conductivity equation. Material properties then are assumed as dependent from temperature only, and Fourier's equation

defines a simple interrelationship between the four basic thermo physical properties: $\lambda(T)$, $c_p(T)$, $\rho(T)$ and the thermal diffusivity a(T).



Figure 1: Heat balance if a body



Figure 2: Basics of a flash experiment

3. Flash technique - parker model and advanced examining modells

In the early 60-ies of the last century Parker et al. used the solution of the 1-dimensional formulation of the thermal conductivity equation to derive the theoretical basis of diffusivity measurement /2,3/. The method is based on an infinitely short heat pulse and the assumption of adiabatic boundaries. This is illustrated above. One sees both the theoretically temperature response calculated from Parker's model, and the real experimentally detected temperature response T(t).

Based on measurements with reference materials the standard deviation of a set of measurements is less than 1% of the measured value. Nevertheless, these data differ minimum 5% from the true value! The reason therefor is the too simple examining model of Parker, which:

- 1. does not consider any heat exchange of the sample with it's environment and
- 2. does not consider the non-negligible duration of the heat impact. Insufficiencies like those became obviously and improved models became developed therefrom.

In cases of non-negligible heat losses of the sample and finite durations of heat impact comparable (in proportion to the run time of the thermal response of the sample), elaborated models like Cape-Lehmann model – incorporating heat losses and finite pulse length correction – capture all relevant effects /4,5/. So far no thermal source or sink becomes evident, and so far samples are homogenous and statistically isotropic, mostly no fault coverage is noticeable.



Figure 3: Temperature response of thermally inert (above) and thermally non-inert (downwards) materials

<u>Current material development often focusses on **processing materials**</u>. Kinetically descriptions of the current status of matter are needed /6,7/ and the basic assumptions mentioned above are not further fulfilled. Nevertheless: for all that flash techniques are applied, and in lots of cases it seems to be possible to examine sufficient data (c.f. figure – left side-above). But from principal reasons examination models do NOT consider any <u>consumption and/or release of heat</u>. The fundamental risk of the insufficient examination of diffusivity data by reason of an inadequate

examining model is evident, because no tool to quantify the descriptive quality of a specific model in terms of an amount to the uncertainty is available till now.

4. Uncertainty estimation in flash methods

Here three causally determined sources of uncertainty are postulated: a first one coming from the sample or material itself, a second one traceable back to the performance of the equipment, and a third one coming from the applied model to examine physical quantities from the measured data. They will be attributed as <u>Sample Specific Uncertainty</u>: *SSU*, <u>Equipment Specific Uncertainty</u>: *ESU*, and <u>Model Specific Uncertainty</u>: *MSU*. They must be formulated strictly in accordance to the recommendations of the GUM. And the outcome of these models is used to improve some examination routines.



Figure 4: Principles of an uncertainty assessment in flash methods

ESU(a): Despite it's insufficiencies Parkers model allows to estimate an "<u>Equipment Specific</u> <u>Uncertainty</u>" of the flash setup as it is shown in the figure on the right side. The used laser flash device NETZSCH® LFA 427 provides a data acquisition rate of about 0,5 MHz /8/. Thus the minimum uncertainty $u(t_{1/2})$ is 2 µs. The numerical simulation of the measured temperature profile at the top side of the specimen needs about 250 data points between the release of the laser and the half time. Thus a minimum half time of $t_{1/2}$ (min) = 0,5 ms must not be gone below. As one specific result of this a minimum sample thickness, depending on the diffusivity of the material, can be estimated.

$$h_{min} \cong \sqrt{\frac{\pi^2}{\ln 4} \cdot a \cdot t^{min.}_{1/2}} \cong 0,06 \cdot \sqrt{a}$$
(3)

SSU(a): The effect of the sample itself will be considered by the standard deviation of the diffusivity data $s(a_i)$ from repeated measurements at a specific temperature. From this the "*Sample Specific Uncertainty*" *SSU(a)* = $(1/\sqrt{n})$. $s(a_i) = s(a)$ is defined.

MSU(a): At the moment there is no possibility to quantify the fit-capability of the examining model in terms of its suitability to gather the relevant thermal transport effects inner the sample. Thus the third significant part of an uncertainty assessment – the so called "<u>Modell</u> <u>Specific Uncertainty</u>" cannot be quantified currently.

5. Summary

Based on three basic sources of uncertainty a concept to formulate a comprehensive description of the uncertainty of diffusivity data from flash measurements is proposed. These sources are the measured sample– causing a <u>Sample Specific Uncertainty SSU</u>, the equipment itself with its <u>Equipment Specific Uncertainty ESU</u> and the examining model used to derive the diffusivity data from the thermal response of the sample: the <u>Model Specific Uncertainty MSU</u>. The SSU and the ESU can easily be formulated using the recommendations of the GUM. But for the formulation of the MSU currently no method does exist. The reason therefor is that modern methods are operated numerically, and that the user does not have access even to the data necessary to transform e.g. the statistics of a fit quality in a dimension of uncertainty. It seems to be a request to the equipment suppliers to give an authoritative estimation of the MSU, implementing the parameters minimum specific for the applied numerical routines. An extension of the theoretical basis of the examining equations to thermally non inert materials seems to be a need too.

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Measurement of apparent thermal conductivity of wet porous building materials by a periodic method

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Abstract: In this paper, we propose a transient method for measuring the thermal conductivity of a wet porous building material and a method of evaluating the measurement uncertainty, on the basis of both theoretical developments for heat and mass transfer and the constructed database of hygrothermal properties. An approximation formula for the measurement uncertainty caused by moisture movement and non-uniform moisture distribution, and thus a determination of the measuring conditions that satisfy the upper limit of measurement uncertainty, is derived. The evaluation of the measurement uncertainty makes possible a simple and thus practical method for measuring thermal conductivity. Based on the above analysis, the apparent thermal conductivity of a wood fiber board was measured at the mean temperature $8.0, 27.5, and 40 \,^\circ$ C.

Keywords: Apparent thermal conductivity, Wet porous material, Non-steady state method, Heat and moisture transfer, Measurement uncertainty

1. Introduction

Most building materials, with the exception of glass and metals, are porous and thus absorb moisture due to condensation, rain, and water uptake from the ground. The absorbed moisture may damage the materials through, e.g., rotting or frost damage, and thus may cause their performance to deteriorate. In particular, an increase in the moisture content of insulation material causes a reduction of its thermal resistance, which must be avoided as much as possible to preserve its performance. However, infiltration of rain water into a brick wall or joints of tiles and uptake of ground water into the foundation (footing) are very difficult to avoid. Therefore, it is important to understand the changes in the thermal properties (thermal conductivity and heat capacity) of porous materials due to changes in their moisture content.

ISO 10051 [1] specifies a steady-state method for measuring the thermal conductivity of a moist building material. In the steady-state method, a nonuniform distribution of moisture content in the test piece is inevitable, since the imposed temperature gradient causes moisture transfer. The nonuniform moisture distribution makes it difficult to define which moisture content the measured thermal conductivity corresponds to. ISO 10051 categorizes the moisture distribution in the test piece into several types and estimates the thermal conductivity corresponding to each type. Since theoretical and experimental research has recently been performed concerning heat and moisture transfer in porous materials [2]-[6], along with measurements and the construction of a database of hygrothermal properties [7], hygrothermal behavior can now be predicted with reasonable accuracy.

This paper proposes a transient method for measuring the apparent (effective) thermal conductivity of a wet porous building material and a method of evaluating the measurement uncertainty, on the basis of both theoretical developments for heat and mass transfer and the

constructed database of hygrothermal properties. The proposed method makes use of a nonsteady-state method that uses a small temperature change with a short period as an input. The evaluation of the measurement uncertainty makes possible a simple and thus practical method for measuring thermal conductivity.

2. Apparent Thermal Conductivity of Wet Porous Materials

2.1 Fundamental equations of vapour, liquid water, and heat transfer

In this research, the following equations describing the simultaneous flow of heat and moisture in a moist porous material are used [4]:

vapour balance
$$c\gamma \frac{\partial X}{\partial t} = \frac{\partial}{\partial x} \left[k_v \frac{\partial X}{\partial x} \right] + \alpha'_i S(X - X_i)$$
 (1)

liquid water balance $\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left[D_{\theta t} \frac{\partial \theta}{\partial x} \right] + \frac{\partial}{\partial x} \left[D_{T t} \frac{\partial T}{\partial x} \right] + \alpha'_{t} S(X - X_{t})$ (2)

heat balar

nce
$$c'\gamma'\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[\lambda \frac{\partial T}{\partial x} \right] + R\alpha'_i S(X - X_i)$$
 (3)
n isotherm $X_i = g(\theta, T)$. (4)

absorption isotherm
$$X_i = g(\theta, T)$$
.

where the sensible heat transported by vapour and liquid is neglected. Assuming α_i is infinite(local equilibrium), using Equation (4), Equations (1)–(3) are transformed as follows:

moisture balance
$$\left(1 + c\gamma \frac{\partial g}{\partial \theta}\right) \frac{\partial \theta}{\partial t} + \left(c\gamma \frac{\partial g}{\partial T}\right) \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left[D_{\theta} \frac{\partial \theta}{\partial x}\right] + \frac{\partial}{\partial x} \left[D_{T} \frac{\partial T}{\partial x}\right]$$
(5)

$$\left(Rc\gamma\frac{\partial g}{\partial\theta}\right)\frac{\partial\theta}{\partial t} + \left(Rc\gamma\frac{\partial g}{\partial T} + c'\gamma'\right)\frac{\partial T}{\partial t} = \frac{\partial}{\partial x}\left[\left(\lambda + RD_{Tv}\right)\frac{\partial T}{\partial x}\right] + R\frac{\partial}{\partial x}\left[D_{\theta v}\frac{\partial\theta}{\partial x}\right]$$
(6)

heat balance

where
$$D_{\theta} = D_{\theta v} + D_{l\theta} = k_v \frac{\partial g}{\partial \theta} + D_{\theta l}, \quad D_T = D_{Tv} + D_{Tl} = k_v \frac{\partial g}{\partial T} + D_{Tl}$$
 (7)

2.2 Implication of the thermal conductivity of a wet porous material

In Equation (3), λ represents the thermal conductivity, which is mainly determined by conduction through the constituents (solid skeleton, water, and air) in the case of no moisture movement, and of course it varies with the water content. On the other hand, as seen in Equation (6), λ and RD_{Tv} appear in the conjunct form $\lambda^* = \lambda + RD_{Tv}$, and λ^* is the coefficient to the temperature gradient.

As mentioned above, λ and RD_{TV} never appear separately in the fundamental equations (5) and (6) or in the boundary conditions. Consequently, D_{θ} , D_{T} , $\lambda^*=\lambda + RD_{T_v}$, and $D_{\theta v}$ are necessary to calculate the heat and mass transfer, while the values of λ and RD_{Tv} are not necessary. Because of these properties of the fundamental equations, only λ^* (not λ) is given by any method of measuring thermal diffusivity. Thus, methods that minimize the effects of moisture movement can mostly minimize the effect of the term $R\partial/\partial x(D_{\theta v}\partial \theta/\partial x)$ and measure λ^* more accurately.

3. Theoretical Analysis of Thermal Diffusivity Measurement by Periodic Method

3.1 Objective of analysis

It is estimated from the above-mentioned result that the thermal diffusivity corresponding to λ^* can be measured in a non-steady-state method minimizing the moisture movement, and thus non-uniform moisture distribution. In order to minimize the nonuniformity, a periodic method is adopted as a transient method of measuring thermal conductivity in this study. Since positive and negative temperature gradients are generated in turn in this method, the (time-averaged) water content distribution can be expected to remain nearly uniform. By measuring the temperatures at two points in the sample, the thermal diffusivity can be determined based on the amplitude ratio or phase difference of these two temperatures. If the input cyclic temperature fluctuation is kept small enough that the change in transport properties is also small enough, the system can be regarded as linear.

The objective of the following analysis is to estimate quantitatively the measurement uncertainty caused by moisture movement and to derive a formula to give the measurement uncertainty that is composed of the material properties and is applicable to any material. This problem will be solved by a perturbation method assuming that the transfer coefficients are linear functions of water content and temperature and that the solution is a power series of the input surface temperature variation amplitude. The influences of moisture are those caused by

- (A) the existence of the moisture movement, and
- (B) variation of the transfer coefficients with water content and temperature.

The first term of the solution can be considered to represent (A), and the second term, (B).

3.2 Formulation

3.2.1 Perturbation from initial conditions

Suppose that the material is semi-infinite and that its surface temperature variations are sinusoidal. The basic equations are Equations (5) and (6) (neglecting smaller order terms in the left-hand side):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial x} \left\{ D^{0}_{\theta t} \left[1 + \eta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \eta_{2} \left(T - T_{0} \right) \right] \frac{\partial \theta}{\partial x} + D^{0}_{\theta v} \left[1 + \zeta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \zeta_{2} \left(T - T_{0} \right) \right] \frac{\partial \theta}{\partial x} \right\} + \frac{\partial}{\partial x} \left\{ D^{0}_{T t} \left[1 + \beta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \beta_{2} \left(T - T_{0} \right) \right] \frac{\partial T}{\partial x} + D^{0}_{T v} \left[1 + \zeta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \zeta_{2} \left(T - T_{0} \right) \right] \frac{\partial T}{\partial x} \right\}$$

$$(8)$$

$$(c'\gamma')^{0} \left[1 + \kappa_{1}(\theta - \theta_{0})\right] \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left\{ \lambda^{0} \left[1 + \gamma_{1}(\theta - \theta_{0})\right] \left[1 + \gamma_{2}(T - T_{0})\right] \frac{\partial T}{\partial x} + RD_{Tv}^{0} \left[1 + \xi_{1}(\theta - \theta_{0})\right] \left[1 + \xi_{2}(T - T_{0})\right] \frac{\partial T}{\partial x} \right\} + R \frac{\partial}{\partial x} \left\{ D_{\theta v}^{0} \left[1 + \zeta_{1}(\theta - \theta_{0})\right] \left[1 + \zeta_{2}(T - T_{0})\right] \frac{\partial \theta}{\partial x} \right\}$$
(9)

with initial conditions, $T = T_0$, $\theta = \theta_0$,

and boundary conditions,

(10)

$$\left\{ D^{0}_{\theta \ell} \left[1 + \eta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \eta_{2} \left(T - T_{0} \right) \right] + D^{0}_{\theta \ell} \left[1 + \zeta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \zeta_{2} \left(T - T_{0} \right) \right] \right\} \frac{\partial \theta}{\partial x} + \left\{ D^{0}_{T \ell} \left[1 + \beta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \beta_{2} \left(T - T_{0} \right) \right] + D^{0}_{\theta \ell} \left[1 + \zeta_{1} \left(\theta - \theta_{0} \right) \right] \left[1 + \zeta_{2} \left(T - T_{0} \right) \right] \right\} \frac{\partial T}{\partial x} = 0 \quad (x = 0)$$

$$(11)$$

 $T = Finite \ (x \to +\infty), \ T = T_0 + I_0 \sin \omega t \ (x = 0), \ T = Finite \ (x \to +\infty)$ (12), (13), (14)

where zero superscripts represent the values at θ_0 and T_0 . Transforming θ and T to θ' and T' by the relation,

$$T' = T - T_0, \quad \theta' = \theta - \theta_0 \tag{15}$$

the transformed equations have the same form as Equations (8)–(14), except that θ_0 and T_0 are 0. Hereafter we rewrite θ' and T' as θ and T.

3.2.2 Moisture content and temperature as functions of small input

We assume a power series solution as

$$T = I_0 T_1 + I_0^2 T_2 + I_0^3 T_3 + \dots, \ \theta = I_0 \theta_1 + I_0^2 \theta_2 + I_0^3 \theta_3 + \dots,$$
(16)

where, I₀ is the amplitude of the surface temperature variation. Substituting these equations into Equations (8)–(14) and equating the coefficients of the same order, we obtain the equations for θ_1 , T_1 , θ_2 , T_2 , etc.

3.3 Solution

3.3.1 First order solution (periodic solution)

$$\theta_{1}(t,x) = \alpha_{1}E_{1}\exp\left(-\alpha_{1}\sqrt{\frac{\omega}{2}}x\right) \times \sin\left(\omega t - \alpha_{1}\sqrt{\frac{\omega}{2}}x\right) - \alpha_{2}E_{2}\exp\left(-\alpha_{2}\sqrt{\frac{\omega}{2}}x\right) \times \sin\left(\omega t - \alpha_{2}\sqrt{\frac{\omega}{2}}x\right), \quad (17)$$

$$T_{1}(t,x) = \alpha_{1} \frac{EE_{1}}{B} \exp\left(-\alpha_{1} \sqrt{\frac{\omega}{2}}x\right) \times \sin\left(\omega t - \alpha_{1} \sqrt{\frac{\omega}{2}}x\right) - \alpha_{2} \frac{EE_{2}}{B} \exp\left(-\alpha_{2} \sqrt{\frac{\omega}{2}}x\right) \times \sin\left(\omega t - \alpha_{2} \sqrt{\frac{\omega}{2}}x\right), \quad (18)$$

where, $E = \frac{B}{(\alpha_1 - \alpha_2) \left[C - (CA - BD) (\alpha_1^2 + \alpha_1 \alpha_1 + \alpha_1^2) \right]}, E_1 = C - (CA - BD) \alpha_1^2, E_2 = C - (CA - BD) \alpha_2^2$ (19)

 α_1 and α_2 are positive roots of the quadratic equation ($\alpha_1 < \alpha_2$)

$$(AC - BD)\alpha^{4} - (A + C)\alpha^{2} + 1 = 0,$$
(20)

where,
$$A = D_{\theta}^{0}, \quad B = D_{T}^{0}, \quad C = \frac{\lambda^{0} + RD_{Tv}^{0}}{(c'\gamma')^{0}}, \quad D = \frac{RD_{\theta v}^{0}}{(c'\gamma')^{0}}.$$
 (21)

3.3.2 Second order solution (periodic solutions)

$$\begin{aligned} \theta_{2}(t,x) &= 2U_{3}\exp\left(-\alpha_{1}\sqrt{\omega}x\right) \times \cos\left(2\omega t - \alpha_{1}\sqrt{\omega}x\right) + 2U_{7}\exp\left(-\alpha_{2}\sqrt{\omega}x\right) \times \cos\left(2\omega t - \alpha_{2}\sqrt{\omega}x\right) \\ &+ 2Q_{1}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) \times \cos\left(2\omega t - 2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) + 2Q_{2}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) \times \cos\left(2\omega t - 2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right), \end{aligned}$$
(22)
$$&+ 2Q_{3}\exp\left[\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \cos\left[2\omega t - \sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] + Q_{4}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) \\ &+ Q_{5}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) + 2Q_{6}^{\prime}\exp\left[-\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \cos\left[\sqrt{\frac{\omega}{2}}(\alpha_{1} - \alpha_{2})x\right] \\ &+ 2Q_{6}^{\prime}\exp\left[-\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \sin\left[\sqrt{\frac{\omega}{2}}(\alpha_{1} - \alpha_{2})x\right] \\ &+ 2Q_{6}^{\prime}\exp\left[-\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \sin\left[\sqrt{\frac{\omega}{2}}(\alpha_{1} - \alpha_{2})x\right] \\ &+ 2Q_{6}^{\prime}\exp\left[-\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) \times \cos\left(2\omega t - 2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) + 2R_{2}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) \times \cos\left(2\omega t - 2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) \\ &+ 2R_{1}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) \times \cos\left(2\omega t - 2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) + 2R_{2}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) \times \cos\left(2\omega t - 2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) \\ &+ 2R_{3}\exp\left[-\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \cos\left[2\omega t - \sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] + R_{4}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{1}x\right) \\ &+ R_{5}\exp\left(-2\sqrt{\frac{\omega}{2}}\alpha_{2}x\right) + 2R_{6}^{\prime}\exp\left[-\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \cos\left[\sqrt{\frac{\omega}{2}}(\alpha_{1} - \alpha_{2})x\right] \\ &+ 2R_{6}^{\prime}\exp\left(-\sqrt{\frac{\omega}{2}}(\alpha_{1} + \alpha_{2})x\right] \times \sin\left[\sqrt{\frac{\omega}{2}}(\alpha_{1} - \alpha_{2})x\right] + V_{18} \end{aligned}$$

3.4 Determination of thermal diffusivity

3.4.1 Approximation of the coefficients appearing in the solution

By assuming, $\frac{BD}{AC} < 1$, etc. (which should be derived from the hygrothermal properties), the following approximate equations are obtained:

$$\alpha_{1} \cong \frac{1}{\sqrt{C}} \left(1 - \frac{BD}{2C^{2}} \right), \quad \alpha_{2} \cong \frac{1}{\sqrt{A}} \left(1 + \frac{BD}{2AC} \right), \quad E = \frac{B}{\sqrt{C}} \left(1 - \frac{\sqrt{A}}{\sqrt{C}} \cdot \frac{BD}{AC} \right),$$

$$E_{1} \cong C \left(1 - \frac{A}{C} \right), \quad E_{2} \cong -\frac{BD}{C} \left(1 + \frac{A}{C} - \frac{BD}{C^{2}} \right), \quad \alpha_{1}E_{1} \frac{E}{B} \cong 1 - \frac{\sqrt{A}}{\sqrt{C}} \cdot \frac{BD}{AC},$$

$$\alpha_{2}E_{2} \frac{E}{B} \cong -\frac{\sqrt{A}}{\sqrt{C}} \cdot \frac{BD}{AC} \left(1 + \frac{BD}{2AC} \right), \quad 2 \frac{1 - A\alpha_{1}^{2}}{B\alpha_{1}^{2}} U_{3} \cong -2(R_{1} + R_{2})$$
(24)

3.4.2 Solution for heat flow without moisture

The solution is

$$T(t,x) = I_0 \exp(-\sqrt{\frac{\omega}{2a}}x) \times \sin(\omega t - \sqrt{\frac{\omega}{2a}}x) + T_m$$
(25)

where T_m is the (constant) average temperature, a is the thermal diffusivity of the sample material, and ω is the angular velocity of the input temperature. By making use of this solution, for example, the method using the phase difference gives the thermal diffusivity a as

$$a = \frac{1}{\phi_0^2} \left(\frac{\omega}{2}\right) (x_1 - x_2)^2 \tag{26}$$

where x_1 and x_2 are any two points in the material and ϕ_0 is the phase difference between the temperatures at x_1 and x_2 .

3.4.3 Solution for heat flow with moisture

By using the fact that generally $\alpha_2 \left(\cong \frac{1}{\sqrt{A}} \right)$ is larger than $\alpha_1 \left(\cong \frac{1}{\sqrt{C}} \right)$, Equation (18) approximately

becomes

$$T_1(t,x) = \alpha_1 \frac{EE_1}{B} \exp\left(-\alpha_1 \sqrt{\frac{\omega}{2}}x\right) \times \sin\left(\omega t - \alpha_1 \sqrt{\frac{\omega}{2}}x\right)'$$
(27)

because of the rapid exponential decay of the second term. Based on this solution, when there is moisture, the apparent thermal diffusivity $\frac{1}{\alpha_1^2}$ can be given by

$$\frac{1}{\alpha_1^2} \cong C\left(1 + \frac{BD}{C^2}\right) = \frac{1}{\phi^2} \left(\frac{\omega}{2}\right) (x_1 - x_2)^2 \,, \tag{28}$$

where ϕ is the phase difference of the temperatures at x_1 and x_2 .

3.5 Observational uncertainty:

The uncertainty in the thermal diffusivity calculated using the phase difference ϕ measured in this case relative to that of Equation (26) is

$$\frac{\phi_0^2}{\phi^2} - 1 = \frac{1}{C} \frac{1}{\alpha_1^2} = 1 - \frac{BD}{C^2},$$
(29)

where the approximation $\frac{1}{\alpha_1^2} \cong C\left(1 + \frac{BD}{C^2}\right)$ (Equation (24)) was used. As expected, Equation (29) represents the influence of the term $R\frac{\partial}{\partial x}\left(D_{\theta},\frac{\partial\theta}{\partial x}\right)$.

Similarly, the perturbation solution T_2 can be used to determine the amplitude of the input temperature variation, because this temperature expresses the influence of the nonlinear change of the hygrothermal properties, i.e., the degree of nonuniform distribution of the moisture content.

4. Measurement of Thermal Diffusivity by Periodic Method

4.1 Outline of measurement by periodic method

A schematic diagram of the apparatus for the periodic method is given in Figure 1. The whole system is installed in a climate chamber whose temperature is kept at the mean temperature of the sample under measurement. The sample is preconditioned at a certain water content, and then the whole surface is made impermeable to moisture movement. A periodic temperature variation is imposed on the sample, and the temperatures at (at least) two points in the sample are measured by thermocouples.



Figure 1: Schematic diagram for measuring thermal diffusivity

4.2 Measurement of Thermal Diffusivity of Wood Fibreboard

As an example, Figure 2 shows the measured temperature profiles at two positions under the conductivities $\omega = 0.265 \text{ rad/s}$ (period 24s), $\Theta = 170 \%$, T₀=26.9 °C, I₀=0.338 K. The thermal conductivities obtained are shown in Figure 3. The mean temperatures of the sample were 8.0, 27.5, and 40.0 °C. In calculating the thermal conductivity, the volumetric heat capacity of the material was used.



Figure 2: Measured temperature profiles at two positions Figure 3 Thermal conductivity of wood fibre board

(moisture content by weight $\Theta = 170$ %

The results obtained for a wood fibre board show that the thermal conductivity increases rapidly with water content, from 0.06 W/m K when it is air dry to 0.21 W/m/K at 200% of water content (at 27.5 °C). This suggests that the variation of the thermal conductivity with water content must be considered. Thermal conductivity increases with the mean temperature, and its change is rather large. This increase is because of the variation of the values of λ and D_{Tv}, which are components of λ^* , with temperature. Making use of this fact, the values of λ and D_{Tv} can be estimated separately by the results obtained.

In these measurements, the maximum theoretical uncertainty of the periodic method calculated by Equation (29) is 0.1 % (at Θ = 10%), which is sufficiently small compared with the uncertainty caused by experimental processes.

5. Conclusion

In this paper, we proposed a transient method for measuring the thermal conductivity of a wet porous building material and a method of evaluating the measurement uncertainty. An approximation formula for the measurement uncertainty caused by moisture movement and non-uniform moisture distribution was derived. Based on the results, the apparent thermal conductivity of a wood fiber board was measured at the mean temperature 8.0, 27.5, and 40°C.

Nomenclature

- a: thermal diffusivity of the material $[m^2/s]$, A, B, C, D: defined in Equation (21), c: porosity $[m^3/m^3]$,
- c': specific heat of the material [J/(kg K)], cs: specific heat of the dry material [J/(kg K)],
- D₀₁, D_{T1}: liquid water conductivity related to water content gradient and temperature gradient, respectively, [m²/s], [kg/(msK)],
- $D_{\theta v},\, D_{Tv},\, D_{\theta},\, D_{T}$: moisture conductivities defined by Equation (7),
- E, E₁, E₂: defined in Equation (19), I₀: amplitude of the input surface temperature [K],
- kv: vapour diffusivity [kg/(m s kg)/kg'], R: latent heat of vaporization [J/kg],
- S: specific surface area inside the material, i.e., ratio of surface area to the pore volume $[m^2/m^3]$,
- t: time[s], T: temperature [K], To: initial temperature [K],
- T₁, T₂, θ₁, θ₂: the first and second terms of the perturbation solution of the temperature and water content, respectively [K], [kg/m³],
- U3, U7, Q1-Q6, R1-R6, V18: coefficients appearing solutions 02 and T2,
- x: coordinate [m], X: humidity ratio of moist air in the pores of the specimen [kg/kg'],
- X:: equilibrium humidity ratio with liquid or capillary water at the interface in the material [kg/kg'],
- α_1, α_2 : defined in Equation (20),
- α' : effective vapour transfer coefficient at the interface [kg/(ms kg/kg')],
- γ : specific weight of dry air [kg/m³], γ ': density of the material [kg/m³],
- $η_1$, ζ₁, $β_1$, ξ_1 , $κ_1$, $γ_1$: water content coefficients of D_θ, D_{θν}, D_{Tl}, D_{Tv}, c'γ', λ,
- $η_2$, ζ₂, $β_2$, $ξ_2$, $γ_2$: temperature coefficients of D_θ, D_θ, D_T, D_T, λ,
- λ : thermal conductivity without moisture movement [W/(m K)], $\lambda^*=\lambda+RD_{Tv}$ [W/(m K)],
- θ : water content of material [kg/m³], Θ : water content by weight [%],
- ω : angular velocity of the input surface temperature [rad/s].

Subscripts: 0= initial, θ=moisture, T=temperature, l=liquid, v=vapour.

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The role of the nano-local heating in photoinduced structural changes in chalcogenide glasses from point of view of the barrier-cluster-heating model

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Abstract: This contribution is devoted to the concise characteristic of barrier-cluster-heating model of amorphous semiconductor and to the description of its possibilities by the explanation of the physical phenomena in chalcogenide glasses. Barrier-cluster-heating model originated as synthesis of two various independently created models - barrier-cluster model and local-heating model. Synthesis of both mentioned insights brought also synergic effect, enabling the deeper understanding of physical processes in amorphous semiconductors. In this article are ushered and discussed a new insights on the observed phenomena, which brings connection of two models.

Keywords: chalcogenide glass, photoinduced changes, structural transformations, weak absorption tail, mid-gap phenomena

1. Introduction

Chalcogenide glasses have recently drawn great attention due to their potential use in various solid state devices [1-8]. Until now doesn't exist such model, which would be able to explain wider area of phenomena observed in these matters [1, 5-10]. In this contribution is described so called barrier-cluster-heating model of non-crystaline matter, e.g. chalcogenide glass, which enables to explain many electrical, optical and photo-structural (photo-induced) phenomena in these matters. BCH model originated as synthesis of two various models of chalcogenide glasses - barrier-cluster model and local-heating model. These were created and developed independently one from the other. It was shown, that these two models are mutually compatible, and that they are mutually complemented and enriched. The compability of both mentioned insights enables us to create extended barrier-cluster-heating model (BCH). But BCH model is not a mechanical connection of the two models. Synthesis brought deeper understanding of physical processes in amorphous semiconductors. In the conclussion of this article are analysed the complex views on the phenomena in chalcogenide glasses.

2. Barrier-cluster-heating model

Barrier-cluster heating model (equal as its former predecessor barrier-cluste model) of the noncrystalline semiconductors is based on the assumption that in non-crystalline semiconductors, there exist nano-regions separated from each other by potential barriers [11-15]. We suppose that these nano-regions in chalcogenide glasses are created by closed clusters. Important starting point of authentic local-heating model was also similar idea, that glasses at nanometer scales are inhomogeneous, consisting of nano-regions. This is in compliance with original BC model. This is important component unit of the compability of both models, which enables to integrate of both models into one model (BCH).

Existence of nanoregions

Authors [1] of local heating model state that the experimental data testifying to the existence of nanoregions in glasses are somewhat indirect. These data (facts) include:

a) pre-peak in the radial distribution function obtained from X-ray structural data.

b) excess heat capacity C(T) and "plateau" in the temperature dependence of thermal conductivity $\lambda(T)$ in the interval T = 10-20 K, which are observed in all glasses and amorphous materials.

c) low-frequency peak (boson peak) found in Raman scattering spectra of light in all amorphous materials.

The assumption of a non-continuous structure is a very effective approach, allowing one to explain quite different features of glass-formers from this simple background [1]. Several important facts confirm the accuracy of the assumptions of described model of the local heating. These include the following relation observed: The maximum frequency of the boson peak allows determining the correlation radius of the structure [1]. It was demonstrated [1-3] that the boson peak has universal shape for a large number of glasses with different chemical compositions and corresponds approximately to one value R = 1 nm. If the characteristic size of nanoregions is somewhat different in different glasses, then these differences have to be in experiments with structural factor measurements and in simultaneously observed estimations based on the low-frequency Raman scattering of light. Indeed, it was shown [1-3]. that the estimations based on the structural factor and on the Raman scattering are the same with good precision. Moreover, one can simultaneously change the boson peak position and the width of the pre-peak in structural measurement. Experiments performed with vitreous SiO₂ modified by high pressure confirmed this rigorous correspondence. Further arguments in favour of local heating model can be find in works [1].

The electron spectrum

BCH model uprises from the assumption (which was noticed already in the original BC model), that electron spectrum of the pure chalcogenide glasses (pure As₂S₃, As₂Se₃) is similar to the spectrum of respektive crystaline matter and that it is characterized practically with pure forbidden band. Many facts confirmed the correctness of such assumption. Chalcogenide glasses possess high transparency in relatively broad interval of photon energies [9,10]. On the other hand it emerges that in forbidden gap of these substances there are curious (usually metastable) states. Up to now there are no arguments for unambiguous answer. The observed mid-gape effects can be in the framework of BCH model explained also without the assumption of the existence of states' density in the forbidden band. BCH model though can concurrently explain also the origin of photoinduced states in the forbidden band and also the origin of ESR signal connected with it [11-15].

Remarks: The barrier-cluster-heating model doesn't exclude the existence of gap states corresponding to the various impurities and some other structural defects, which arise at neutron scattering in a sample etc. These states have other character than photoinduced states and they are not primary source of appearance exponential tails of an optical absorption.

The potential barriers

Potential barriers between nano-regions (which was supposed already in the BC model) hinder the transport of the carriers at the margin of the conduction or valence bands. This explains the origin of sub-bands of lower mobility. At the same time, however, the barriers also influence significantly the optical absorption at the optical absorption edge. It is caused in the first line by their inducing a strong electron-phonon interaction. Another important factor - as far as influence of barriers is concerned - is that the absorption of light in the region of the optical absorption edge is usually connected with tunneling of carriers through the barrier. These facts enable us to explain successfully the photoconductivity, electroabsorption and photoluminescence.

Exponential tails

Barrier-cluster-heating (BCH) model comes out from an image that exponential tails of an optical absorption doesn't appear as a result of the existence of density states in forbidden band. According to BCH model [11-15] those tails appear as a result of energetic participation of phonons in an "optical" transition of electrons from valence into conduction band. An electron with "deficit energy" overcomes the forbidden gap only by obtaining the energy from a photon and phonon energies. This leads (due to the statistics of phonons) to exponential dependence of the absorption coefficient on photon energy and also to appearance of exponential tails. This enables us to explain the origin of "normal" exponential tails in the area of higher absorptions without assuption, that in the forbidden band exist tails of states' density. About physical background of origin of weak absorption tail in the area of very low absorptions will be from point of view of BCH model discussed in the conclusion of this article.

3. Photoinduced changes in glasses

The glass is known to exibit a variety of radiation effects [1,3,5]. The most famous may be the deffect formation and radiation compaction in silica glasses, which is now comercially utilized for producing Bragg-grating fibers. However, since the oxide glass has a wide bandgap of 4-9 eV and the structure comparative rigid, intense pulsed lasers or ultraviolet source are needed for inducing these phenomena. It is his disadvantage.

Photoinduced changes in chalcogenide glasses

The chalcogenide glass (unlike to the oxide glass) has a band gap of 1-3 eV and flexible structures and accordingly, it exibits many kinds of prominent photoinduced phenomena [1, 4-10]. These phenomena have been extensively studied during the last decades because of their potential applications, especially in optics and optoelectronics. Chalcogenide glasses show several photoinduced changes in structure and properties, including volume, amorphization, devitrification, mechanical (e.g. plasticity), rheological (e.g. viscosity), optical (e.g. darkening, birefringence, luminescence), electrical (e.g. conductivity, dielectric constant), or the chemical (e.g. etching, dissolution), doping properties of glass. Shimakawa et al have in [16] reviewed such phenomena which can be permanent, metastable or temporary with regard to light exposure. Numerous interesting applications have been conceived and designed based on these properties of chalcogenide glasses, especially in amorphous thin film form.

Previous effort to explain the photoinduced changes

Many models, which strive to explain photoinduced changes, assume the existence of various centers in a matter [17,18], to which energy levels in the forbidden gap correspond. Among them, one most frequently used for covalent chalcogenide glasses such as As₂S₃ are the charged-defect and valence-alternation pairs models proposed by Street and Mott [17] and Kastner et al [18]. Existence of such centers wasn't proved in experiments up to now. Tanaka on the base of precise measurements of pure materials of the type As₂Se₃, As₂S₃ is in doubt about existence of such centers. On the other side in pure materials some photo-mid-gap effects precede [19-23]. It points out at the existence of mid-gap states. It is some inconsistency, which represents an open problem.

Remark: In works [24,25] there are the optically induced *"e-h-e* centers" introduced, which give the new of view on this problems and enables to explain the actual contradiction.

In addition, in spite of extreme purity of the glass that substance preserves also weak absorption tail, appearance of which was by some authors attributed to the presence of impurities. Experiments by Tanaka have shown that it isn't conditioned by impurities. A critical viewpoint of models proposed to explain photoinduced effects in chalcogenide glasses was presented by Fritzsche [26], one of the founders of the science of photo-induced transformations in chalcogenide glasses. He believes that there are two kinds of effects inducing changes in chalcogenide glass optical properties. Effect of the first type is related to reconstruction of bistable centers, whereas the second type is associated with reconstruction of the entire glass structure. We thing, that the reality respond the second possibility.

Photoinduced changes from point of view BCH model

The original BC model doesn't deal with explanation of photoinduced structural effects. The priority of the primary BC model was primarily to explain simple processes and patterns in physics of amorphous semiconductors. It was for example the explanation of electrical conductivity (including MNR), photoconductivity, optical absorption, electroabsorption, photoluminescence. Structural photoinduced changes are in any case more complicated and complex set of phenomena. Complex explanation always requires first understanding the subprocesses. The barrier-cluster-heating model accepts the vision, which was proposed and elaborated already in the framework of the primary local-heating model. The barrier-clusterheating model uses the feature, that photoinduced structural changes (both scalar and vector ones) in glasses occur in each single act of light absorption. They are related to reconstruction of nanoregions owing to local heating and subsequent quenching. Podľa BCH modelu photoinduced effects in glasses are caused by heating of the nanoregion during energy quantum absorption above the glass transition temperature. Subsequent quenching of nanoregions from the liquid state fixed the photo-induced transformation. They are related to reconstruction of entire glass structure in nano-cluster (nano-region) after the energy absorption. It is shown in [1] that in the case of chalcogenide glasses the reasonable estimations (in the case of the photon absorption by one nanoregion) indeed lead to such heating. It seems that the nanometer structure of chalcogenide glasses is reminiscence of its crystalline analog, implying the polarization dichroism for nanoregions. In the frame of the model, photoinduced vector changes occur because of selective absorption predominantly in those nanoregions whose maximum absorption axis coincides with the direction of polarization in the light wave. The BCH (equally as the local heating model [1]) explains the existence of photo-induced vector effects even after long-time irradiation of the chalcogenide sample.

Which is the synergetic acquisition of the BCH model?

We have said, that the connection of barrier-cluster model with local-heating model and creating of integrated BCH model, is not only mechanical coupling of both models, but it create advantageous synergetic effects. It provides deeper insight on the physical processes in chalcogenide glasses. BCH model explains e.g., why the energy released by non-radiant recombinations of some *e*-*h* pairs is concentrated on some certain nano-region. This energy then evokes the increasing of nano-region's temperature, and under the suitable conditions also its overheating above the transformation temperature. This is related with the structural changes of this nano-region. BCH model provides information about the relationship of photoluminiscence processes with structural change of nano-region. Just the funnel of energetical states [11, 12] belonging to the bound *e*-*h* pair and gradually approximating of electron of such pair to the hole, is this mechanism, which leads to the concentration of released energy into certain nano-cluster. The releasing of energy occurs namely above all in the state, when electron and hole are already localized in the same nano-region. If the concerning recombination is nonradiant, then energy will be released in form of set of phonons and is practically fully transferred to this nano-region. The consequence of this are intensive vibrations of this nanoregion, vibration which cover the tera-hertz (THz) range, which is identical with range belonging to the known bose-peak, resp. Raman's tail. Just in such region occurs corresponding structural change. On the basis of BCH model can be expected certain connectivity of photostructural changes with known low-temperature anomal phenomena. Further study of these phenomena can contribute also to deeper understanding of anomal phenomena in the glasses. On the basis of BCH model is comprehensible also experimentally observed context between level of photoluminescence and photo-expansion [11-15]. For the photo-expansion are responsible the nano-regions, in which the structural changes occurred, and that occurred there, where happened the non-radiant recombination of *e*-*h* pair.

Weak absorption tails (WAT)

The important preference of integrated BCH model is, that it is able to explain also origin of the weak absorption tails [11-15]. WATs arise according of BCH model with analogical mechanism, as standard exponential tails, therefore in the consequence of energetical participation of phonons of optical origin on the optical absorption of photons of deficit energies [4-7]. The difference is only in this, that in the case of standard exponential tails, on the optical absorption shared "diffuse" phonons (phonons diffused through the whole volume of the sample), while in case of WAT on the optical absorption are sharing phonons released and concentrated in one nano-region. In such case the significant warming of given nano-region occurs in consequence of whole set of released phonons in it. The localization of phonons take (remain) some time [1]. The probability of the participation of phonon on the optical transition of electron in case of such localized phonon is then markedly higher, as by the free diffusing phonons. In other words: Electron of given heated nano-region easier acquires needed number of phonons for refilling of wanting energy, necessary for the optical transition. For the electron of cold nanoregion is it not so easy. This then explains markedly lower WAT steepness. More detailed explanation of the formation of WAT from the view point of BCH model will be devoted other article, which will be published in the near future.
Which recombinations are responsible for the photoinduced structural changes?

From the point of view of the BCH model can be assumed that the structural phase change in nano-region is caused first of all by phonons produced by non-radiative recombination of such e-h pairs, which both components (ie, electron and hole) after earlier skidding diffusion transfers within the catchment energy funnel fall into the same cluster [11-13]. Such pairs will be marked e+h to make distinction with bound pairs e-h in general. Pairs of e+h type generally can recombine with radiation, resulting in photoluminescence. Such pairs may, however, recombine without radiation, which is associated with the emission of monoenergetic phonons. It can be assumed that released monoenergetic phonons cause in the clusters the resonant excitation of atomic lattice of the given region. This ultimately leads to increased temperature, and finally (in case of the sufficiently high temperature) to a modification of the original structure of the microregion. (This does not exclude the possibility that the effect of conversion can also have non-thermal nature).

Reconstruction of nanoregion

Monoenergetic phonons which are liberated in the nano-region cause high diffusivity of atoms in the own nano-region (in terms of band model of diffusion [15]). Some atoms are excitated from band of zero mobility to "diffuse" band of non-zero mobility. This process is likely to have resonant character. Therefore, the restructural effect of monoenergetic phonons can be larger than in the case of thermal (Planck's) phonons.

Relation between photoluminescence and photoexpansion.

Hamakawa et. al. [27] have discovered that bandgap illumination upon annealed As₂S₃ films and bulk samples produces photoinduced volume expansion of ~ 0,4 %, which can be recovered with annealing at the glass-transition temperature of ~ 200 °C. However, Hisakuny and Tanaka [28] have demonstrated for anneled AS₂S₃ films and bulk samples that 2,0 eV sub-gap photons can induce greater volume expansion of ~ 5 %, which can be referred to as giant expansion. In the previously described view on monoenergetic phonons resulting from the recombination of *e*+*h* pair, which two components (ie, electron and hole) are already located in the same microregion, supports the experimentally observed correlation between thermal relations and photoluminescence and photoexpanse. According to the BCH (BC) model [11-12] level of photoluminescence is directly proportional to the concentration of *e*+*h* pairs. Photoluminescence is due to radiant recombination of such pairs. However, the number of non radiative recombinations of *e*+*h* pairs is also proportional to the concentration of *e*+*h* pairs. This suggests that the probability of photo-changes must be directly proportional to the concentration of *e*+*h* pairs.

Photoinduced mid-gap absorption

After excitation of the glass As₂S₃ (or As₂Se₃) with radiation from Urbach-tail region the glass will be able to absorb the photons of low energy (IR) radiation from mid-gap region of spectra [15]. This absorption without action of the primary excitation radiation of the higher photon energy is impossible. The optical transition excited by IR-radiation with low photons energy (trough the pure forbidden band) without presence of the phonon is impossible. At very low temperatures in semiconductor thermal phonons practically do not exist. But how to explain

the mid-gap absorption on the base of the BCH model, when it assumes the pure forbidden band? We believe that mid-gap absorption at low temperature is enabled by the phonons of an optical origin, which are produced by non-radiate recombination of the *e*-*h* pairs, created mainly by the primary "Urbach's tail" radiation. If electron accepts - besides of energy of the low-energy photon - at the same time sufficiently large energy of phonons of optical origin, "cooperative" optical mid-gap absorption will be possible.

4. Conclusion

Barrier-cluster-heating (BCH) model was originated as synthesis of two different models of the chalcogenide glass - the barrier-cluster model and local heating model. BCH model is based on the notion that glasses at nano-meter scales are inhomogeneous, consisting of nano-regions clusters. Between clusters there are potential barriers affecting not only the electrical transport, but optical absorption as well. BCH model is capable to explain the number of important electrical, optical effect in chalcogenide glasses - the conductivity (Meyer-Neldel rule), optical absorption, Urbach's rule, electroabsorption, photoluminiscence, relation between MNR and Urbach's rule. The closed-cluster structure can explain the results of X-ray structure measurements and the absence of an ESR signal in the case of chalcogenide glasses. The model provides a new explanation for the density of states within the forbidden band and explains, why the attempts at identification of gap-states (the charged-defect and valence-alternation pairs) by various optical and other methods fail. Energy released by non-radiative recombination of electron-hole pair localized in one nanoregion is absorbed by the respective clusters. It causes the increase of temperature of the cluster. The photoinduced structural effects in chalcogenide glasses are caused by heating of the nanoregion during energy quantum absorption above the glass transition temperature. Subsequent quenching of nanoregions from the liquid state fixed the photoinduced transformation. BCH model is capable to explain various photoinduced changes, and relations, such as the relation between photoluminescence and photoexpansion. It is able to explain the weak absorption tail and some further mid-gap effects, too. We assume, that the barrier-cluster-heating model can be expected stimulate a development of new interpretations of physical phenomena in chalcogenide glasses.

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Thermal and elastic properties of kaolin Sedlec

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Abstract: Thermal and elastic properties of the kaolin produced by the company Sedlecký kaolín Corp. (Czech Republic) are studied. Its content of kaolinite is at least 90 wt.% (as guaranteed by the producer). The analyses DTA, TDA, TGA, and mf-TMA were used to study the changes that occur in kaolin during heating. The mass changes, volume changes, and Young's modulus were also determined at room temperature as well as after firing at different temperatures, and the results were analyzed. The DTA curve shows three peaks in the temperature range 25 - 1030 °C. These thermal peaks correspond to significant changes in kaolin and could thus affect the measured quantities. The most significant changes between the results at room temperature and during heating were observed in the values of Young's modulus and the bulk density.

Keywords: kaolin, thermal analysis, Young's modulus.

1. Introduction

Kaolin is a material broadly used in the ceramic industry. For a proper ceramics production it is important to have a detailed knowledge about specific parameters of kaolin, such as Young's modulus, the mechanical strength, thermal expansion, density, and porosity. These properties are often measured during firing, but in general they are different from those measured at the room temperature after cooling the samples. For the simulation of the sintering process the knowledge on the temperature dependence of such parameters as Young's modulus, coefficient of thermal expansion, or bulk density is necessary. These parameters also play a very important role in the determination of an optimal firing program. Producers have a profound interest in what properties a product will have at their operating temperature (for building ceramics this is usually room temperature) after firing at a given temperature. For this reason it is rather interesting to determine the values of thermal and mechanical parameters after firing.

Thermal properties of kaolin have already been studied, for example in [1-5]. The properties of kaolinite are strongly influenced by its structure which can be well or poorly ordered [6, 7]. That is why it is important to study thermophysical and mechanical properties of kaolins from various deposits.

From the microscopic viewpoint, kaolinite is a two-layer mineral. It consists of repeating tetrahedron-octahedron (T-O) layers. The tetrahedron layer consists of a connected net of [SiO₄]⁴⁻ cells. The octahedron layer consist of a 2D net of [AlO₃(OH)₃]⁶⁻ cells in which atoms are arranged so that the central atom of Al is connected with three oxygen atoms and three OH molecules. All of these elements are in each layer arranged in a hexagonal network. The T-O layers are bound by the ion-covalent bonds via oxygen atoms. The individual two-layer sheets are connected together via the week van der Waals or hydrogen bonds. Most of kaolinite is

formed from mica and feldspar [6, 8]. The ideal formula of the kaolinite is $(Al_2Si_2O_5(OH_4))$ or, in the oxides form notation, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ [9].

In this paper, we study the kaolin produced by the company Sedlecký Kaolin Corp., Czech Republic, using the differential thermal analysis (DTA), thermodilatometry (TDA), thermogravimetry (TGA), and modulated force thermomechanical analysis (mf-TMA).

2. Experimental

2.1 Samples

In this study we used a kaolin with at least 90 wt.% of kaolinite. It was made by the process of floating from the basic material which consisted of ~25 wt.% of kaolinite. The samples were prepared by extruding from a plastic mass. Extruded samples had a cylindrical shape with the diameter ~11 mm and a varying length (specified below). After extruding, the samples were dried in the open air at room temperature and the relatively humidity ~30 %. After free drying the samples contained ~2 wt.% of physically bound water.

2.2 Measurement methods

The differential thermal analysis (DTA) and thermogravimetry (TGA) was carried out by the analyzer Derivatograph 1100° [10] in the static air atmosphere with a heating rate 5 K·min⁻¹. We drilled a hole into the prepared cylindrical samples (their length was ~20 mm) whose diameter was ~3 mm and depth ~8 mm. The samples were attached to a holder containing a thermocouple. The reference compact sample was made from a pressed Al₂O₃ powder with the same geometry as the measured samples. Three samples were measured via this analysis in order to obtain a representative value.

Thermodilatometry (TDA) was performed by a horizontal push-rod dilatometer described in [11]. The dimensions of cylindrical samples used in the measurements were \emptyset 11×40 mm.

The bulk density during heating was calculated using the experimental results from the TDA (thermal strain) and TGA (relative mass changes) as

$$\rho = \rho_0 \frac{1 + \Delta m / m_0}{1 + 3\Delta l / l_0},\tag{1}$$

where ρ_0 is the initial density.

The resonant mf-TMA, which is based on the resonant vibration of a sample in the fundamental flexural mode, was used for the measurement of Young's modulus, *E*, during heating at a rate 5 K·min⁻¹ from room temperature to 1100 °C on samples with the initial dimensions ~11×140 mm. The resonant frequency, *f*(*t*), at a temperature *t* was used to calculate the modulus, using the formula [12, 13]

$$E(t) = 1.65623 \frac{m_0 l_0^3}{d_0^4} \frac{1 + \lambda(t)}{1 + \varepsilon(t)} f^2(t),$$
⁽²⁾

where l_0 , d_0 , and m_0 are the sample length, diameter, and mass at room temperature, respectively. The relative thermal strain $\varepsilon(t) = \Delta l(t)/l_0$ and the relative mass loss $\lambda(t) = \Delta m(t)/m_0$ of

the sample were measured by the TDA and TGA, respectively. We used the mf-TMA apparatus that was described in detail in [13].

The mass loss, volume changes, and Young's modulus of the samples were also evaluated at room temperature after firing at the temperatures 100, 200, ..., 1100 °C. For this purpose we used a set of ten cylindrical samples. The samples were subject to a controlled thermal program with a heating rate 5 K·min⁻¹, soaking time 5 min, and cooling rate 10 K·min⁻¹ to room temperature. At room temperature the bulk density was determined from the dimensions and mass of the sample.

3. Results and discussion

3.1 Differential thermal analysis (DTA)



Figure 1: DTA curve of the studied kaolin

The results from the DTA analysis (see Figure 1) show a shallow endothermic peak in the temperature range 70 - 250 °C. It corresponds to the liberation of the physically bound water. A sharp endothermic peak appears in the temperature range 535 - 675 °C where the dehydroxylation of kaolinite takes place. During this process the chemically bound OH groups condense and leave the crystal lattice as H₂O molecules, turning kaolinite into metakaolinite. This phase transition can be described in the form of the chemical reaction as [3]

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O \text{ (kaolinite)} \rightarrow 2SiO_2 \cdot Al_2O_3 \text{ (metakaolinite)} + 2H_2O.$$
(3)

In the temperature range 950 – 990 °C a sharp exothermic peak occurs. It is related to the crystallization heat of the Al-Si spinels formation [1, 5] which can be formally written as [3]

 $2(2SiO_2 \cdot Al_2O_3) \rightarrow 3SiO_2 \cdot 2Al_2O_3 \text{ (spinel)} + SiO_2 \text{ (amorphous)}$ (4)

3.2 Thermodilatormetry

The thermodilatometric results are given in Figure 2a. They imply that the total shrinkage after firing at the temperature of 1100 °C is about 3.6 %. In Figure 2b the coefficient of thermal expansion α is shown along with the DTA curve. The coefficient α was calculated from the TDA curve of kaolin during heating as its derivative [14]. The first endothermic peak in the range (25 – 200 °C) on the DTA curve does not correlate with the curve for α . Hence, the liberation of

physically bound water does not cause significant volume changes of the samples. The endothermic peak between 535 °C and 675 °C is connected to the shrinkage of the kaolin samples. The most obvious volume changes correspond to the exothermic reaction with a maximum at 970 °C (on the DTA curve). At this temperature the spinel phase is formed (see Eq. (4)). This formation is rather fast and can be accelerated by the presence of the liquid phase if impurities (for example K₂O), which reduce the glass transition temperature, are present [3]. Because of rapid volume changes, the samples or a product made of the kaolin may be damaged due to the stresses induced in its volume. The response to the dehydroxylation (535 – 675 °C) and spinel phase formation (950 – 990 °C) is practically identical for both measurements during and after firing. The differences between the relative expansion measured during heating and at room temperature occur because in the former case reversible processes affect the thermal expansion, which is not so in the latter case.



temperatures (black) and during firing (gray).

Figure 2b: Coefficient of thermal expansion of (black) and DTA curve (gray).

3.3 Thermogravimetry

The results on the relative mass loss both during heating and after firing are in Figure 3a. Clearly, both curves are practical identical. From Figure 3b it is clear which reactions are connected with a mass loss. The first endothermic peak on the DTA curve corresponds to the liberation of the physically bound water from the pores is present also on the dTG curve. At the temperatures between 535 and 675 °C there is a sharp endothermic peak connected with a rapid decrease of the mass. It is related to the dehydroxylation of kaolinite. Our measurements yield ~12.4 wt.% of the mass loss during dehydroxylation. If we had kaolinite without impurities it would be ~14 wt.% [9]. The formation of the spinel phase in the range 950 – 990 °C is not connected with a mass change.



Figure 3a: Relative mass loss after firing (black) and thermogravimetry during heating (gray).



Figure 3b: dTG (black) and DTA curves (gray).

3.4 Bulk density

The results on the bulk density are shown in Figure 4. Obviously, the density measured during firing is approximately the same as the density measured at room temperature, until the temperature of firing reaches 1000 °C. Above this temperature the sintering process affects the isothermal heating results, causing differences between the two measurements.



Figure 4: Bulk density at room temperature (black), and bulk density computed from the results of the TDA and TGA (gray).

3.5 Young's modulus

The results on Young's modulus are shown in Figure 5. We may observe differences between the Young's modulus values measured during firing and at room temperature. At 25 °C (the first point on both curves in Figure 5) the two values do not coincide, which should be the case. We attribute this fact to the difference in the moisture content in green samples. After drying (at 100 °C) Young's modulus is identical in both cases.



Figure 5: Young's modulus measured at room temperature (black) and during firing (gray).

The values of Young's modulus measured during firing exhibit a local minimum at ~686 °C, soon after the dehydroxylation (within 535 – 675 °C). The values of Young's modulus measured at room temperature have a local minimum corresponding to the firing temperature 600 °C. The dehydroxylation causes a decrease of Young's modulus. The difference originates from the fact that the samples measured at room temperature stay, at the firing temperature, longer in the regime of dehydroxylation.

After the dehydroxylation, both values of Young's modulus are increasing. As for the measurement during heating, the increase clearly correlates with the exothermic DTA peak at ~970 °C. The value of Young's modulus of kaolin fired at 1000 °C measured at room temperature does not have such a sharp growth. The increase in the values of Young's modulus measured at room temperature continues as the firing temperature grows, while those measured during heating exhibit a much smaller increase.

4. Conclusions

Thermal and elastic properties of the kaolin Sedlec were studied. The changes in these properties during heating and after firing at different temperatures were compared. It was found that values of the parameters measured at room temperature correlate quite well with the same parameters measured during heating. A noticeable difference was observed only in the case of Young's modulus, where the values measured at room temperature do not reflect the trend of Young's modulus values measured during the heating. The examined parameters were also compared with each other and it was found that the dehydroxylation influences all of them. The formation of spinel also strongly affects all parameters, except the mass change.

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Chemical and physical characterization of untreated and treated fly ash from a modern MSWI facility

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Abstract: Chemical and physical characterization of untreated and treated fly ash from a modern MSWI facility is performed from the perspective of its possible utilization as pozzolan. The acid washing applied in incinerator in order to leach out heavy metals from fly ash is found to reduce the content of chlorides but it does not solve the high sulfates' content.

Keywords: fly ash, municipal solid waste incinerator, characterization

1. Introduction

About 900 Municipal Solid Waste incinerators are operating worldwide [1]. There are not any data on the total installed capacity but assuming that one incinerator burns 100 kt of waste per year (conservative estimation) it represents about 2.25 Mt of fly ash produced worldwide per year (and about 23 Mt of bottom ash). The MSWI fly ash is a solid "product" of Air Pollution Control line; its chemical and physical properties vary from plant to plant in dependence on design of APC line. Generally MSWI fly ash contains inorganic components (silicates, salts) and organic compounds. Since lot of fly ash's components represent an environmental risk it is usually not possible to landfill it in a raw state and some treatment technique has to be applied. There is about 20 – 30 technologies of fly ash management [2] which can be roughly grouped to i) material recovery/utilization and ii) disposal of a treated (stabilized, solidified) ash.

Various ways of MSWI fly ash are under investigation and eventually in use; it can be used filler in pavement asphalt [3], as a component for ceramic tiles [4] or glass-ceramics [5], as a raw material for Portland clinker production [6], but probably the highest attention is paid to its potential utilization as concrete admixture. Such application is inspired by coal fly ashes but MSWI fly ashes feature by different chemical composition which requires certain treatment which should get MSWI fly ash properties closer to coal ash; the goal is mainly to reduce the salts content. There are basically two methods for MSWI fly ash treatment: thermal treatment and washing. Thermal treatment consists in melting of ash without [7] or with an additive. Washing can be performed by water [8] or by means of more sophisticated multiple step procedures [9]. The aim of present work was to evaluate feasibility of MSWI fly ash utilization as cement substitute in state before and after treatment (acid washing) as it is applied directly in the incinerator.

2. Experimental

MSWI fly ash was studied in two states; firstly in raw state as collected in APC system of MSWI (denoted FA). It is mixture of ashes collected in boiler and in electrostatic precipitator. The second studied material was fly ash from the same incinerator after treatment - leaching of FA by means of acid water solution coming from flue gas absorber; this washed ash is denoted as FAWI. Chemical composition of ashes was examined by XRF (Thermo, ARL 9400 XP). Matrix density was determined by helium pycnometer (Pycnomatic ATC) and loose bulk density by

help of calibrated vessel. Particle size distribution was measured conventionally as grading curve by means of standard sieves and also by laser diffraction analysis (Fritsch, Analysette 22 MicroTec plus). Simultaneous TG/DSC thermal analysis was performed by Setaram calorimeter Labsys Evo under inert atmosphere from ambient temperature to 1000 °C. Morphology of ashes was observed by Scanning Electron Microscopy (Jeol JSM 6510); nature of selected species was revealed by EDS analysis. The pozzolanic activity was tested according EN 196-5 [10]; Portland cement and ash was mixed in proportions as were used for mortars (Table 1). The influence of ashes on initial and final setting time of standard consistency cement paste was evaluated by Vicat apparatus (EN 196-3, [11]). Cement mortars where Portland cement was partially substituted by ashes were prepared in order to evaluate possibility of utilization of MSWI ashes as Portland cement substitute. The water/binder ratio was increased slightly in order to maintain constant consistency of mortar (flow table 140 mm) (Table 1). The mortars were cast to 160 mm x 40 mm x 40 mm standard prisms and stored at 100 % relative humidity for 28 days and than compressive strength was measured.

10				
	CEMI 42.5			
	R	Fly ash	Sand	w/b
	kg/m³			
Control	460	-	1380	0.52
10 %	414	46	1380	0.52
20 %	368	92	1380	0.53
30 %	322	138	1380	0.56

Table 1: Composition of mortars with fly ashes.

3. Results and discussion

The main purpose of fly ash acid leaching applied directly in incineration facility is dissolution of heavy metals salts but the leaching influences also the content of major components (Table 2). The most important change is decrease of chlorides and alkali metals content; on the other hand the concentration of sulfates in FAWI relatively increased due to dissolution of soluble salts. Not surprisingly both ashes exceed the standard (EN 450, [12]) requirements on chloride and sulfate content in fly ash intended to be used as pozzolan in concrete. Solubility of FAWI in water (Table 3) is lower when compared to FA as may be expected. The simultaneous DSC/TG analysis (Figs. 1 and 2) was performed in order to provide more information about chemical composition. There was observed significant increase of gypsum (CaSO4.2H₂O) content from 5 % (in FA) to 17 % (FAWI) (endothermic peak at 165 °C). Another significant peak at 600 °C belongs to thermal decomposition of a soluble compound which has not been identified yet. Gradual endothermic loss of weight from app. 650 °C is caused by complex of various processes – evaporation of volatile salts and thermal decomposition of unstable salts (especially CaCO₃ - DSC signal between 800 and 900 °C).

	FA	FAWI
SiO ₂	15.6	12.2
Al ₂ O ₃	9.2	7.6
Fe ₂ O ₃	2.6	2.4
CaO	23.9	31.4
MgO	1.8	1.1
Na ₂ O	9.4	0.5
K ₂ O	6.6	0.9
Cl	11.2	0.3
SO ₃	11.5	37.2
P_2O_5	1.3	1.1
ZnO	3.7	2.0

Table 2: Chemical composition of ashes – major elements (in wt. %).

Table 3: Fundamental physical properties of ashes.

	Density	Loose bul density	kSpecific surface	d 50	Solubility
	g/cm ³	g/cm ³	m²/kg	m	%
FA	2.663	0.955	394	84	13.6
FAWI	2.622	0.910	750	46	5.6



Figure 1: DSC/TG analysis of sample FA.



Figure 2: DSC/TG analysis of sample FAWI.

The acid leaching of FA influenced also its morphology. FAWI is somewhat finer than FA which is illustrated also by its higher specific surface and lower d_{50} (Table 3). The diversity between grading curves obtained by sieves (Figure 3) and by optical particle size analyzer (Figure 4) – the first one reports somewhat larger particles than the latter – is caused by different measurement environment; MSWI ashes generally tend to form agglomerates due to its salty nature and these agglomerates have been disrupted during the particle size analysis which was performed in water medium. Hence the grading curves correspond to agglomerates and particle size analysis to individual detached and insoluble particles.



Figure 3: Grading curves of ashes.



Figure 4: Particle size analysis of ashes.



Figure 5: SEM image of untreated sample FA.

The appearance and morphology of MSWI ashes was checked by SEM. The raw fly ash FA (Figure 5) contains mainly very fine salt particles which were entrained by flue gas during the combustion or precipitated from gas phase during the cooling of flue gas along the APC line (condensing salts). Siliceous spherical particles are present as well in FA but salt crystals cover

and stick together all species. Character of fly ash was markedly changed during the acid washing procedure. The treatment caused dissolution of most of soluble components (especially chlorides) and also recrystallization of other salts. It resulted to larger crystals (Figure 6) and also spherical particles are more distinct. The spherical species compose mostly from SiO₂, CaO and Al₂O₃ and thus are the valuable portion of the ash. An ideal washing procedure of MSWI fly ash would preserve only the silicate particles.



Figure 6: SEM image of treated FAWI ash.

The influence of fly ashes on initial and final setting time of cement paste of standard consistency was evaluated. A fly ash was used as partial substitute of Portland cement (10, 20 and 30 %). The untreated FA increased significantly initial and especially final setting time (Figure 7); the latter one was longer than 24 hours even for 10 % substitution. The washed fly ash FAWI featured much better performance; it influenced the setting time as well but in a moderate extent. The reason is reduction of chloride content in FAWI which – in high concentration – reduces the rate of hydration.

The possible ability of ashes to replace Portland cement (PC) was checked by help of mortars (Table 1) where ashes were dosed as pozzolanic admixture. Even the lowest substitution (10 % of PC) caused the decrease of mortar's compressive strength despite cementitious mixtures containing 10 and 20 % of both ashes (and also 30 % of FAWI) were found to fulfill standard requirements on pozzolanic cement. The washed ash FAWI influenced the strength in more negative way than the raw untreated FA.

The acid washing of FA as performed in MSW incinerator changes its physical and chemical properties. The reduced chloride content in FAWI is the most important difference caused by

washing from the perspective of possible utilization of studied ash in civil engineering as cement substitute. It is sufficient for significant reduction of setting time compared with unwashed ash FA but the performance as pozzolanic admixture is not sufficient. The reason is low content of hydraulic oxides and high content of sulfates, especially gypsum.



Figure 7: Influence of FA and FAWI on initial and final setting time.



Figure 8: Influence of FA and FAWI on compressive strength of mortars.

4. Conclusions

Chemical and physical characterization of untreated and treated fly ash from a modern MSWI facility was performed from the perspective of its possible utilization as pozzolan. Such application of untreated fly ash is limited mainly by its highly negative influence on setting time. The acid washing applied in incinerator in order to leach out heavy metals from fly ash reduces the content of chlorides what has positive effect on setting time. Unfortunately the washing procedure does not solve the high sulfates' content; only the recrystallization to larger crystals is taking place. Due to low content of hydraulic oxides and very high content of sulfates even the washed ash FAWI is not able to substitute Portland cement effectively. The studied fly ash has to be treated in another way when one would intend to use it as concrete admixture.

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A computational analysis of heat transfer in hollow bricks

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Abstract: In the brick industry, during the last decades the standard clay bricks are being replaced by hollow brick blocks which are more effective from the point of view of thermal insulation properties. However, heat transfer in such kind of bricks is more complex, and new methods are being sought to determine their thermal properties. In this paper, the heat transfer in hollow bricks is analysed by a computational approach utilizing the finite element method.

Keywords: hollow bricks, heat transfer, computational methods

1. Introduction

In last decades, there appeared a great human pressure on saving earth natural resources due to permanent increase of the total energy consumption in all kinds of human activities. More than 40 % of energy is consumed in buildings and therefore there is significant potential for reducing consumption with cost-effective measures. Since building heating and cooling contributes significantly to the global energy demand, it is crucial to improve the thermal efficiency of building materials and building technologies.

In 2002, the European Union introduced legislation to ensure lower energy consumption. The key part of this legislation is Energy Performance of Buildings Directive [1]. This directive required all EU countries to enhance their building regulations and to introduce energy certification schemes for buildings.

In 2010 there was introduced new adoption of re-cast EPBD [2], which toughened the regulations given by original EPBD. The EU Members are facing new tough challenges, among them moving towards new and retrofitted nearly-zero energy buildings by 2020 (2018 in the case of public buildings), the application of cost-optimal methodology for setting minimum requirements for both envelope and technical systems.

To fulfill the new requirements coming from EPBD II, such as demand for low-energy and nearly-zero energy buildings, it is essential to use the best building materials in terms of their thermal efficiency to increase the building envelope thermal resistance. Although the crucial role in the thermal resistance of building envelopes is played by thermal insulation, also the load bearing structures should meet high demands on thermal insulation properties.

However, it is not only the EPBD what led the brick producers to develop new materials. In brick industry, there were noticed many attempts to improve the standard clay bricks during the past with one simple reason – just to ensure better quality of indoor environment. With the knowledge of positive thermal properties of dry air, the producers tried to involve the air as a regular component of brick body. Such approach supported by research [3-5] results in development of new generation of bricks, known as hollow bricks.

With ongoing research, there appeared new types of hollow bricks in recent time. As the original hollow bricks contain cavities filled with air, the new types are filled with different insulation materials, such as mineral wool, expanded polystyrene, perlite [6], etc. At first glance,

this innovation seems to be useless, as the thermal insulation of the dry static air is lower than common thermal insulation materials. But it is important to notice, that when the cavities are filled with solid materials, the heat transfer by radiation is negligible and the total effective heat transfer of new types of hollow bricks may be lower than traditional hollow bricks filled with air.

In this paper, a computational approach is applied for the determination of effective thermal conductivity of hollow bricks with the cavities filled with hydrophilic mineral wool and recycled (crushed) polyurethane. At first, the thermal properties of brick body and selected thermal insulation materials are determined. Then, a finite element approach is applied for the calculation of steady-state temperature fields in the hollow bricks. The effective thermal conductivity is then determined using Fourier's law. The computational data are verified by the results of semi-scale experimental measurements.

2. Experimental

The data for basic physical properties of brick body were obtained by helium pycnometry and by the gravimetric method. The thermal conductivity of brick body and thermal insulation materials was determined in normal temperature range using impulse method (Isomet 2104). This device applies a dynamic measurement method, which is able to reduce the time of thermal conductivity measurements. The principles of this method lie in analysis of the temperature response of the analyzed material to heat flow impulses. The heat flow is induced by electrical heating using a resistor having direct thermal contact with the surface of the sample. The device is equipped with various types of optional probes such as needle probes (suitable for porous, fibrous or soft materials) or surface probes (suitable for hard materials). The measurement range of thermal conductivity is 0.015 to 6 W/mK, the accuracy is 5 % of reading + 0.001 W/mK, the measurement reproducibility is 3 % of reading + 0.001 W/mK.

The measured results are summarized in Table 1.

Material	Bulk density [kg/m³]	Thermal conductivity [W/mK]
Brick body	1398	0.3000
Hydrophilic mineral wool	100	0.0383
Recycled polyurethane	12*	0.0395
*powder density		

Table 1: Bulk density and thermal conductivity of involved materials

3. Computational

All calculations were performed using computer code SIFEL (Simple Finite Elements) [7], which uses finite element method to simulate heat and moisture transport. It enables simulation of constructive building details in 1-D or 2-D arrangement. The software was developed at

Department of Mechanics, Faculty of Civil Engineering, Czech Technical University in Prague. A particular advantage of SIFEL code is the possibility of investigation of variants concerning different constructions, different materials and different climatic loads. Constructive details of buildings and building materials can be optimized using the numerical simulation, and the reliability of constructions for different given indoor and outdoor climates can be judged. SIFEL works with different extension, such as HEMOT [8] that is able to provide the parameters from material database. This simplifies computations and allows obtaining more complex results.

The hollow brick (including cavities) was meshed and the materials were assigned to respective elements. In total the mesh was formed by 78 687 nodes and 77 819 quadrilateral elements. The meshed cross-section of the hollow brick is shown in Figure 1, a detail of the mesh near the face side is given in Figure 2.



Figure 1: Cross-section of the hollow brick



Figure 2: Detail of the mesh

For the sake of subsequent comparison with experimental data, the boundary conditions were chosen exactly in the same way as in the semi-scale experimental analysis performed by [9].



Figure 3: Scheme of the simulation

The hollow brick was very well insulated on the lateral sides, so that the heat losses there were not taken into account. The heat transfer coefficient on both faces of the brick, α , in the Newton's boundary conditions was set according to the Czech National Standards as 7.69 W/m²K [10] The air temperatures in the cold and hot chambers were 10.68 °C and 25.33 °C (average temperatures during all the course of the experiment). The scheme of the simulation with boundary conditions is shown in Figure 3.

All simulations were performed until the steady-state heat transfer was reached, i.e.,

$$q = -\lambda \frac{dT}{dx} = q_s \tag{1}$$

where *q* is the heat flux [W/m²], λ is the thermal conductivity [W/mK], and *q*^s is the heat flux in steady-state conditions [W/m²].

The effective thermal conductivity of the hollow bricks, λ_{eff} , was calculated using the equation

$$\lambda_{eff} = q_b \, \frac{\Delta x}{\Delta T} \,, \tag{2}$$

where $\Delta \xi$ [m] is the total thickness of the brick block (0.5 m), ΔT [K] is the temperature difference be-tween the hot and cold face of the brick, and q_b [W/m²] is the heat flux in the boundary element of the hollow brick which is calculated according to

$$q_b = \lambda_{bb} \frac{\Delta T_e}{\Delta x_e},\tag{3}$$

where λ_{bb} [W/mK] is the thermal conductivity of the brick body (λ_{bb} = 0.300 W/mK), $\Delta \xi_e$ [m] is the thickness of the boundary element ($\Delta \xi$ = 0.001 m), and ΔT_e [K] is the temperature difference between the opposite sides of the rectangular element in the direction of the heat flux.

The first simulation was performed with the measured values of thermal conductivity of involved materials shown in Table 1. The calculated steady-state heat fluxes which are given in the first line of Tables 2, 3 marked as Step 1 differed from the aver-age heat fluxes measured in the semi-scale experiment (Table 4); for the hydrophilic mineral wool the difference was less significant than for recycled polyurethane.

Parameter	λмw	q	λ_{eff}
	[W/mK]	$[W/m^2]$	[W/mK]
Step 1	0.0383	2.175	0.0744
Step 2	0.0380	2.164	0.0741

Table 2: Calculated thermal parameters of hollow brick filled with hydrophilic mineral wool

Table 3: Calculated thermal parameters of hollow brick filled with recycled polyurethane

Parameter	λpur	q	$\lambda_{e\!f\!f}$
	[W/mK]	$[W/m^2]$	[W/mK]
Step 1	0.0395	2.217	0.0759
Step 2	0.0487	2.529	0.0871

Table 4: Average heat flux in the hollow bricks measured in the semi-scale experiment (Pavlík et al., 2013)

Hydrophilic mineral wool	2.165	W/m ²
Recycled polyurethane	2.530	W/m ²

The main source of these differences was, apparently, the uncertainty in the measurement of thermal conductivity of the thermal insulation materials; the material in the holes could differ from that measured in the laboratory, for instance in the density. Therefore, the values of thermal conductivity of insulation materials were optimized in the subsequent step while the thermal conductivity of brick body was fixed. For that purpose a simple trial-and-error approach was used. The aim of the optimization was to achieve an agreement between the measured and calculated steady-state heat fluxes in the hollow brick.

The results of the Step 2 calculations are presented in Tables 2, 3. The value of thermal conductivity of the hydrophilic mineral wool had to be changed only slightly to achieve the measured heat flux, the difference was within the error range of the measurement method. On the other hand, the optimized thermal conductivity of recycled polyurethane was more than 20% higher than the measured value.

4. Discussion

It is obvious from both experimental and computational point of view, that cavity filler has significant impact on the effective thermal conductivity of hollow bricks. Assuming that the experiment was conducted with a good accuracy, the results of computational simulation provided useful complementary information about thermal performance of hollow bricks.

In this paper, hollow bricks with two different insulation fillers were compared: one brick was filled with hydrophilic mineral wool, the other one with recycled polyurethane. Before any comparison is done and the results are summarized, it is essential to explain the difference in manufacturing technology of both kinds of bricks.

The process of manufacturing of the hollow brick filled with mineral wool was completely machine-operated. The customers get the ready-to-use brick and no further modification or final preparation is needed on the site. The 100 % machine production ensured that the cavity filling was homogenous in whole cavity volume and all cavities were filled identically, in other words, the thermal properties of the cavities were very similar.

The manufacturing process of the other type of hollow brick, filled with recycled polyurethane, was substantially different. The producer supplied the hollow bricks and the insulation material separately and the process of filling of the cavities was done manually on the site. Therefore, it was not ensured that the cavities were filled precisely. Due to manual filling by inexperienced people it was very likely, that each hollow was filled in different way. The hollows could contain different amount of the filling material, as the insulation was not compacted, the density may vary across the cavity volume and last but not least, when the cavity was filled imperfectly, some air gaps could appear in the insulation material and the heat transfer by radiation could occur, which was against the philosophy of production of this kind of hollow bricks.

The average heat flux for hollow brick filled with hydrophilic mineral wool was measured as 2.165 W/m². In the first phase of simulation the initial value of thermal conductivity equal to 0.0383 W/mK was used (measured by Isomet device). The difference between simulated and measured heat fluxes was 0.46 %. In the second phase, the thermal conductivity of mineral wool had to be modified to 0.0380 W/mK. In this way, the difference between measured and simulated heat fluxes was reduced to 0.046 %. The slight modification of thermal conductivity of mineral wool can be easily explained by the measurement accuracy of Isomet device, which is 5 % of reading + 0.001 W/mK. The effective thermal conductivity of hollow brick block filled with hydrophilic mineral wool with 0.046 % error in heat fluxes was determined as 0.0741 W/mK.

The average heat flux for hollow brick block filled with recycled polyurethane was measured as 2.530 W/m². The initial value of thermal conductivity of polyurethane was set to 0.0395 W/mK, but due to high inhomogeneity of cavity filling, this value was expected to be changed dramatically. The difference between simulated and measured heat fluxes was 12.39 % and therefore the thermal conductivity of polyurethane was changed to 0.0487 W/mK in the second phase. The difference in heat fluxes was reduced to 0.02 % and the effective thermal conductivity of hollow brick was determined as 0.0871 W/mK.

The difference in effective thermal conductivities of both hollow bricks was very high, even though the thermal properties of both the original filling materials measured in the laboratory were very similar. Therefore it can be concluded that the technological process of cavity filling has a crucial impact on the effective thermal conductivity of hollow brick.

5. Conclusions

Based on the results presented in this paper it can be concluded, that development of new types of hollow bricks filled with different kind of insulation materials can be a prospective solution. A comparison of two kinds of hollow bricks filled with hydrophilic mineral wool and recycled polyurethane revealed that hollow brick filled with hydrophilic mineral wool exhibited significantly better thermal properties than the brick with the cavity filler made of recycled polyurethane. As the thermal conductivity of polyurethane measured in the laboratory is very similar to expanded polystyrene or mineral wool, the difference in thermal performance of the whole hollow brick is caused by the loose character of the recycled form of polyurethane. Therefore, an improvement of the filling technology can be recommended as a topic for further research and manufacturing.

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Computational analysis of coupled heat and moisture transport in building envelopes: the effect of moisture content

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Abstract: Many current computational simulations of temperature and moisture fields in building envelopes are performed with material parameters which do not depend on moisture content. This paper brings a comparison of simulation results based on constant and moisture dependent input parameters. This allows emphasizing the differences between both approaches and contributes to a possible avoidance of design errors caused by poor quality of input data of computational models.

Keywords: coupled heat and moisture transport, building envelopes, moisture content

1. Introduction

On a theoretical level, most currently used computational models of heat and moisture transport can be considered as appropriate for predicting hygric and thermal conditions in building envelopes. However, any model can provide reliable information only in the case that the quality of input data is very good. This is not always true because the standard list of thermal and hygric parameters given by the producers as well as the material databases included in the simulation tools are usually far from complete. They also often do not include the dependencies of heat and moisture transport and storage parameters on moisture and temperature. Therefore, in today's scientific practice the computational simulations of temperature and moisture fields are performed either with moisture dependent parameters, constant parameters or partially moisture dependent, partially constant parameters, based on the availability of measured data. This makes comparisons of simulated data difficult even for experienced scientists, not speaking of building professionals in construction companies.

This paper brings a comparison of simulation results based on constant and moisture dependent input parameters. This allows emphasizing the differences between both approaches and contributes to a possible avoidance of design errors caused by poor quality of input data of computational models.

2. Computational analysis

The computational analysis was accomplished by computer code HEMOT [1-2], which was developed at the Department of Material Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague on the basis of the general finite element package SIFEL [3]. As basic input parameters of the mathematical model, material parameters, scheme of construction detail, initial and boundary conditions and time specification of simulation were required.

2.1 Mathematical model

Künzel's mathematical model of heat and moisture transport [4] was used in the simulations which can be formulated as

$$\frac{d\rho_{v}}{d\varphi}\frac{\partial\varphi}{\partial t} = div\left[D_{\varphi}grad\varphi + \delta_{p}grad(\varphi p_{s})\right]$$
(1)

$$\frac{dH}{dT}\frac{\partial T}{\partial t} = div(\lambda gradT) + L_v div[\delta_p grad(\varphi p_s)]$$
⁽²⁾

where ρ_v is the partial density of moisture, φ relative humidity, δ_v permeability of water vapour, p_s partial pressure of saturated water vapour, H enthalpy density, L_v heat of evaporation, λ thermal conductivity and T temperature,

$$D_{\varphi} = D_{w} \frac{d\rho_{v}}{d\varphi} \tag{3}$$

is liquid moisture diffusivity coefficient, D_w is capillary transport coefficient.

2.2 Scheme of construction detail

Three variations of building envelope based on autoclaved aerated concrete (AAC) were chosen for simulation, in order to analyze the consequences of dependence of materials parameters on moisture content on the calculated moisture and temperature fields in a building envelope. We assumed load bearing wall in a thickness of 375 mm provided with three different types of thermal insulations (expanded polystyrene, hydrophobic and hydrophilic mineral wool) 50 mm thick. Thermal insulation was connected to the wall using adhesive layer made from Mamut M2 mortar in a thickness of 10 mm. The whole building envelope was provided on the interior and exterior side with MVR Uni plaster (developed especially for AAC constructions).

2.3 Material parameters

All the material parameters were measured in the laboratory of transport processes at the Department of Materials Engineering and Chemistry, Faculty of Civil Engineering, Czech Technical University in Prague [5-7]. They are summarized in Tables 1 and 2 and Figure 1 where the following symbols are used: ρ – bulk density [kg/m³], porosity %], *c* – specific heat capacity [J/kgK], μ – water vapour diffusion resistance factor [-], w_{hyg} – hygroscopic moisture content by volume [m³/m³], λ – thermal conductivity [W/mK], _{app} – apparent moisture diffusivity [m²/s].



Figure 1: Moisture diffusivity as a function of moisture content

	Expanded polystyrene	Rockwool hydrophobic mineral wool (HFOB)	Rockwool hydrophilic mineral wool (HFIL)
ρ [kg/m³]	16.5	100	170
ψ[%]	98.4	96.6	92.9
c [J/kgK]	1570	790	770
µdry cup [-]	58	2.6	2.7
µwet cup [-]	29	1.3	1.6
λ _{dry} [W/mK]	0.037	0.036	0.041
$\lambda_{sat}[W/mK]$	0.0513	0.766	0.694
$\kappa_{app} [m^2/s]$	1.5e-09	6.1e-11	4.1e-05
<i>Whyg</i> [m ³ /m ³]	0.0001776	0.00021	0.000539

Table 1: Material characteristics of thermal insulations

Table 2: Material characteristics of other materials

	AAC P1.8-300	Mamut M2	Baumit MVR Uni
		mortar	
ρ [kg/m³]	304	1430	1402
ψ[%]	87.4	42.6	44.4
c [J/kgK]	1080	1020	1020-1780
µdry cup [-]	7.10	12.40	12.4
µwet cup [-]	2.20	-	4.5
λ _{dry} [W/mK]	0.075	0.481	0.443
λ _{sat} [W/mK]	0.704	2.022	1.380
$\kappa_{app} [m^2/s]$	2.08e-09	1.07e-9	1.59e-9
<i>Whyg</i> [m ³ /m ³]	0.0152	0.0201	0.042

2.4 Boundary conditions and time interval of simulation

Because the boundary conditions should be as realistic as possible, climatic data in the exterior in the form of Test Reference Year for Prague was used. Test reference year contains average data for 30 years. On the interior side we used constant value of relative humidity 55% and temperature 21°C (see Figure 2). The climatic data were obtained using Meteonorm software [8]. The simulation started with the data for 1st July and was performed for 5 consecutive years. The presented results refer to the last simulated year where the effect of initial conditions was assumed to vanish.



Figure 2: Boundary conditions

3. Computational results

Analyzed moisture and temperature profiles are presented in a set of figures which are given below. Each figure contains vertical lines corresponding to the material interfaces described in Section 2.2. In these figures, interior is on the left side, that means, the layers are sorted in order (from left side): interior plaster, AAC block, connecting layer, thermal insulation and exterior plaster.

Temperature field

Figure 3 shows temperature profiles of building envelopes in a typical winter day (15th January). The differences between temperature values are not so high, however they are apparent particularly in the zone of connecting layer. The highest temperatures are obtained when building envelope with expanded polystyrene with moisture dependent parameters is assumed. On the other hand, lowest values are obtained when hydrophilic mineral wool assuming constant material parameters is under consideration.

Temperature profiles in a typical summer day are captured in Figure 4. Similarly to the previous case, the differences are not very significant but they are apparent in the AAC block near to the material interface between AAC and connecting layer. The lowest temperature values are obtained when hydrophilic mineral wool assuming constant material parameters is considered, the highest values are given when hydrophobic mineral wool assuming moisture dependent material parameters is considered.

The differences between simulation results assuming constant and moisture dependent parameters are obvious at most in Figure 5, where building envelope provided with expanded polystyrene is presented. The highest difference was detected on the material interface between AAC block and connecting layer and reached 1.2 °C, which is approximately 0.5 %.



Figure 3: Temperature profiles in a typical winter day



Figure 4: Temperature profiles in s typical summer day



Figure 5: Temperature differences between simulation results assuming constant and moisture dependent parameters

3.2 Moisture field

As the moisture transport and accumulation parameters of investigated thermal insulating materials were significantly different (see Table 1), it was to be expected that relative humidity profiles will differ more substantially than temperature fields. This was confirmed, as it is illustrated in the relative humidity profiles in Figure 6.



Figure 6: Relative humidity profiles in typical winter day

The highest differences (Figure 6) in relative humidity are located near the connecting layer and reach almost 22 %. The highest relative humidity is obtained when hydrophilic mineral wool is assumed.

In the case of the relative humidity profiles in summer period (Figure 7), the highest values are achieved when expanded polystyrene is assumed. However, while during the winter period the differences between particular variations were almost 22 %, during summer period it is only 11 %.



Figure 7: Relative humidity profiles in typical summer day



Figure 8: Relative humidity differences between simulation results assuming constant and moisture dependent parameters

According to the results presented in Figure 8, the building envelope provided with hydrophobic mineral wool seems to be the most sensitive to the quality of input material parameters. The differences between simulation results assuming constant or moisture-dependent values of material parameters is 3.72 percentage points of relative humidity.

3.3 Energy efficiency

Annual energy consumption is calculated as integral of time function of heat flux according to the relation

$$Q = \int_{1Jan}^{31Dec} q(t)dt , \qquad (4)$$

where *Q* denotes the energy efficiency per annum [kWh/m²_{envelope}a] and q(t) is time function of heat flux [W/m²_{envelope}] calculated from nodal temperatures in interior boundary element,

$$q = -\lambda \frac{dT}{dx}, \tag{5}$$

where *q* denotes the heat flux [W/m²_{envelope}], λ is thermal conductivity [W/mK], *dT* is difference between temperatures of two nodes defining the element [K] and *dx* is size of the element [m].

The value of thermal conductivity λ is determined from calculated moisture content according to the linear function characterized by values of λ_{dry} and λ_{sat} in Table 2 of Baumit MVR Uni plaster.

Figure 9 compares hourly values of heat fluxes of investigated types of building envelope. The differences in hourly values are low, but integration of their time function according to (4) reveals relative distinctions (see Table 3).

Thermal insulation	Annual energy consumption [kWh/m ² envelopea]
EPS – constant	18.743
EPS – moisture dependent	19.954
HFOB – constant	18.788
HFOB – moisture dependent	19.875
HFIL – constant	19.535
HFIL – moisture dependent	21.021

Table 3: Annual energy consumption of the studied envelopes



Figure 9: Heat fluxes on interior side

Assuming only constant values of material characteristics, best results are achieved when expanded polystyrene is used. However, taking into account the effect of moisture content, the best energy efficiency is obtained for building envelope provided with hydrophobic mineral wool.

4. Discussion

Based on the results presented in this paper it is obvious that the quality of simulation outputs is closely related to the quality of input parameters. Therefore, during experimental analysis it is essential to focus on measuring not only constant values of materials characteristics, but also on their dependence on moisture content.

Temperature field of building envelope is primarily influenced by thermal conductivity of materials which are involved. Considering the fact, this parameter can be increased due to moisture up to 10-20 times (see Tables 2 and 3). More convenient, but not correct results will be obtained, when constant material parameters will be assumed. This is proved by results presented in Figures 3-5. Temperatures across the envelope as result of simulation assuming only constant values of material characteristics are lower than results of simulation with moisture dependent values. The highest temperature difference was detected on the material

interface between AAC block and connecting layer and reached 1.2 °C (0.5 %) (building envelope with expanded polystyrene – see Figure 5). This value seems to be very small, however it can lead to underestimation of water vapour condensation inside building envelope. Unfortunately, possible condensation can be located near to the connecting layer between AAC block and thermal insulation, so its damage may lead to separation of layers.

Deterioration of thermal properties will also negatively affect energy efficiency of building envelope. According to the results presented in Figure 9 and Table 3, poor quality of input data can create incorrect image about thermal capability of building envelope and magnitude of the error can be up to 7 %. It is also worth to mention that from the point of view of energy efficiency, expanded polystyrene seems to be the best choice when only constant material parameters are assumed, while under real conditions hydrophobic mineral wool gives slightly better results (see Table 3). Similar discrepancies are often misused by producers of building materials presenting only dry state values of their products.

The moisture diffusivity influencing moisture field inside building envelope at most is far from a constant as it is obvious in Figure 1. Therefore, there are differences in simulation results based on different approaches (assuming moisture dependent or only constant material parameters). The graphs presented in Figures 6 and 7 show that hydrophilic mineral wool gives almost identical results during the year, regardless of quality of used material characteristics. Building envelope with expanded polystyrene gives worse results, when moisture dependent material parameters are used. The difference is 1 percentage point of relative humidity. The biggest difference is obtained in summer when building envelope provided with hydrophobic mineral wool is assumed (see Figure 8). However, in case of moisture fields, all the differences are on the safety side, because better results are obtained when moisture dependent material parameters are used.

5. Conclusions

In this paper, effect of moisture dependent thermal and hygric parameters on the moisture and temperature fields in building envelopes was analyzed. The studied envelope consisted of AAC (as load bearing material) provided with thermal insulation (expanded polystyrene, hydrophobic and hydrophilic mineral wool) and exterior and interior plaster. It was confirmed that the presence of moisture in building materials affects many of their parameters, one the most significantly impacted are thermal properties. During their service life, building materials contain almost permanently certain amount of moisture, thus it is necessary to calculate with their deterioration. The producers of building materials very often present only values in dry state, but this can be very misleading. It is necessary to point out that the quality of input parameters has a significant impact on the quality of calculation results. This was proved quite clearly in this paper. Regarding this fact, the primary experimental analysis of porous materials must be done very well. If the quality of input parameters is not so good (e.g., the dependence on moisture content could not be measured), it is essential to consider the possible uncertainties of the computations and to perform at least a sensitivity analysis within the expected margin of error.

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Experimental investigations of thickness effect curve in polystyrene foam (Styrofoam)

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Abstract: In the paper results of investigations of thermal conductivity reduction effect k(l) for small thicknesses of layers l in expanded polystyrene (EPS), i.e. styrofoam are presented. White styrofoam in dots manufactured by Termoorganika (Poland) and graphite styrofoam manufactured by Austrotherm (Poland) were selected for investigations. The measurements were carried out in plate apparatus Fox 314 (made by LaserComp, USA) for samples with a thickness l of from about 10 mm to about 100 mm, with black ($\varepsilon = 1$) and shining ($\varepsilon = 0.04$) sample's edges in the range of temperature from 0 oC to 50 oC. The study showed a significant share of heat transfer by radiation in white styrofoam in dots. Furthermore, the addition of graphite to the EPS beads significantly reduces contribution of heat transfer by radiation in graphite styrofoam.

Keywords: thickness effect curve, styrofoam, radiative-conductive heat transfer

1 Introduction

Expanded polystyrene (EPS), i.e. styrofoam is used mainly as thermo-insulating material for insulation of residential buildings. Recently, new varieties of styrofoam, such as white styrofoam in dots or graphite styrofoam appeared on the market. Especially the latter pays special attention because of better thermo-insulating properties (in comparison to white styrofoam). Silver gray color of graphite styrofoam is obtained by adding graphite to the EPS beads. In white styrofoams radiative-conductive heat transfer occurs, which results in the so called "thickness effect". It means that thermal conductivity obtained by measurements varies with the thickness of styrofoam layer. Investigations on thermal conductivity k are carried out under conditions of steady state heat transfer. As an example, it is considered the sample of thickness l_{A_i} assuming the temperature difference is $\Delta T = const$ and not greater than a few degrees. For such data we obtain the value of thermal conductivity of k_A – Figure 1. For a thicker sample l_{B} , assuming the same value of $\Delta T = const$ a different value of thermal conductivity k_{B} is obtained. The more different thicknesses of the sample *l* we consider on investigations of the thermal conductivity the more precise curve k(l) we obtain that illustrates thermal conductivity reduction effect – Figure 1. The range of layers' thicknesses that it concerns depends on many parameters, for example on the emissivity of the layers' boundaries. The value k_c is the conductive component of thermal conductivity k. We can assume that the conductive component k_c is fixed for small values of ΔT . White styrofoam in dots Gold Fasada manufactured by Termoorganika (Poland) with density $\rho = 15 \text{kg/m}^3$ and graphite styrofoam *Fassada Premium* manufactured by Austrotherm (Poland) with density $\rho = 14.7$ kg/m³ were selected for investigations of k(l).


Figure 1a:. Disc-shaped sample of thickness l placed between two copper plates of temperatures, $T_2 > T_1$, $\Delta T = T_2 - T_1$



Figure 1b:. Thermal conductivity reduction effect k(*l*) *for samples of small thickness l.*

The measurements were carried out in plate apparatus Fox 314 for samples with a thickness *l* changing from about 10 mm to about 100 mm (every 10 mm), with black ($\varepsilon = 1$) and shining ($\varepsilon = 0.04$) sample's faces [4]. Black faces were provided by the apparatus. Shining faces were obtained by covering each sample with a tin aluminum foil with low emissivity of about $\varepsilon = 0.04$ [1, 2]. The *k*(*l*) measurements were performed in temperature ranges: 0÷10 °C, 20÷30 °C, 40÷50 °C, i.e. for average temperature: \overline{T} : 5 °C, 25 °C, 45 °C, respectively. In each case, the heat transfer was from bottom to top, i.e. temperature of the lower plate T_2 was always higher than the temperature of the upper plate T_1 .

2 Experimental results

Results of the k(l) dependencies on sample thickness for selected styrofoams were illustrated in Figs. 2 and 3. For white styrofoam in dots there is a strong effect of reducing the thermal conductivity as a function of sample thickness l – Figure 2. This means that the contribution of heat transfer by radiation is significant in total heat exchange. Additionally, the k(l) curves obtained with black and shining sample edges are markedly different. For graphite styrofoam the k(l) curves with black and shining sample faces are flat and there is practically no effect of reducing the thermal conductivity as a function of sample thickness l. This means that the contribution of heat transfer by radiation in graphite styrofoam is significantly smaller as compared to white styrofoam in dots. It should be noted that the authors' previous studies have shown that the convective heat transfer in styrofoams is negligible [3]. Comparison of the k(l) reduction curve for the both styrofoam types are similar. However, graphite styrofoam has 20% lower thermal conductivity than the white one. Additionally, shining sample faces do not affect the effect of reducing the thermal conductivity k(l) in graphite styrofoam.



Adding graphite to the EPS beads results in almost complete elimination of the radiative heat transfer. It should be noted that the white styrofoam in dots with aluminum foils partially block the radiative heat transfer, in graphite styrofoam their influence is negligible – Figure 4.



Figure 4: Comparison of dependences k(l) on sample thickness for white styrofoam in dots (Gold Fasada) and graphite styrofoam (Fassada Premium) with black and shining sample's faces.

3. Calculation of radiative heat transfer

The impact of layer surface emissivity on the effect of reducing of thermal conductivity under steady state conditions was the subject of research that the authors of this paper presented in the monograph – Figure 5 [1]. For the shining sample faces ($\varepsilon = 0.04$) maximum of the radiative heat flux density $\dot{q}_r(l)$ dependence and typical inflection of the k(l) curve for small samples thickness l is observed. In the vicinity of styrofoam walls temperature gradients increase with decreasing surface emissivity. This means that conductive heat flux density in this region becomes a larger part of the total heat flux density of the sample $\dot{q}(l)$ [1, 2].



Figure 5: Thermal conductivity k(l) and radiative heat flux density $\dot{q}_r(l)$ along sample thickness l according to radiative transfer equation (RTE) calculations with surfaces emissivity ε less than one [1].

Table 1 summarizes the experimental values, i.e. the values from the Fox 314 apparatus, heat flux density $\dot{q}(l)$ for white styrofoam in dots in the temperature range 40÷50 °C. Then by extrapolation of the k(l) curve for that styrofoam to the sample thickness l=0 mm, value of the conductive component of thermal conductivity $k_c = 0.032$ W/(m·K) was obtained - Figure 6. Subsequently, the values of the conductive component of heat flux density, i.e.: $\dot{q}_c(l) = k_c \frac{\Delta T = 10\text{K}}{l}$ and radiative component of heat flux density for l=0 mm were evaluated, i.e. $[1, 2]: q_r(0) = \frac{\sigma \cdot (T_2^4 - T_1^4)}{2/\varepsilon - 1}$, where $\sigma = 5.67 \cdot 10^{-8}$ W/(m² · K⁴) is the Boltzmann constant.

The results of calculations are $[\dot{q}_r(0)]_{\varepsilon=1} = 73.1 \text{ W/m}^2$ and $[\dot{q}_r(0)]_{\varepsilon=0.04} = 1.5 \text{ W/m}^2$. Other values of radiative component of heat flux density were calculated from the expression $\dot{q}_r(l) = \dot{q}_c(l) [1, 2]$. The values $\dot{q}_c(l)$ and $\dot{q}_r(l)$ for white styrofoam in dots are summarized in Table1, and the k(l) and $\dot{q}_r(l)$ dependencies for white styrofoam in dots were additionally illustrated in Figs. 6+8. Comparison of the $\dot{q}_r(l)$ dependencies for white styrofoam (for the same value of $k_c = 0.032 \text{ W/(m \cdot K)}$) radiative heat flux density as a function of sample thickness values $\dot{q}_r(l)$ both for black and shining sample edges are many times lower (to 1.6 W/m²), than in the case of white styrofoam.

Table 1: Heat flux density experimental data $\dot{q}(l)$ for white styrofoam in dots within temperature rangefrom 40 °C to 50 °C (Fox 314).

<i>l,</i> mm	10.0	20.4	30.0	41.0	48.1	59.7	70.2	80.3	90.0	99.6
$\dot{q}(l)$, W/m², $\varepsilon = 1$	37.9	19.8	14.2	10.2	8.8	7.2	6.2	5.3	4.9	4.4
$\dot{q}(l)$, W/m ² , $\varepsilon = 0.04$	34.5	18.5	13.4	9.8	8.5	7.0	6.0	5.2	4.8	4.3
$\dot{q}_{\mathcal{C}}(l)$, W/m²,	32.1	15.7	11.0	7.8	6.7	5.4	4.6	3.9	3.6	3.2
$\dot{q}_r(l)$, W/m ² , $\varepsilon = 1$	5.9	4.1	3.2	2.4	2.1	1.8	1.6	1.4	1.3	1.2
$\dot{q}_r(l)$, W/m², $\varepsilon = 0.04$	2.4	2.8	2.4	2.0	1.8	1.6	1.4	1.3	1.2	1.1



There is also no typical maximum of the $\dot{q}_r(l)$ curve – Figure 8.



Figure 8: Comparison of dependences $\dot{q}_r(l)$ *on sample thickness l for white styrofoam in dots with graphite Styrofoam, with black and shining sample's faces.*

4 Conclusions

The addition of graphite to the EPS beads significantly reduces the share of heat transfer by radiation and thus reducing the reduction effect of thermal conductivity k(l). In white styrofoams there is typical maximum of $\dot{q}_r(l)$ curve for a low emissivity, e.g. $\varepsilon = 0.04$, that is for sample faces with high reflectance of radiation. The inflection of k(l) curve for $\varepsilon = 0.04$ could not be confirmed, because it is difficult to make samples of styrofoam with layer thicknesses below 10 mm. In graphite styrofoam, in which the contribution of heat transfer by radiation is negligible, curves $\dot{q}_r(l)$ for layer faces emissivities $\varepsilon = 1$ and $\varepsilon = 0.04$ are the same.

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Moisture dependence of water vapour permeability

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Abstract: In simulations of an isothermal hygric performance of a capillary-porous building material, moisture transport by surface diffusion can be involved into moisture dependent water vapour permeability. Generally, the water vapour permeability is a function of moisture content but it is often modelled as vapour permeability/relative humidity relation using directly the standard cup method measurements results. In this work the real dependence of the water vapour permeability on moisture content was determined. The water vapour permeability of the samples was measured by the standard cup method using the RH differences: 0 - 53%, 11.3 - 53%, 33 - 53%, 53 - 75.4%, 53 - 84.7%, 53 - 94% and 53 - 100%. The weight of the samples was checked before and after the cup measurements and at the end of the measurements the tested samples were oven dried at temperature of 105° C in order to determine their actual moisture content. The measurements were carried out for burnt clay bricks and autoclaved aerated concretes. Based on the obtained results a suitable approximation function of the vapour permeability moisture dependence was suggested.

Keywords: water vapour permeability, surface flow, moisture dependency, burnt clay brick, autoclaved aerated concrete

1. Introduction

In capillary-porous materials, besides the moisture transport by water vapour diffusion the moisture transport by surface diffusion occurs in hygroscopic range. It arises at higher moisture content as a result of presence multilayer water molecules sorption. The actual value of a threshold moisture content at which formation of the surface diffusion starts depends on pore structure of the material and therefore is different for particular materials [1]. On the other hand, the determined threshold moisture content can serve as a characteristic of the material pore structure.

At isothermal conditions, the surface diffusion flow and water vapour diffusion flow directions are identical. Therefore, at standard cup measurements [2], it is impossible to separate the water vapour diffusion and the surface diffusion. Really, the isothermal vapour permeability is a function of moisture content but it is often modelled as vapour permeability/relative humidity relation using directly the standard cup method measurements results [3, 4]. However, the actual moisture content in the sample during the cup method test depends not only on the applied relative humidity (RH) difference but reflects also used way of drying as well as previous history of the sample. Moreover the vapour permeability/RH relation is not usable for simulation of the hygric performance of a building material/structure in cases when hysteretic effects could be of importance.

In the presented work the water vapour permeability/moisture content dependence of chosen building materials was determined and a suitable approximation function of the vapour permeability moisture dependence was suggested. The measurements were carried out for two types of burnt clay bricks and autoclaved aerated concretes.

2. Materials and methods

The tested bricks are commonly used burnt clay bricks produced by two different Slovak factories. The bricks are manufactured from a clay-sand mixture (the proportion of the sand ranged from 30% to 50%); the temperature of burning is 900–1000°C.

The tested AAC samples are produced by two different manufacturers – Ytong and Hebel. They have a similar chemical composition (lime-cement binder, sand filler) and practically identical basic material parameters (bulk density, open porosity, capillary moisture content cf. Table 2).

Basic material parameters of the tested materials - bulk density, total open porosity and capillary moisture content as well as water vapour sorption isotherms were determined in previous works [5, 6]. The water vapour adsorption curves were determined by standard gravimetric desiccator method, which consists in conditioning the samples in desiccators under constant RH and temperature (23°C) until the static equilibrium is achieved [7].

The water vapour permeability of the tested materials was measured by the standard cup method [2] using the RH differences: 0 - 53%, 11.3 - 53%, 33 - 53%, 53 - 75.4%, 53 - 84.7%, 53 - 94% and 53 - 100%. The mass of the sample was checked before and after each cup test. At the end of all cup measurements the samples were oven dried at temperature of 105° C in order to determine actual moisture contents of the samples. All water vapour permeability measurements were performed in an air-conditioned room at temperature of $23 \pm 0.5^{\circ}$ C and RH equal to $53 \pm 1\%$. The required RH inside the cup was established by using silica-gel, water or saturated salt solutions (Table 1).

Table 1: Silica-gel, water and saturated salt solutions used for controlling RH inside cups

RH	0 %	11.3 %	33 %	75.4 %	84.7 %	94 %	100 %
	Silica- gel	LiCl·H ₂ O	MgCl2·6H2O	NaCl	KCl	KNO3	water

3. Results and discussion

The basic material parameters of the tested materials are presented in Table 2.

Material	Bulk density [kg/m³]	Open porosity [-]	Capillary moisture content [m³/m³]
Brick P	1370	0.42	0.37
Brick D	1724	0.30	-
AAC Y	500	0.80	0.28
AAC H	512	0.80	0.27

Table 2: Basic material properties of tested materials

Analysis of the measured water vapour resistance factor/moisture relations has shown that for all tested materials they can be approximated by following hyperbolic function:

$$\mu = \mu_0 - a \cdot \frac{\exp(\frac{u_m - u_{m1}}{u_{m2}}) - \exp(\frac{u_{m1} - u_m}{u_{m2}})}{\exp(\frac{u_m - u_{m1}}{u_{m2}}) + \exp(\frac{u_{m1} - u_m}{u_{m2}})}$$
(1)

Where u_m is moisture content, μ_0 , a, u_{m1} and u_{m2} are parameters.

The approximation function (1) has a form suitable for numerical simulations of hygric performance of building materials or structures.

The obtained water vapour resistance factor/moisture content dependences and their approximations are presented in Figure 1 - 3. The parameters of equation (1) are in Table 3.

As can be seen from Figure 1 – 3, the transition from the higher value of water vapour resistance factor, corresponding to the water vapour diffusion without the surface diffusion, to the lower value, following from cumulated effect of the water vapour diffusion and the surface diffusion takes place in a relatively narrow transition zone. The mean moisture content at which the transition occurs corresponds to parameter u_{m1} of equation (1). The width of the transition zone is expressed by the parameter u_{m2} and corresponds to value of $2 \cdot u_{m2}$.

The relative humidity corresponding to the threshold moisture content of the surface diffusion formation can be evaluated from the obtained water vapour resistance factor/moisture relation (Figure 1 -3) and respective sorption isotherm. In Figure 4, the water vapour adsorption isotherms of the tested materials, determined in previous works [5, 6] are shown. As can be expected from previously published results [1], there is no unique threshold relative humidity value for the surface diffusion flow of the tested materials. In case of both AAC materials the surface diffusion starts at relative humidity of about 25%, in case of brick P it is of about 45% while in case of brick D it is of about 60%.



Figure 1: Water vapour resistance factor vs.moisture content for brick P



Figure 2: Water vapour resistance factor vs.moisture content for brick D



Figure 3: Water vapour resistance factor vs.moisture content for AAC Y and AAC H

Conclusions

The water vapour permeability/moisture content dependence of ceramic bricks and AAC materials was experimentally determined.

Material	μο	а	Um1	Um2
Brick P	9.2	3.7	0.0098	0.0037
Brick D	13.7	2.9	0.0024	0.0005
AAC Y	8.5	3.0	0.022	0.001
AAC H	6.0	2.6	0.0185	0.0026

Table 3: Parameters of approximation (1)



Figure 4: Water vapour adsorption isotherms for AAC H, AAC Y, brickP and brick D [4,,5]

The measurements have shown that a transition from the higher value of water vapour resistance factor, corresponding to water vapour diffusion without surface diffusion to the lower value, corresponding to the cumulated effect water vapour diffusion and surface diffusion takes place in a relatively narrow transition zone.

Based on analysis of the experimental data the approximation of moisture dependent water vapour permeability by the hyperbolic function was suggested.

In future work the identified relation between water vapour resistance factor and moisture content should be verified for other types of building materials.

Acknowledgments

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Suitability of different multilayer film models of water vapour adsorption isotherms

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Abstract: Several studies confirmed that the deposition of sorbate molecules on the pore walls surface is a dominant process during the adsorption. A previous analysis of the results of water vapour and nitrogen adsorption in combination with the mercury intrusion porosimetry showed the suitability of these methods to identify the pore structure and to model the water vapour and nitrogen sorption and the sorption hysteresis. A similarity between ratios of specific surface areas and sorbate volumes at 95 % relative pressure confirms that the forming of the multilayer film on the pore walls is dominant process during adsorption. The adsorption isotherm can be then modelled as the product of adsorbate layer film thickness and specific surface area. The formation of multilayer film can be in these cases described by several models, for example Halsey, Harkins Jura, GAB, etc. This paper is focused on the analysis of the suitability of different models describing the formation of multilayer film on the pore surface. The analysis was performed on calcium silicate plates, lightweight plasters and burnt clay bricks.

Keywords: Sorption, pore structure, multilayer film, water vapour, nitrogen

1. Introduction

For a correct computational simulation of the dynamic moisture behaviour of building structures it is necessary to know the hygric parameters of their materials. The important material parameter is the moisture capacity, which in the hygroscopic region is defined as the slope of the sorption isotherm. The determination of the moisture capacity from only a few measured values introduces considerable inaccuracies into the calculation.

Several studies confirmed that the forming of water molecules layer on the pore walls surface is a dominant process during the adsorption. This paper discusses the applicability of various models based on formation multilayer water film on the pores surface.

2. Studied models

An extensive review of water vapour adsorption models is presented in [7] and [8]. We will compare the application of some of them.

Brunauer-Emmert-Teller (BET) equation

The BET equation [1] represents a fundamental milestone in the interpretation of multi-layer sorption isotherms. The method serves as the basis for an important analysis technique for the measurement of the specific surface area of the material. The concept of the BET theory is an extension of the Langmuir theory, which is a theory for monolayer molecular adsorption, to multilayer adsorption. The resulting BET equation the adsorbed multilayer capacity at given relative pressure:

$$w(p / p_0) = \frac{C \cdot w_m \cdot (p / p_0)}{[1 - (p / p_0)] \cdot [1 - (p / p_0) + C \cdot (p / p_0)]}$$
(1)

where w_m is monolayer capacity and C is the BET constant, p/p_0 is the relative pressure.

Halsey model

Halsey [2] proposed as an alternative to the BET equation the model of polymolecular adsorption. In this model he assumed that the adsorbate bonding energy of is the power function of adsorbate amount. The thickness of the adsorbate layer $t(p/p_0)$ at the adsorbate relative pressure p/p_0 is expressed in (nm) in the form:

$$t = \tau \left[\frac{a}{\ln(p_0 / p)} \right]^{1/n}$$
(2)

where = the effective diameter of sorbate molecule equal to 0.277 nm for water, a and n are constants, p₀/p is inverse value of relative pressure.

Water sorption can be consequently modelled with use of Halsey equation as the product of adsorbate layer thickness *t* and specific surface area:

$$w(p/p_0) = t(p/p_0) \cdot A \tag{3}$$

Harkins Jura (HJ) method

The forming of the statistical fim in the empirical HJ equation [4] is given as:

$$t = \left[\frac{a}{b - \log(p_0 / p)}\right]^{1/n} \tag{4}$$

Where parameters *a*, *b* and *n* are constants. For nitrogen DeBoer [4] determined the constants a = 13.99, b = 0.034 and n = 2.0. The original HJ model assumed n = 2.0 as a fixed constant.

Guggenheim, Anderson and de Boer (GAB) equation

The GAB equation is based on the BET model. The mathematical formulation is as follows:

$$w(p / p_0) = \frac{C \cdot w_m \cdot K \cdot (p / p_0)}{[1 - K \cdot (p / p_0)] \cdot [1 - K \cdot (p / p_0) + C \cdot K \cdot (p / p_0)]}$$
(5)

where *K* is the empirical parameter. In case of K = 1, the equation simplifies to the BET model.

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Authors [5] proposed the modification of the GAB isotherm in order to correlate the sorption data for relative pressures higher than 0.9. The isotherm retains the desireable properties of GAB isotherm, i.e. good fitting in the range of relative pressures 0.05 and 0.8, and also provides noticeable improvement in the fitting quality for high values of relative pressures:

$$w(p / p_0) = \frac{C \cdot w_m \cdot K \cdot (p / p_0)}{[1 - K \cdot (p / p_0)] \cdot [1 - K \cdot (p / p_0) + C \cdot K \cdot (p / p_0)]} + \frac{C \cdot K \cdot K_2 \cdot (p / p_0)^2}{[1 - K \cdot (p / p_0)] \cdot [1 - (p / p_0)]}$$
(6)

For $K_2 = 0$ this equation simplifies into GAB and for K=1 and K₂ = 0 into original BET.

3. Measurements

For three burnt clay brick materials from various locations, four calcium silicate materials, the lightweight carbonate and lightweight lime-cement plasters the water vapour sorption tests were carried out. The water sorption isotherms were determined with Aquadyne DVS Water Sorption Analyser, an integrated microbalance system for the automatic study of dynamic water sorption at ambient pressure. The isotherms were determined in 0.1 - 0.98 relative pressure range. The basic parameters of the analysed materials are presented in table 1.

Material	Bulk density	Porosity	Water
	(kg/m³)	(-)	specific surface area (m²/m³)
brick from Zilina	1510	0.45	2.87x10 ⁶
brick from Lucenec	1840	0.32	19.10x10 ⁶
brick from Pezinok	1500	0.50	59.22x10 ⁶
Calcium silicate A	240	0.67	5.27 x10 ⁶
Calcium silicate B	240	0.91	4.48 x10 ⁶
Calcium silicate C	200	0.93	4.32 x10 ⁶
Calcium silicate D	280	0.90	6.57 x10 ⁶
Lightweight lime-cement plaster	670	0.63	8.39 x10 ⁶
Lightweight carbonate plaster	610	0.67	12.65 x10 ⁶

Table 1: Basic parameters	of analysed	materials
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4. Analysis

A prerequisite for the application of all considered models the knowledge of the specific surface area of a material. Therefore the multipoint BET method was applied to estimate it in common with monolayer capacity and C constant. The validity range of BET equation was tested in linearised BET diagram. The vertical axes were therefore transformed into the form (p/p0)/[u.(1-p/p0)]. The linear trend in the linearized BET plot shows the region of the model validity. Typical linearised BET plots are in figure 1.



Figure 1: Characteristic linearized BET-plot courses.

Roughly linear trend in the wide range of relative pressure (approx. up to 95%) is characteristic for macro-porous materials where the water vapour condensation does not occur during the adsorption. On the contrary, an exponential increase in the vertical axis indicates the presence of condensate. The applicability of the models based on the formation of the film thickness on the pore walls is therefore limited to this linear region. If there is condensation in pores, the reduction in specific surface area occurs, and thus the capacity of the monolayer reducdtion. In [6] an algorithm for determining the pore size and pore structure, taking into account changes in specific surface is indicated. In the case of modelling the sorption isotherm beyond the BET model validity, we have already the statistical film thickness including formed condensate which is recalculated into equivalent film thickness on the overall pore surface area.

In Figure 2 the typical adsorption isotherms of analysed building materials with corresponding approximated models are depicted.





Parameters of the compared models giving the best approximations for tested materials are listed in table 2.

Table 2: Parameters of analyzed models for various materials

Material	BE	Т	Hal	sey	Harkir	ns Jura	Harkins	Jura-mo	dified	GAB	Viollas a	nd Rovedo
	w _m	С	а	n	а	b	а	b	n	К	К	K ₂
Calcium silicate A	6.546E-03	49.03	1.5	1.4	0.050	0.000	0.100	0.010	1.4	0.98	0.95	1.0E-06
Calcium silicate B	4.472E-03	35.16	0.8	1.5	0.030	0.000	0.090	0.001	1.5	0.97	0.95	1.0E-06
Calcium silicate C	5.174E-03	339.62	0.4	1.7	0.010	0.000	0.090	0.001	1.5	0.94	0.84	1.0E-06
Calcium silicate D	6.546E-03	30.46	1.3	1.4	0.090	0.000	0.095	0.001	1.5	0.95	0.89	1.0E-05
Brick from Zilina	7.817E-04	61.20	5.0	2.5	0.140	0.030	0.100	0.000	2.7	0.78	0.65	1.0E-06
Brick from Pezinok	9.451E-03	202.51	2.5	1.7	0.065	0.000	0.085	0.000	1.7	0.94	0.94	1.0E-07
Brick from Lucenec	2.139E-03	17.87	1.3	2.0	0.040	2.000	0.050	0.010	1.8	0.80	0.73	1.0E-05
Lightweight lime-cement plaster	3.463E-03	2.66	0.7	1.3	0.025	0.000	0.060	0.000	1.1	0.80	0.78	1.0E-04
Lightweight carbonate plaster	5.222E-03	176.41	2.0	2.3	0.060	0.005	0.060	0.010	2.2	0.84	0.84	1.0E-07

In the case of mainly macro-porous materials (i.e. calcium silicates) validity of BET equation is evident up to 0.80 - 0.95 relative pressures. These types of materials are characterized by a low portion of the meso-pores where condensation occurs at lower relative pressures, so the forming of water film on the pores surface is dominant during the adsorption. At higher relative pressures the BET model overestimates equilibrium moisture content, due to assumption of non-existing free specific surface area of the capillaries that are filled with water. This is evident in case all other analyzed materials.

The unrealistic increase of moisture content due to presence condensate and reduction of the specific surface area was empirically taken into account in GAB model by reduction of parameter *K*. For calcium silicates with wide range of validity of BET theory, high values of parameters *K* (0.94 - 0.98), i.e. the low reduction, were determined. For all other materials the lower values of parameters *K* are suitable. For these materials GAB model correlates with measurements up to 0.8 relative pressures.

The limit of GAB equation for modeling the equilibrium moisture content at higher pressures compensates the equation proposed by Viollas & Rovedo [5]. This model based on the extension of BET equation and subsequently GAB equation enables to model the whole hygroscopic range. For this model the reduction of parameter K and very low values of parameter K₂ are

characteristic. Both GAB and Viollas & Rovedo only slightly change the character of monolayer film forming at low relative pressures.

In the original model describing the formation of the multilayer film on the pore walls proposed by Harkins Jura the exponent parameter value n = 2 was suggested. As it is shown in figure 2, the existence of condensate prevents a further application of this model. Therefore the modification of this parameter was tested and the results give a satisfactory correlation with the measurements.

Halsey found that his model gives a good fit for differing absorbents and absorbates with prior data for exponent n = 1 to 15. For all analysed materials, value of n equals to 1.3 - 2.3. The existence of condensate and the associated reduction of pore surface area were in this work taken into account by suitable constant parameters. Modelling the forming of multilayer film using the two-parameter equation represents an elegant tool for modelling the sorption isotherms.

5. Conclusions

Five models describing the formation of multilayer film on the pores surfaces were tested. Physically well defined BET equation proved the limit of validity of pure multilayer film forming. At higher relative pressures, an alternative model had to be used. Modelling of forming a multilayer film using two-parameter Halsey equation provides an elegant tool for modelling sorption isotherms. Modification of the original BET model applied by Viollas and Rovedo constitutes an appropriate alternative preserving the essence of BET theory.

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Influence of the sieving process on thermophysical properties of brick clay

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Abstract: Milling and sieving are an important part in the preparation of materials for the manufacture of ceramics. The paper deals with thermal analysis of brick clay from the locality of Radobica (Central Slovakia). The dependence on the grain size from 50 to 500 μ m was studied by two different thermal analyses (the DTA and TDA). It was found out that samples with a low granularity contain more soft minerals, such as illite. On the other hand, the samples with a high granularity contain more hard minerals (such as quartz) that were difficult to sinter. The milling and sieving processes affected not only the grain size but also the composition of mixtures.

1. Introduction

Brick clay is usually rich in clay minerals with traces of metal oxides and organic matter. Clay minerals are typically formed over long periods of time by gradual chemical weathering of rocks, usually silicate-bearing, by low concentrations of carbonic acid and other diluted solvents [1, 2]. In the ceramic industry these clays are used for its fine properties, such plasticity and the ability to receive non-plastic materials [3].

One of the important part in the preparation of materials for the production of ceramics are grinding and sieving. The particle size and shape affect many material properties, such as sintering speed or pressing ability of green ceramics, which influence the final strength of a ceramic body. The ambient conditions have a significant influence on the results of the sieving process . For example, during dry sieving agglomerates formations may occur due to electrostatic forces between powder particles [4].

Thermal analyses are a group of methods which allow observing reactions during heating or cooling. Widely used thermal analyses include the Differential Thermal Analysis (DTA) and Thermodilatometry Analysis (TDA). The DTA allows us to monitor the temperature difference between the studied and reference materials. If any physical or chemical reaction does not occur in the sample, the resulting curve is a zero line. If a reaction takes place in the sample, the resulting curve forms an exothermic or an endothermic peak whose area is proportional to the reaction heat and mass of the sample [5, 6]. The TDA allow us to observe linear expansion of the studied material during heating or cooling. This is particularly important for ceramic samples in which phase transition and sintering occurs during heating [7].

Samples and Methods

In this work was used clay samples from the locality of Radobica rich in illite minerals used in the brick production in the past. The mineralogical composition before and after firing is presented in Table 1.

Table 1: Mineralogical composition before and after firing from the locality of Radobica (Central Slovakia)

Raw	smectite	illite	feldspar	quartz	calcite
Fired	cristobalite	mullite	feldspar	quartz	

Collected samples were dried and crushed. After milling by a laboratory mill, the samples were sieved by laboratory sieves with a mesh size 50, 100, 200, and 500 μ m. The results of the sieve test are shown in Figure 1.

As we can observe, the largest representation has grains of size 200-500 μ m, which represent ~ 65% of the whole sample. The smallest representation was observed for grains of size under 50 μ m. This result may be affected by the formation of agglomerates in the sample which do not pass through the sieve. The agglomerate formation can be explained by accumulation of electrostatic charges between particles and sieve component [4, 8].



Figure 1: Results of the sieve test.

The samples for the two thermal analyses were prepared by two different ways. The samples for the TDA were prepared from dry clay (with different grain sizes <50, 50 – 100, 100 – 200, 200 – 500 μ m) and water. From this mixture compact samples were made with dimensions $10 \times 10 \times 40$ mm³. Thus prepared samples were measured using the TDA with the temperature regime from the laboratory temperature (LT) up to 1100 °C and back to 100 °C with a heating and cooling rate 5 °C/min.

The samples for the DTA were prepared from dry clay with different grain size (<50, 50 – 100, 100 – 200, 200 – 500 and >500 μ m) with mass ~1.5 g. The DTA was measured from LT up to 1050 °C with a heating rate 5 °C/min. Powder samples were subject to a second heating from which reversible reactions taking place in the samples could be observed.

2. Results and Discussion

During the firing of ceramic materials many changes occurs in samples that we can identify through thermal analyses. On the DTA record (Figure 2) we can observe several reactions which occur during firing in the sample. Up to the temperature 200 °C we can observe an endothermic reaction which is connected with the liberation of physically bonded water. The next exothermic reaction with a maximum at ~350 °C is connected with burning out of organic compounds contained in the clay bearing. The next endothermic reaction in the range 450 -

750 °C is connected with two step illite dehydroxylation [9]. This reaction overlays another reversible reaction (the α - β quartz transformation) which can be observed during second heating of the sample. In the temperature range 850 – 950 °C we can observ a weak endothermic reaction connected with the calcination of the sample [10].



Figure 2: DTA record of RA sample.

The dimension response of the sample to temperature changes during heating and cooling can be observed on the TDA record (see Figure 3). Up to the temperature ~550 °C the sample expands approximately linearly. The largest changes of samples can be observed at 573 °C were the α - β quartz transformation occurs. Another significant change occurs at ~850 °C where a significant shrinkage caused by sintering of the sample can be observed [11].



Figure 3: TDA record of RA sample during heating (grey line) and cooling (black line).

On the cooling curve (Figure 4) several reactions can be also observed. In the temperature interval 1100 - 1050 °C the sintering still occurs, which is reflected by a rapid shrinkage of the sample. Bellow the temperature 1050 °C the dimensions change approximately linearly. At the

temperature 573 °C we can observe the reversible α - β quartz transformation again. Bellow this temperature we do not observe any reactions.



Figure 4: The TDA curve of RA sample during cooling.

In evaluating the TDA curves we focused on two parameters. The first was the maximal shrinkage of the sample depending on the grain size. The second parameter was the contraction the sample during the α - β quartz transformation. Whereas during heating the sample this reaction is partially overshadowedby dehydroxylation, we followed the α - β quartz transformation during cooling. The results of our observations are summarized in Table. 2.

RA samples	Maximal contraction / %	SiO ₂ contraction / %
< 50 µm	7.49	0.07
50 - 100 μm	4.64	0.09
100 - 200 μm	2.15	0.13
200 - 500 μm	-0.47	0.20

Table 2. Maximal contraction and SiO2 contraction of samples by TDA.

As we can see, the largest shrinkage was achieved for the samples with a particle size <50 μ m. On the other hand, the samples with the initial grain size 200 – 500 μ m at temperature 1100 °C were by 0.5 % larger than at the beginning of the measurement. These differences could be caused by differences in the specific surface area of particles in the samples [12, 13]. Another reason may be a different initial composition of samples caused by sieving. From the obtained data we can see the relative expansion of the sample near the temperature where the α - β quartz transformation occurs is for samples with grain size 200 – 500 μ m three times larger than for the samples with the initial grain size bellow 50 μ m. This difference can be caused by a different hardness of particles of clay. Softer illitic particles can be grounded easier and faster than harder quartz particles. After sieving this mixture the small particles are predominantly of the illitic type and, conversely, quartz particles will be more present in samples with higher granularity.



Figure 5: DTA record of RA sample during 2nd heating.

Our findings are further verified by the DTA analysis. In contrast with the dilatometric measurements in this method we used powder samples. This difference allow us to observe the samples up to a particle size >500 μ m. For each sample, we performed measurements during the second heating. Our aim was to eliminate dehyroxylation which covers the reversible reaction of the α - β quartz transformation. In the obtained curve (see Figure 5) we can observe two reactions. The first reaction in the temperature region 50 – 150 °C is connected with the liberation of physically bonded water. The second one is the α - β quartz transformation at temperature 573 °C.

We observed the changes in the peak areas according to the grain size of the sample. Our findings are summarized in Table 3. The largest peak area occurs for the samples with the larger granularity, while the lowest peak areas were observed for the samples with the smallest grain size. From these results we can make similar conclusions as in the dilatometry measurements. The largest peak area in the α - β quartz transformation region was observed for the samples with higher granularity. These differences can be attributed to an uneven distribution of illitic and quartz particles due to the sieving process.

RA samples	DTA / °C ² .g ⁻¹
< 50 µm	23.9
50 - 100 μm	25.2
100 - 200 μm	27.8
200 - 500 μm	30.7
> 500 µm	34.0

Table 3: The comparison of the area of peaks associated with α - β *quartz transformation.*

3. Conclusions

In the studied brick clay samples it was shown that significant influence of sieving process on DTA and TDA curves was present. The differences between samples with a different granularity were observed during sintering and also during the α - β quartz transformation. Both

analyses confirmed that the sieving process affected the initial composition of samples after sieving. This may be caused by a different hardness of particles of clay. Softer illitic particles can be grounded easier and faster than harder quartz particles. Under this assumption, after sieving this mixture the small particles are predominantly of the illitic type and quartz particles will be more present in the samples with a higher granularity. An important role during dry sieving is played by agglomeration formations due to electrostatic forces between fine powder particles.

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Investigation of heat transfer in cavity brick block using laboratory methods suitable for large-scale specimens

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Abstract: Cavity brick blocks were originally designed for residential houses. However, they can be beneficially applied also for smaller administrative and public buildings. Since the cavity brick blocks should find application in outer walls of buildings, their thermal conductivity together with mechanical properties represents the most important material parameter for their usage. In this paper, the thermal conductivity as the main parameter characterising the heat transfer is analysed using an experimental facility where laboratory methods can be applied on large-scale specimens.

Keywords: cavity brick blocks, heat transfer, large-scale

1. Introduction

Thermal comfort and indoor air quality are important factors to be considered during building design and operation. The most important variables that influence the condition of thermal comfort are: air temperature, water vapour pressure, relative air velocity and mean radiant temperature [1].

In Central European countries, there is paid specific attention to the design and manufacturing of single-layer building envelope systems based on lightweight cavity bricks, whereas the cavities are filled either by air or thermal insulation materials as polystyrene balls, mineral wool, crushed polyurethane foam, etc. Filling the cavities by thermal insulation materials reduces the heat transfer by radiation and contributes to the higher thermal resistance of brick block compared to materials with air cavities only.

Cavity brick blocks are originally designed for residential houses. However, they can be beneficially applied also for smaller administrative and public buildings. Since the cavity brick blocks should find application in outer walls of buildings, their thermal conductivity together with mechanical properties represents the most important material parameter for their usage. Here, thermal conductivity as the main parameter characterising the heat transfer represents crucial factor that influences the thermal comfort of buildings.

Besides thermal comfort, indoor air quality is another important issue that should be considered in buildings. It is affected by heating, ventilation, air conditioning, construction quality, applied materials and building operation. These aspects should be always considered during design, construction and building maintenance stages [2]. Hence, the studied brick blocks must obey also the conditions that ensure the indoor air quality. From this point of view, the water vapour transport from the interior through the building envelopes represents important parameter.

For determination of thermal conductivity, several steady state methods can be used, whereas reference standard methods [3] are often considered. As for the practical experimental setups, the guarded hot plate arrangement is the most frequently used [4].

Since achieving the steady-state conditions within the thermal conductivity measurement is a time consuming and relatively expensive procedure, application of the transient methods of

thermal conductivity measurement is also popular. Among them, the hot wire method is the most frequently applied technique [3]. In materials research, there are also applied devices working on dynamic measurement principle. Here, the measurement is based on the analysis of the temperature response of the analysed material to heat flow impulses [5].

A number of advanced apparatuses for thermal conductivity measurement is available on the current market, which are based on the above principles. However, most of the laboratory methods allow determination of thermal conductivity on small samples or for a plate sample configuration with small specimen thickness. This makes possible measurement of homogeneous materials with no large-scale discontinuities only. Therefore, in this paper a steady state technique based on semi-scale experiment principle is applied for the assessment of thermal conductivity of entire brick blocks.

2. Semi-scale experiment and its evaluation

Within the semi-scale experiment, the climatic chamber system originally developed for investigation of hygrothermal performance of building materials and structures was used. Details on the system were published in [6] and [7]. It consists of two commercial climatic chambers for simulation of relative humidity and temperature, and a specially developed connecting tunnel for placing the studied samples. The tunnel is vapour proof and thermally insulated from the environment.

The measured brick block was provided with necessary temperature and heat flux sensors and thermally insulated in the tunnel between the climatic chambers (Figure 1).



Figure 1: Sample arrangement and insulation.

In the climatic chambers, specific different temperatures were set, nominally temperature difference 15/30°C and 30% relative humidity were used. In this way, the 1-D heat transport through the studied brick block was simulated until the steady state heat flux was obtained.

Calculation of thermal conductivity λ (W/m/K) was done using the measured data of heat fluxes according to the equation

$$q = -\lambda \cdot gradT,\tag{1}$$

where q (W/m²) is the heat flux and T (K) temperature.

For temperature and relative humidity monitoring, commercially produced combined minisensors by Ahlborn, Germany, were employed. The accuracy was as follows: the capacitive relative humidity sensors were applicable in the 5-98% relative humidity range with a \pm 2% accuracy, the resistance thermometers had an accuracy of \pm 0.4°C in the temperature range from -20°C to 0°C, and \pm 0.1°C in the temperature range from 0°C to 70°C. The heat flux through the studied brick was monitored by the heat flux plate sensors Ahlborn FQA020C of a cylindrical shape having diameter 33 mm, which were fixed on both front sides of the brick block. The accuracy of these sensors was \pm 5% of the measured value. In both climatic chambers were additional sensors for temperature and relative humidity control.

3. Studied cavity bricks

Three types of brick blocks with internal cavities produced by company Heluz Brick Industry, Czech Republic, were analysed in the paper. Two types of bricks had the cavities filled by mineral wool (Figure 2) or polystyrene balls, whereas the third brick had air cavities only, without additional filling thermal insulation. The bricks were designed for application in thermal insulation masonry having a width of 500 mm.



Figure 2: Brick block with cavities filled by mineral wool.

Scheme of the brick block with air cavities is given in Figure 3 [8]. The basic physical properties of the brick body are given in Table 1.

	e 11 2000 prope	The of erren cong
Bulk	Matrix	Total open porosity
density	density	(-)
(kg/m ³)	(kg/m ³)	
1 389	2 830	0.51

Table 1: Basic properties of brick body



Figure 3: Scheme of the studied brick block with air cavities.

4. Result and discussion

Figures 4 – 6 present the typical results of temperature and relative humidity monitoring in both climatic chambers.



Figure 4: Typical temperature course in the cold chamber.



Figure 5: Typical temperature course in the warm chamber.



Figure 6: Typical relative humidity course in the climatic chamber system.

Apparently, the temperature steady state conditions were maintained well during all the course of the experiments; only small fluctuations could be observed. The variations of relative humidity were also relatively low, based on the particular chamber performance. Therefore, the basic conditions for a proper evaluation of the performed experiments were met.

The temperature profiles given in Figure 7 gave information on thermal performance of particular studied bricks. We can see relatively low differences between temperature data obtained for different types of cavities filling what demonstrates the achievement of steady state conditions within the studied samples.

Similar data are presented in Figure 8. Here, typical temperature variations measured for air cavities brick block are given at specific times of experiment.



Figure 7: Temperature profiles in the studied brick blocks.



Figure 8: Temperature profiles measured for air cavities brick block at specific time intervals of experiment.

The typical heat fluxes measured for specific researched materials are given in Figures 9 - 11. For one cavity brick, four heat flux sensors were used. The data were averaged over a time interval of several days and then used for thermal conductivity calculation.



Figure 9: Typical heat flux measured at air-cavities brick surface.



Figure 10: Typical heat flux measured at mineral-wool filled cavities brick surface.



Figure 11: Typical heat flux measured at polystyrene-balls filled cavities brick surface.

Thermal conductivity of tested cavity brick blocks calculated from the measured heat flux data is summarized in Table 2.

Air cavities	Polystyrene balls filled cavities	Mineral wool filled cavities
0.123	0.091	0.075

Table 2: Thermal conductivity of brick blocks (W/mK)

Looking at the thermal conductivity data one can see improvement of bricks thermal resistance by application of thermal insulation materials as cavity fillers. From the quantitative point of view, the best thermal insulation performance exhibited brick block with mineral-wool filled cavities. Its thermal conductivity was about 40% lower compared to brick block with air cavities. Also the application of polystyrene filler led to the significant improvement of thermal insulation properties. In Table 3, there are presented thermal transmittances of particular brick blocks calculated from measured thermal conductivity values. According to the Czech standard ČSN 730540-3, all the measured materials are up to this standard that specifies required value of thermal transmittance for external wall equal to 0.3 W/m²K and recommended value equal to 0.25 W/m²K.

Table 3: Thermal transmittances of brick blocks (W/m²K)

Air cavities	Polystyrene balls filled cavities	Mineral wool filled cavities
0.246	0.182	0.150

5. Conclusions

A steady-state experiment in semi-scale conditions was applied for the determination of the effective thermal conductivity of a brick blocks with internal cavities. The result of the experiment presents valuable information for the building practice, where the measured thermal conductivities can find use at the thermal design of brick masonry. The obtained data pointed to the effectiveness of tested cavity fillers for improvement of thermal resistance of single-layer brick building envelopes.

In future work, the designed experimental setup can be used for the determination of thermal conductivity of other types of building materials with large-scale inhomogeneities, as well as for testing the thermal performance of critical segments of building structures.

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Reusing of ceramic waste powder in concrete production

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Abstract: The possible applicability of waste ceramic powder as partial Portland cement replacement in concrete production is studied in the paper. For the finely ground ceramic powder, measurement of chemical composition was done using XRF and XRD analysis. The particle size distribution of ceramics was accessed on laser diffraction principle. The ceramic powder was used in cement based pastes composition in weight cement placements of 8, 16, 24, 32, and 40%. For the tested pastes, basic physical and mechanical properties were accessed. The hydration process of particular studied mixtures was monitored by calorimetry and XRD analysis.

Keywords: waste ceramic powder, hydration heat, XRF and XRD analysis, mechanical and physical properties, cement replacement

1. Introduction

Concrete is beyond question the most important building material. Its worldwide annual production is presently more than 10 billion tons [1], and one can expect rapid increase of its manufacturing in the near future especially in the developing countries whose economies rapidly grow. Instead of the concrete excellent mechanical and durability properties that are the main reasons for its usage, its production brings several harmful secondary effects to the human society and environment. First, there is the vast amount of natural resources needed to produce such high amount of building material each year. Cement manufacturing implies extraction of 1.7 tonnes of rock to produce 1 tonne of clinker. Then, production of one tonne of cement for concrete industry generates 0.55 tonnes of chemical CO2 and requires an additional 0.39 tonnes of CO2 in fuel emissions, accounting for a total of 0.94 tonnes of CO2 [2]. Worldwide, the cement industry alone is estimated to be responsible for about 7% of all CO₂ generated [3], [4]. Additionally, the cement production requires high energy impact, which is approximately 850 kcal per kg of clinker [5]. To ensure the future competitiveness of concrete as a building material, it is essential to improve the sustainability of concrete structures [6]. Therefore the replacement of cement in concrete by any type of industrial waste represents a tremendous saving of energy and has important environmental benefits. Besides, it will also have a major effect on decreasing concrete costs, since the cost of cement represents more than 45% of the concrete cost [5].

The history of building technology shows that reuse and recycling of wastes have been practised for several millennia. For example, brick, mortar and ceramic tile have long been recycled as rubble fillings for solid masonry walls [7]. Here, emplecton masonry represents typical representative of waste reuse in the past. With current moves towards performance-related specifications of materials it has become practicable as well as desirable to utilise materials classified as industrial wastes or secondary raw materials. Industrial wastes have

continued to increase due to the continued demands of resource use by humans. For these wastes to be incorporated into concrete, they can either be used as partial cement replacement or as aggregate in concrete in order to maintain the sustainability of this construction material [8]. For concretes which are developed, produced and used in an environmentally friendly manner the term "Green Concrete" [9] is commonly used. Several by-products have already found their utilization in concrete production. Incorporations of coal combustion fly ash (FA), ground granulated blast furnace slag (GBFS), and silica fume (SF), are typical examples of reuse of industrial by products in concrete manufacturing. In the last few decades, FA has been one of the most widely used supplementary cementitious materials in concrete. FA is an important pozzolan, which has a number of advantages compared with regular Portland cement. It has lower heat of hydration compared to cement and moreover concrete produced with FA can have better strength and durability than concrete produced without it [10]. Concrete with incorporated FA has lower permeability to chloride ions and other aggressive environments [11], [12] it has higher freeze-thaw resistance and abrasion resistance [13], [14]. The recommended FA replacement level for high strength concrete is usually 15-25% [15], but considerable research has been conducted on the properties of concrete using higher proportions of fly ash, such as 30-70% of the total binder [16], [17]. Also GBPS improves positively properties of concrete, especially its mechanical properties and rheology of fresh mixtures even in high volume applications [18], [19]. Here, the frost, sulfate attack and chloride resistivity were also improved using the GBFS as cement replacement [20]. SF as a by-product of induction arc furnaces of production silicon metal or ferrosilicon alloys has long been used as a mineral admixture to produce high-strength and high-performance concrete. Owing to the pozzolan reaction between calcium hydroxide and SF, compared with Portland cement, the hydration of concrete containing SF is much more complex resulting in high quality concrete with high durability and mechanical resistivity [21]. In addition, due to energy-saving and resource-conservation, both ecological and economical benefit can be achieved using SF blended Portland cement [22], [23].

However, instead of these generally accepted materials for concrete production, also other type of wastes must be characterized and studied for their reuse in concrete mix design. In this paper, problem of possible usage of waste ceramics in concrete production is addressed. In Europe, the amount of wastes in the different production stages of the ceramic industry reaches some 3–7% of its global production meaning millions of tons of calcined-clays per year that are just land filled [1]. Because of the worldwide ceramic industry, high amount of waste ceramics is produced annually over the world. Although the reutilization of ceramic wastes has been practiced, the amount of wastes reused in that way is still negligible and most of the ceramic waste is landfilled. Because of increasing restrictions on landfills, the cost of deposition will increase, and the ceramic industry will have to find ways for reusing their wastes. Application of waste ceramics in concrete production would lead to reduction of cost, energy savings, promoting ecological balance and conservation of natural resources [24]. As stated above, one of the effective ways to reduce the environmental impact of cement and concrete industry is to use mineral additions, as a partial cement replacement. An increasing interest in the pozzolanic admixture of calcined clays with calcium hydrate has been shown recently by researchers dealing with the production of new hydraulic materials for the masonry and concrete industry [25]. A portion of ceramic products formed within the burning illite-group minerals and having suitable fineness can become active pozzolana [26], [27], [28]. Therefore, waste ceramic materials may have a potential to become a cheaper but almost equivalent alternative to metakaolin as supplementary binder in mortar and concrete [29].

Waste ceramics can find use also as fine aggregate in concrete mix design. About successful application of ceramic aggregate reported for example Torkittikul and Chaipanich [9] who found that the compressive strength of Portland cement mortar and concrete containing ceramic waste aggregate (CWA) was higher than that of the control mix due to a rougher surface of the CWA particles enhancing strength. Recently, Medina et al. [30] substituted 20 and 25 wt.% recycled sanitary ware for gravel in coarse aggregate and studied whether the structural recycled concrete is resistance to water. They found that the slightly higher porosity in the recycled concrete does not translate into greater permeability. These new recycled concretes, which prove to be as durable as the conventional material, will therefore perform well throughout their design service life.

In summary, the waste ceramic has great potential to be used as partial cement replacement or natural aggregate substitution, taking into account the ceramics chemical composition, thermal treatment and fineness. It is clear that the calcination of the raw ceramic clay have an effect on the hydraulicity and pozzolanic action. The loss of combined water due to thermal treatments causes a demolition of the crystalline network of the clay constituents and the silica and alumina remain in a disordered but, invery case, unstable amorphous state. Therefore, waste ceramic as artificial pozzolan usually assume pozzolanic character [25]. Because of the complexity of the studied problem and specific production technologies of particular ceramic factories, detail research on possible use of waste ceramics in concrete industry must be carried out. On this account, fine ceramic powder coming from Czech brick factory is studied as possible partial Portland cement replacement in concrete mix design.

2. Studied materials, sampling

Ceramic powder is a by-product of brick company HELUZ Brick Industry that is the second biggest producer and deliverer of the brick material on the Czech market. The ceramic powder is produced within the cutting highly precise cavity brick blocks that are manufactured in width from 250 mm to 500 mm. The company has production facilities in three locations, whereas the ceramic waste used in this work is coming from production plant Hevlín, located in South Moravia. See Figure 1 for Hevlín brick factory.



Figure 1: Hevlín production plant.

Chemical and mineralogical composition of ceramic powder was measured by X-Ray Fluorescence (XRF) analysis and X-Ray Diffraction (XRD) analysis and the results are given in Tables 1, 2. X-Ray diffractograms were measured with a diffractometer PANalytical X'PertPRO (PANalytical, Almelo, Holand) with Bragg-Brentano configuration (CoK radiation source, voltage of 4 kV at mA) and fast linear detector X'Celerator. Measured diffractograms were analysed by computer code HighScorePlus 3.0.5 (PANalytical Almelo, Holand, 20012) comparing with database data from JCPDS PDF2, Sets 1-54, International Centre for Diffraction Data, Newton Square, Pennsylvania, U.S.A., 2004. Weight substituion of particular crystallic phase was done using Rietveld method using code DiffracPlus Topas 4.2. Here, models obtained from database ICSD, release 2012/1 (FIZ Karlsruhe, SRN) a American Mineralogist Crystal Structure Database were used. In Table 1, only main oxides are given. Looking at the data presented in Table 2, we can see high amount of amorphous particles what is good for prospective pozzolanic activity of the researched ceramics. X-Ray diffractogram of ceramic powder is given in Figure 2. Blain specific surface of the ceramics was 665 m²/kg.

Substance	Amount [mass
	%]
SiO ₂	51.3
Al ₂ O ₃	20.0
Fe ₂ O ₃	6.0
CaO	11.5
MgO	4.5
SO ₃	1.0
Na ₂ O	1.3
K ₂ O	3.2
TiO ₂	0.8
Σ	99.6

Table 1: Chemical composition of waste ceramic powder

Table 2: Mineralogical composition accessed by XRD analysis (in wt.%)

Amorphous fraction		46.7
Silica	51.3	23.6
	Albite	6.5
Feldspar	Microcline	7.2
	Orthoclase	2.8
	Biotite	0.9
Mica	(Black mica)	
	Muscovite	2.6
Other	Akermanite	4.4
silica		
	Hedenbergite	3.8
Hematite		1.4
Σ		99.9




Figure 2: X-Ray diffractogram of waste ceramics.

For the cement-based mix preparation with incorporated ceramic waste powder, Ordinary Portland cement (CEM I 42.5 R) was used. Blain specifica surface of the cement was 330 m²/kg. Ceramic powder was applied at 8, 16, 24, 32 and 40% replacement by weight of cement, while water/binder ratio was 0.5 and was kept constant for all the studied pastes. With a view to evaluation of ceramic powder effect of pastes performance, also a reference mixture with Portland cement as the only binder was studied as well. For the mechanical parameters assessment, the fresh mixtures were cast into the moulds having dimension of 40/40/160 mm. Basic physical properties were measured on cubes of side 50 mm. After 24 hours, the samples were unmoulded and left in water. The measurement of mechanical properties and basic physical properties was done after 28 days of wet curing. For XRD analysis and hydration heat measurement, specific samples were cast and tested at chosen time of curing.

3. Experimental methods

3.1 Measurement of basic material properties

For the researched pastes, measurements of bulk density, matrix density, and total open porosity were performed. The experiments were done on 5 cubic samples of side 50 mm. The relative expanded uncertainty of applied testing method is expected 5%. Bulk density was determined from the measurement of sample sizes (using digital length meter) and its dry mass. The matrix density was accessed by helium pycnometry using Pycnomatic ATC (Thermo Scientific). The accuracy of the gas volume measurement using this device is $\pm 0.01\%$ from the measured value, whereas the accuracy of used analytical balances is ± 0.0001 g. On the basis of bulk density and matrix density measurements, the total open porosity was calculated [31], [32].

3.2 Particle size distribution and specific surface area

For the dry ceramic powder, particle size distribution was measured. The measurement was done on laser diffraction principle using the device Analysette 22 Micro Tec plus, FRITSCH. It allows measurement of particle size in the range 0.08 – 2000 m. The measuring range is obtained with the utilization of two lasers with different wave length. A green laser is used for the small particle range whereas an IR-laser is utilized for the measurement of larger particles. Due to the movability of the measuring cell, the captured angle area of the diffracted respectively scattered laser light can be matched to the requirements of the individual sample. With larger particles a large distance between measuring cell and detector is chosen, so the here appearing small diffraction angles can still be detected very well. With fine and very fine powders, optimal conditions for the measurement of large scattering angles are obtained by selecting a small distance between measurement cell and detector distance. This results in high resolution and sensitivity. Instead of pure ceramic powder, also the data for cement and studied ceramics/cement mixtures were accessed.

3.3 XRD analysis of hydration process and measurement of hydration heat

At early age, the heat released was measured during 48 h using an isothermal conduction calorimeter operating at 20 °C. Thereafter, the assemblage of hydration products was studied at 2, 7 and 28 days by XRD analysis. Ground paste samples were measured on diffractometer (Philips X'Pert PW 3710) equipped with a graphite monochromator using CuK α radiation and operating at 40 kV and 20 mA. Scanning was made from 5 to 60 20 a scan speed of 2°/min and a sampling interval of 0.02°.

3.4 Mechanical properties

The bending strength of hardened mortars that were stored 28 days in water was determined using the procedure described in the standard ČSN EN 12390-5 [33]. For the measurement, prismatic samples having dimensions of 160/40/40 mm were used. The compressive strength was measured according to the standard ČSN EN 12390-3 [34] on the portions of prisms broken in bending test; the loading area was 40 x 40 mm. Young's modulus was measured by the dynamic pulse ultrasonic method [35]. In the experiments, the samples were prisms having dimensions of 160/40/40 mm, and the measurements were performed in longitudinal direction. The ultrasonic pulse method is based on the measurement of travel time of ultrasonic wave

launched from the device and passing through the material. For the measurement we used device DIO 562 working on the frequency of 50 KHz. The relationship between dynamic Young's modulus *E* [MPa], wave velocity v [m/s] and material's bulk density ρ_b [kg/m³] is given as

$$E = \rho_b v^2 \tag{2}$$

3. Results and discussion

The measured particles size distribution is given in Figures 3, 4. Here, also the data for cement are given. Cement CEM I 42.5R exhibited maximal volume of particles at size of 26 m, whereas the waste ceramic powder has maximum at particle size of 34 m. This finding is good in general, since the observed slightly worse fineness of ceramics compared cement is for intended application as partial cement replacement quite sufficient.



Figure 3: Particle size distribution of studied materials – distribution curve.



Figure 4: Particle size distribution of studied materials – cumulative curve.

Basic physical properties of the pastes investigated are presented in Table 3. Here, the presented results exhibited average value from 5 measurements. Mechanical properties are summarized in Table 4.

Replacement level [mass %]	Bulk density	Matrix density	Total open porosity
	[kg/m³]	[kg/m³]	[-]
0	1 570	2 165	27.5
8	1 513	2 255	32.9
16	1 549	2 269	31.7
24	1 480	2 334	36.6
32	1 436	2 310	37.8
40	1 511	2 379	36.5

Table 3: Basic physical properties of researched pastes

Replacement	Compressiv e strength	Bending strength	Young's modulus
lever [mass 76]	[MPa]	[MPa]	[GPa]
0	52.9	9.8	21.6
8	45.7	8.7	22.9
16	49.3	8.7	20.9
24	41.8	8.4	19.5
32	36.7	7.2	18.7
40	36.4	7.7	18.3

Table 4: Mechanical properties of researched pastes

A clear relation between porosity and mechanical properties may be seen from the data of Tables 3 and 4. Typically, as high porosity was measured, as low compressive and bending strength. From the quantitative point of view, the best performance from the materials containing waste ceramics exhibited paste with 16 wt% of cement replacement. The compressive strength of this material decreased of less than 7% compared to reference mixture, the similar behaviour was found in the case of Young's modulus, compressive strength decreased of about 11%. Generally, all the tested mixtures exhibited sufficient mechanical strength even in the case of high level of cement replacement.

Results of calorimetric measurement are given in Figure 5.



Figure 5: Results of calorimetric measurement.

We can see that with higher cement replacement systematically decreased the heat released during the hydration process. However, all the studied materials exhibited the maximum of the hydration heat at approximately 14 hours. Therefore, the kinetics of the hydration reaction of all studied materials looks similar. From the practical point of view, limitation of hydration heat development is highly beneficial for casting and production of high volume structures, where the high hydration heat usually brings number of technological problems.

X-ray diffractograms are for 2, 7, and 28 days of samples hardening graphed in Figures 6, 7, 8. From the measured data, there is obvious rate of hydration and pozzolan reaction. At two days, there is a clear peak of portlandite,. At seven days of hardening, the portlandite peak significantly decreased because of pozzolanic reaction with ceramics compounds.



Figure 6: X-ray diffractogram for 2 days of hardening.



Figure 7: X-ray diffractogram for 7 days of hardening.



Figure 8: X-ray diffractogram for 28 days of hardening.

4. Conclusions

Analysis of reuse of waste ceramic powder as partial Portland cement replacement was done in the paper. Application of waste ceramics in 16 wt% cement replacement gave sufficient mechanical properties of the cement-based paste what is highly promising for future research that will be focused on design and development of new types of cement-based composites with incorporated ceramics waste powder. However, also other tested mixtures with applied ceramics gave sufficient properties and this knowledge can be used for instance in the production of low strength concretes and composites. Low hydration heat of ceramic powder/cement mixtures will allow casting and manufacturing of high volume structures without any advanced technological solution.

From the economical and environmental point of view are the obtained results highly perspective, since the possible reuse of the ceramic waste will bring savings in natural resources, decrease of CO₂ production and reduction of landfilling.

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Preliminary analysis of possible use of dried sewage sludge in cement based composites mix design

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Abstract: The effect of application of municipal sewage sludge as partial Portland cement replacement in cement based composites mix design is studied. Thermally pretreated dry sewage sludge produced in municipal wastewater treatment plant in Patras, Greece, was used. The researched materials were prepared by replacement of 10, 20, 30, 40, and 60% of cement in cement pastes composition by sludge, whereas the water/binder ratio was kept constant for all the studied mixtures. For the thermally untreated sludge, measurements of chemical composition, powder density, matrix density, grain size analysis, TGA, XRD, and SEM analyses were performed. Then, the sewage sludge was thermally treated for two hours at 700°C and milled. For this treated material, XRF and particle size distribution analyses were performed as well as measurement of basic physical properties. For the tested cement pastes with incorporated sewage sludge, mechanical and basic physical properties are measured in order to access the effect of partial Portland cement replacement by wastewater sewage sludge on materials performance.

Keywords: municipal sewage sludge, thermal treatment, partial cement replacement, concrete and cement composites production

1. Introduction

Large quantity of sewage sludge coming from municipal wastewater treatment plants is produced annually over the world. This feature is not characteristic for the developed countries only, but also in the developing countries, due to the rapid progress in urbanization and industrialization, there can be observed high increase in production of sewage sludge [1]. Sludge is an unavoidable byproduct of primary, secondary, and advanced wastewater treatment processes. It is typically generated at a rate of 70–90 g/person equivalent per day [2], [3].

Probably the most common method of sewage sludge disposal represents landfilling, in some countries also disposal into the ocean [4], [5]. In addition, sewage sludge is applied also in the agriculture, for example as organic fertilizer and for soil management [6], [7], [8]. Here, one must take into account that sludge contains pollutants and unstable pathogen content leading to potential health and environmental hazards, and its landfilling represents substantial risk of soil contamination and degradation of the urban landscape [9], [10]. The properties of sewage sludge depends on the quality of wastewater, for example industrial wastewaters containing heavy metals yield a contaminated sewage sludge, which, in most of the cases, cannot be used in agriculture. Therefore, taking into account the sustainability principles, it is becoming

impossible to landfill the sludge and alternatives of its recycling and reuse must be found and researched in the near future.

An alternative way of sludge disposal is incineration that achieves significant reduction of material volume. After incineration at high temperatures, the main components in sewage ash include SiO₂, CaO, Al₂O₃ and Fe₂O₃, whereas these compounds are also common in ordinary Portland cement [11], [12], [13]. Incineration makes possible to obtain incinerator sewage sludge ash with pozzolan properties. Therefore, the sewage sludge ash (SSA) retained in filters and sewage sludge bottom ash (SSBA) can be used in production of building materials. For example SSA has found application in mortars [14], concrete mixtures [15], [16], as light-weight aggregate in light-weight concretes [17], [18], asphalt paving mixtures [19]. In case of cementing matrix, possible heavy metals content in sludge is stabilized and solidified, whereas the metals are converted into highly insoluble salts, which do not leach at appreciable rates. The sewage sludge found application also in brick manufacture [20], [21], [22]. The prospective benefits of using sludge or SSA as the brick or tile additive include immobilizing heavy metals in the fired matrix, oxidizing organic matter and destroying any pathogens during the firing process, and reducing the frost damage based on the results of several full or bench scale studies [23].

For the energy and environment conservation by virtue of decreasing energy necessary for cement production, reducing CO₂ emission, reducing the natural resources for cement and reducing the load of disposal sites, the reuse of wastewater sewage sludge looks like beneficial solution. In view of the aforementioned disposal problems and the increasing cost of construction materials, experimental laboratory studies have been conducted in this paper in order to evaluate the use potential of sewage sludge as a cement replacement material.

3. Sewage sludge

The sludge used in this study was obtained from a municipal wastewater treatment plant located in the suburbs of Patras, Greece. The sewage sludge was collected after being concentrated by centrifugation in the plant. Since sludge contains between 1 and 4 wt% of solid materials, and the rest is water, it was dried in laboratory oven at 70°C for one week. For the untreated sludge, chemical composition was measured by X-Ray Fluorescence (XRF) analysis. Here, the measurements of powder density, matrix density, and sieve analysis were also performed. Powder density reached value of 0.712 g/cm³, matrix density measured by helium pycnometry was 1.62 g/cm³. Chemical composition of raw sludge is given in Table 1. Here, only main oxides are given.

Several EU member states have chosen to establish limit values for heavy metals in sludge and for maximum annual average loads of heavy metals. In fact, the United Kingdom is the only member state in which regulations on the use of sludge do not specify limit values for heavy metals in sludge, but define limit values for quantities of metals introduced in the soil. Results of XRF analysis of heavy metals content are presented in Table 2. These data were compared with limits set in Greece that are mostly similar to the limit values set by the European Directive 86/278/EEC [24]. We can see that amount of all researched heavy metals was typically lower compared to the limits for sludge. Hence, the studied sludge can be classified as non-hazardous waste. However, the leaching test must be recommended before the practical use of research sludge in practical applications.

Substance	Amount [mass
	%]
SiO ₂	18.02
Al ₂ O ₃	6.36
Fe ₂ O ₃	8.67
CaO	26.71
MgO	5.29
SO ₃	10.61
ZnO	0.35
Na2O	3.56
K ₂ O	1.54
TiO ₂	1.29
P ₂ O ₅	12.64
Cl	4.23
Σ	97.73

Table 1: Chemical composition of raw sludge

Morphology of the raw sludge material was studied using Scanning Electron Microschopy (SEM) analysis and is presented in Figures 1 -3. For the measurement, device LEO- SUPRA 35VP with a Bruker EDX microanalysis probe was used. The morphology of the crystalline material showed that it consisted of prismatic and plate-like crystallites, whereas their size being less than 200 nm. Both the prismatic and plate like morphology is typical for struvite crystallites.

Substance	Concentration	Limits for sludge
	[mg/kg solid]	[mg/kg solid]
Ag	<1	
As	<1	15
Cd	<1	20 - 40
Со	<1	
Cu	80	1 000
Mn	60	
Мо	<1	
Pb	<1	750
Rb	5	
Se	<1	
Sr	10	
Zn	80	2 500
Ti	100	
Ni	<1	300
Cr	<1	500
Hg	<1	16

Table 2: XRF analysis of heavy metals content



Figure 1: SEM morphology of raw sewage sludge.



Figure 2: SEM morphology of raw sewage sludge.



Figure 3: SEM morphology of raw sewage sludge.

Granulometric analysis was done by standard sieve method using normalized sieves. Here, two samples were analysed in order to see the inhomogeneity of the raw material (see Figure 4).



Figure 4: Grading analysis of raw sludge.

Within the mineralogical analysis of sludge, the dried material was powdered to a fine powder in an agate mortar with pestle and X-Ray diffractograms were obtained with a Siemens D-5000 X-Ray diffractometer with Bragg-Brentano configuration (CuKa Source, λ =1.5405). Phase identification was performed with Crystallographica Search Match (Version 2.0.3.1, Oxford Cryosystems). The characteristic reflections corresponding to struvite were identified. There is a possibility of the presence of calcite or SiO_2 (reflection at 29.8 20°), what corresponds with the data of XRF analysis. Despite the fact that amorphous material was also present (organic matter), it seems that the crystallinity of the material was higher than anticipated.

With a view to extract organic compounds from the raw sludge, thermal treatment was performed at 700°C for 2 hours and the burnt material was milled in order to achieve similar fineness as cement. The XRF chemical composition after thermal treatment is given in Table 3. We can see that the amount of SiO₂ increased of about 5 wt% compared to the reference material, and the amount of Al₂O₃ increased of about 2 wt%. Powder density of the thermally treated sludge increased compared to the raw material, as well as matrix density. Here, the powder density reached the value of 0.959 g/m³, and matrix density 2.549 g/cm³.

Substance	Amount [mass %]
SiO ₂	22.85
Al ₂ O ₃	8.89
Fe ₂ O ₃	5.89
CaO	25.41
MgO	5.36
SO ₃	6.73
ZnO	0.26
Na ₂ O	4.83
K ₂ O	1.47
TiO ₂	1.00
P_2O_5	12.54
Cl	4.14
Σ	99 37

Table 3: Chemical composition of thermally treated sludge



Figure 5: X-Ray diffraction pattern of raw dried sludge. Standards and the respective ICCD numbers are shown at the lower part of the graph.

The effect of thermal treatment on sludge changes was in detail observed by Thermo Gravimetric Analysis (TGA). TGA was performed using apparatus Labsys Evo (Setaram) that allows simultaneous TGA-DTA and TGA-DSC measurements. The operating temperature range of this device is 25 – 1600°C. In our experiments, the studied samples were exposed to linear heating of 5 °C/min up to 1000°C under argon atmosphere. Here TGA and DTG curves are presented (Figure 6), whereas DTG data were obtained from derivation of TGA curve.



Figure 6: TGA (black) and DTG (gray) curves, heating rate 5°C/min.

Looking at the measured data, one can identify 4 remarkable weight drops. At temperature intervals 25 – 70°C and 70 – 150°C physically bounded water is evaporated and struvite (NH₄MgPO₄·6H₂O) decomposition took place [25]. Significant weight loss was observed for temperature range 200 – 500°C. This finding we assign to the decomposition of organic compounds with long carbonyl chain [26]. The decomposition at 300–350°C was found to be the decomposition of hemicellulose [27], cellulose [28], micro algae [29], leather [30], and some aliphatic amino acid [31]. The decomposition at higher temperature, 400–500°C is believed to be the decomposition of the complex and/or aromatic structures in various materials such as API separator sludge, bituminous coal, plastics, etc. [32]. At temperature interval 650 – 750°C, decomposition of calcite took place.

For the milled, thermally treated sludge, particle size distribution was measured. The measurement was done on laser diffraction principle using the device Analysette 22 Micro Tec plus. This device uses red laser for measurement of bigger particles and green laser for finer particles, whereas the laser analyser allows measurement of grain size up to 2 mm. The measured particles size distribution is given in Figure 7. Here, also the data for cement are given. Cement CEM I 42.5R exhibited maximal volume of particles at size of 26 m, whereas the sludge has maximum at particle size of 56 m. Although the sludge grinding gave slightly worse fineness, its particle size distribution is for intended application as partial cement replacement quite sufficient.



Figure 7: Particle size distribution of studied materials.

4. Composites studied and testing methods

Ordinary Portland cement (CEM I 42.5 R) was used in the experimental study. Thermally treated sludge was applied at 10, 20, 30, and 60% replacement by weight of cement, while water/binder ratio was 0.4 and was kept constant for all the studied pastes. For the sake of comparison, also a reference mixture with Portland cement as the only binder was studied as well. The fresh mixtures were cast into the moulds having dimension of 40/40/160 mm. After 24 hours, the samples were unmoulded and left in water. The measurement of mechanical properties and basic physical properties was done after 28 days of wet curing. Among the basic properties, the bulk density, matrix density, and total open porosity were measured on gravimetric principle combined with helium pycknometry. The bending strength of cured composites was determined using the procedure described in ČSN EN 12390-5 [33]. The compressive strength was measured according to the ČSN EN 12390-3 of fragments of samples from bending strength testing [34].

5. Results and discussion

Basic physical properties of the composites investigated are presented in Table 4. Mechanical properties are summarized in Table 5. Here, the presented results exhibited average value from 5 measurements.

A clear correlation between porosity and mechanical properties may be seen from the data of Table 5. Typically, as high porosity was measured, as low compressive and bending strength. Similar strong relationship between the compressive strength and pore structure of a cementitious material has been reported in the literature [35]. Rö ler and Odler [35] used four expressions to find the relationship between the porosity and compressive strength of porous solids; furthermore, they concluded that the linear relation (Hasselmann model) fit their results best. Similar results published also C.-L. Yen et al. that characterize eco-cement paste produced from waste sludge [11]. From the quantitative point of view, the highest porosity exhibited material with 60 wt.% cement replacement by sludge. This material exhibited lowest

mechanical resistivity. However, it still remains almost 50% of its compressive strength compared to the reference mixture, what is in general positive finding. From the point of view of production of high quality concrete, the 10 and 20 wt% replacement of cement looks like possible solution.

Replacement	Bulk density	Matrix density	Total open porosity
level [IIIass 76]	[kg/m³]	[kg/m ³]	[-]
0	1 686	2 197	0.233
10	1 597	2 168	0.264
20	1 560	2 199	0.291
30	1 494	2 203	0.321
60	1 350	2 211	0.390

Table 4: Basic physical properties of researched pastes

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1 able 5: Mechanical	properties	of researchea	pastes

Replacement	Compressive strength	Bending strength
level [mass 76]	[MPa]	[MPa]
0	61.82	10.64
10	58.99	7.77
20	48.92	7.60
30	44.94	7.33
60	28.66	5.92

6. Conclusions

Analysis of possible use of dried sewage sludge coming from wastewater treatment plant in Patras, Greece, in cement based composites mix design, was done in the paper. The sludge investigated exhibited proper chemical composition for its incorporation into the cement matrix. The material has also very low content of heavy metals that were for all investigated metals identified in concentration under required limits of toxicity.

The thermal treatment of pre-dried sewage sludge and its grinding gave material that can be applied as partial cement replacement in cement based composites and concrete design. For production of high quality and strength concrete, 10 and 20 wt% replacement of cement can be recommended. However, also higher content of sludge in materials composition can be used, especially for production of materials with lower demands on mechanical resistivity and durability.

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Effect of extraction methods on performance of Municipal Solid Waste Incineration fly ashes as admixtures in cementitious Composites

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Abstract: Probably the most perspective field of utilization of Municipal Solid Waste Incineration (MSWI) ashes consists in its application as admixtures in cementitious building materials. Bottom ash, due to its wide particle size distribution, is usually intended to be used as aggregate while fly ash can feature pozzolanic properties and thus be used as Supplementary cementitious material (SCM). Unfortunately the raw MSWI fly ash may contain – in dependence on applied Air Pollution Control (APC) technology – also environmentally hazardous components (POPs, heavy metals) and salts (chlorides, sulfates). The utilization of fly ash as admixture in fact solves the problems related to POPs and heavy metals due to stabilization and solidification effect but chlorides and sulfates represent problem due to its negative effect on hydration of Portland cement and reactive components of fly ash itself. Hence content of chlorides and sulfates in fly ash has to be reduced in order of its successful application as SCM. The technologically simplest way represents extraction of fly ash and filtration of solid residuum. The present paper deals with influence of various water-based extraction solutions on chemical composition of MSWI fly ash and its applicability as SCM. The washing of untreated MSWI fly ash by water was found to be an effective way to improve its properties being important for utilization of the ash as partial Portland cement substitution.

Keywords: Municipal Solid Waste Incineration ashes, Supplementary cementitious material, Ash treatment

1. Introduction

The aim of present study was to find a simple and efficient treatment method for MSWI fly ash generated at a modern incinerator equipped with electrostatic precipitator and catalytic PCDD/PCDF removal system. The treated ash is intended to be used as cement substitute in cementitious materials. Generally the MSWI residues treatment methods can be sorted to three fundamental groups [1]: separation processes, solidification/stabilization (s/s) and thermal processes. One of the widely used s/s process is mixing of MSWI residues (particularly fly ash) with Portland cement which ensures stabilization of heavy metals by its alkaline environment and limited rate of possible transport of heavy metals and other pollutants out of the solidification and a practical application – properly treated MSWI fly ash can be an admixture bringing an added value to cementitious composites similarly as coal fly ash does. Both waterbased separation processes and thermal treatment can be used in order to improve MSWI fly ash behavior in cementitious systems. Each MSW incinerator (and its Air Pollution Control system) is to certain extent a unique technology and thus – together with influence of varying waste composition – composition of generated ashes is different from place to place [1], [2].

Nevertheless the presence of large amounts of sulfates and chlorides is typical for all MSWI fly ashes and represents the main problem complicating the utilization of these ashes as admixtures in cementitious materials; the salts in untreated fly ash cause the increase of setting time and reduction of strength [3]. Bertolini [4] performed water washing of MSWI FA till chlorides concentration reached 0.4 % but the ash was not able to replace Portland cement effectively. Gao [5] proposed to use water washed MSWI fly ash as maximum 20% cement replacement. Aubert [6] studied the fly ash treated by Revasol process (water washing, phosphation, calcination) and found it to behave as inert aggregate. The goal of the present study was to find a simple washing procedure for MSWI fly ash intended to be used as cement substitute.

2. Experimental

The object of study was untreated MSWI fly ash (UFA) collected in boiler and electrostatic precipitator of a MSWI facility in Czech Republic. The fly ash was subjected to following treatment procedures: water washing performed in agitated vessel with L/S (liquid/solid) ratio equal to 5 (signed W 5); water washing L/S = 10 (W 10); washing by 0.1% solution of (NH₄)3PO₄ with L/S = 10 (WP 10). The washing time was 20 minutes and then the solid residuum was filtered out and dried. All above listed treated ashes were used as cement substitute as whole or just separated fine particles (passed through 125 µm sieve) were applied – such ashes are signed by F (fines). For comparison also fly ash washed directly in incinerator by acid solution coming from flue gas water absorption was involved (FAWI). The ability of ashes to replace Portland cement was tested by means of mortars where individual ashes were used as 10 and 20% cement (CEM I 42.5 R) substitution (Table 1). The mortars were casted to 160x40x40 mm standard prisms and stored at 100 % RH for 28 days and then compressive strength was measured. The compressive strength was measured according to ČSN EN 12390-3, whereas the loading sample area was 40x40 mm. The most promising treated ash was studied in detail. Chemical composition of ashes was examined by XRF (Thermo, ARL 9400 XP). Particle size distribution was measured conventionally as grading curve by means of standard sieves. Simultaneous TG/DSC thermal analysis was performed by Setaram calorimeter Labsys Evo under inert atmosphere from ambient temperature to 1000 °C. Morphology of ashes was observed by Scanning Electron Microscopy (Jeol JSM 6510); nature of selected species was revealed by EDS analysis. The influence of ashes on initial and final setting time of standard consistency cement paste was evaluated by Vicat apparatus (EN 196-3). The resistance to freezing/thawing cycles was quantified by means of compressive strength measurement after the proper number of cycles (between -20 and 20 °C).

Substance	CEMI 42.5 R	Fly ash	Sand	w/b
	kg/m ³			
Control	460	-	1 380	0.52
10%	414	46	1 380	0.52
20%	368	92	1 380	0.52
30%	322	138	1 380	0.52

Table 1: Composition of mortars with treated fly ashes.



Figure 1: X-Ray diffractogram of waste ceramics.

3. Results and discussion

The influence of treated ashes on mortars compressive strength was applied as screening criterion in order to select the most promising way of UFA ash treatment (Figure 1). As it was analysed elsewhere [7] neither UFA or FAWI ash (treated in incinerator in order to leach out heavy metals) can not be used as adequate Portland cement substitute. The separation of fine portions (< 125 μ m) of these two ashes did not provide a better results; the strength of mortars was even lower compared to whole ashes. Hence three ways of washing treatment were performed and the washed ashes were again tested as whole and fines only. The best performance featured material W 10 F, i.e. fine portion of fly ash washed in water (L/S = 10). This material was found to be able to substitute 10% of Portland cement and also 20% substitution provided only moderate reduction of strength compared to control.



Figure 2: Compressive strength of mortars where Portland cement was substituted by various treated ashes in level of 10 and 20 %.

The main change in chemical composition of UFA and W 10 F ash (Table 2) consists in reduction of soluble chlorides (NaCl, KCl) content. The total solubility of UFA in water (1:10) was 13.6 % (Table 3). The concentration of other components correspondingly increased in W 10 F – insoluble aluminosilicates, species containing Fe₂O₃ and phosphates. The chemical analysis indicated also higher content of sulfates in W 10 F. Thermal analysis (Figure 2) revealed somewhat higher content of gypsum in W 10 F (signal from beginning to 200 °C) what corresponds with higher concentration of SO₃ and CaO as well. The DSC peak at 600 °C belongs to a soluble compound. Peaks around 900 °C are due to calcite (CaCO₃) thermal decomposition.

Substance	UFA	W 10 F
SiO ₂	15.6	19.1
Al ₂ O ₃	9.2	11.6
Fe ₂ O ₃	2.6	3.0
CaO	23.9	29.9
MgO	1.8	2.5
Na ₂ O	9.4	2.9
K ₂ O	6.6	2.7
Cl	11.2	2.8
SO ₃	11.5	14.1
P ₂ O ₅	1.3	`1.7
ZnO	3.7	5.5

Table 2: Chemical composition of untreated fly ash UFA and treated W 10 F (in wt. %).

Table 3: Chemical composition of untreated fly ash UFA and treated W 10 F (in wt. %).

	Solubility [1:10]	рН	
	%		
UFA	13.6	11.4	
W 10 F	3.0	11.4	

The influence of water washing on the nature of fly ash was documented by means of SEM microscopy. The untreated UFA ash (Figure 3) is constituted of agglomerated fine species which were entrained by flue gas leaving the fire and of salt particles condensing gradually from flue gas due to its decreasing temperature. The water washing procedure caused (besides the soluble salts dissolution) also recrystallization of some salts to larger particles and the silicate spherical particles were "washed" from salt cover and became more distinct (Figure 4). The composition of several particles was checked by EDS; calcium silicate and various other silicates (with Al₂O₃, Na₂O, CaO and MgO) were found.



Figure 3: SEM image of untreated sample UFA.



Figure 4: SEM image of W 10 F ash.

The influence of washing on particle size distribution was evaluated by grading analysis (Figure 5). The simple washing (W 10) caused just minor particles refinement compared to UFA. The separation of particles larger than 125 μ m (W 10 F) obviously moved the particle size

distribution and this ash is – concerning its fineness – close to requirements on pozzolanic fly ash intended to be used as concrete admixture (EN 450).



Figure 5: Grading curves of ashes.

The untreated fly ash UFA had highly negative influence on initial and final setting time of fresh cement paste (Figure 6). The final setting time of paste with UFA was above 10 hours. The washing and fines separation improved significantly these parameters; the paste with cement substitution up to 30% got stiff faster than the control paste. The reason was the reduction of chlorides content by washing from 11.2 to 2.8 %.



Figure 6: Influence of FA and FAWI on initial and final setting time.

The effect of W 10 F treated ash on mortar's durability was evaluated by means of subjecting mortars to freezing/thawing cycles and determination of its compressive strength (Figure 7).



Figure 7: Influence of FA and FAWI on initial and final setting time.

The compressive strength of unloaded mortars with 20 and 30% cement substitution was lower than strength of Control and W 10 F 10 mortar (10% substitution). The compressive strength of individual mortars did not change much up to 75 freezing cycles. Nevertheless difference between Control and W 10 F 10 on one side and W 10 F 20 and 30 on the other side was observed after 100 cycles. The latter materials preserved its compressive strength also after 100 freezing cycles while strength of Control was reduced.

4. Conclusions

The washing of untreated MSWI fly ash by water (L/S = 10) was found to be an effective way to improve its properties being important for utilization of the ash as partial Portland cement substitution. The washing has to be accompanied by excluding of particles larger than 125 μ m. The remaining fine portion W 10 F was distinguished mainly by significant reduction of chlorides content compared to untreated ash. It resulted to shorter setting time of cement paste. The particle size distribution of W 10 F was close to requirements on pozzolanic fly ash. The treated ash improved the resistance of mortar to freezing water action. The explanation lies probably in modification of porous system of mortars. Unfortunately the proposed treatment was not able to reduce high sulfate content what means a long-time durability risk.

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Experimental analysis of physical properties of different types of flours

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Abstract: In this paper, basic physical properties of different types of flours, namely four types of smooth flour, whole-meal flour, semolina, and graham flour are studied at first. The characterization of flours is done using FTIR spectroscopy. Powder density and matrix density are measured using the gravimetric method and helium pycnometry. Particle size distribution is measured on laser diffraction principle. For the studied materials, measurement of thermo physical properties is done using the impulse method; the measurement is performed in dependence on moisture content. Among the hygric properties, sorption and desorption isotherms are measured using dynamic water vapor sorption device. The electrical properties, specific resistance, capacity, and electrical impedance is determined in the dependence on different frequency with LCR meter. The results presented in this paper can find utilization in food industry. They can be applied for instance for the adjustments of the drying rate, for the calculations of the economical drying time and for the determination of energetic balances of drying processes.

Keywords: smooth flour, whole-meal flour, semi-meal flour, physical properties, food industry

1. Introduction

Cereals are from the national economy point of view the most significant agriculture product. They are basic and essential part of human and livestock nutrition as well as important commodity for food industry. For the bread production, wheat and rye are used. Instead of these main mill materials, barley, oat, corn, rice, buckwheat, pea and soya are also processed [1]. Each wheat flour mill has characteristic mill flows that produce unique flours and coproducts [2]. Fundamental knowledge of physical characteristics and their variability, such as true density, bulk density, moisture and particle size distribution, are helpful to ensure proper handling, storage, and drying, as well as help to determine the overall design of the processing system. Accurate description of particle size in a raw material is essential to feed formulation and manufacturing because it affects the feed's processing conditions and nutritional efficiency. The importance of particle size in feed manufacturing was reported by several researchers [2], [3]. Cereal products are subjected to various types of thermal processes such as cooking, cooling, drying, extrusion, and freezing before consumption. Therefore, thermal parameters are important physical properties of food and agricultural materials, and are critical parameters in the engineering design of any thermal processes [4], [5], [6]. The hydration properties of cereals can be considered as critical factors that partly control how cereals may be stored and processed, as well as the quality of processed products. Mechanisms involved in the hydration of flours particles, kinetics of dough formation, and their effects on the properties of doughs and their products constitute an important field of investigation [7], [8]. Dielectric properties of materials are those electrical characteristics of poorly conducting materials that determine their interaction with electric fields. These properties are important factors for agricultural and food products in any processes involving radio-frequency (RF) or microwave dielectric heating [9].

As stated above, characterization of agricultural materials is the first step in food products formulation and development. Basic understanding of the properties of these materials can lead to improvement of both the products quality and ease of product development. On this account, chosen physical properties of four types of smooth flour, whole-meal flour, semolina, and graham flour are studied in the presented paper.

2. Materials and sampling

Four different types of smooth flour (wheat flours 00Extra, T650, 1050, and wheat - rye RL90), whole-meal wheat flour (WM), wheat semolina (S), and wheat graham flour (GF) are studied in this paper. All the researched materials are products of Vitaflóra, mill Kolárovo, Slovakia, and were studied in the dry state, initial state from the market and after exposure to 75% of relative humidity at 20 and 40°C. The drying was performed for 90 minutes at 130°C according to ISO 712.

3. Experimental methods

3.1 Measurement of basic material properties

Firstly, FTIR spectroscopy with ATD diamond crystal was used for the characterization of flours. Among the basic properties, powder density (sprinkled and compacted), and matrix density were measured on gravimetric principle combined with helium pycnometry. Initial moisture content was calculated from the mass before and after drying for 90 minutes at 130°C.

3.2 Particle size distribution

The measurement was done on laser diffraction principle using the device Analysette 22 Micro Tec plus, FRITSCH. It allows measurement of particle size in the range 0.08 – 2000 m. The measuring range is obtained with the utilization of two lasers with different wave length. A green laser is used for the small particle range whereas an IR-laser is utilized for the measurement of larger particles. Due to the movability of the measuring cell, the captured angle area of the diffracted respectively scattered laser light can be matched to the requirements of the individual sample. With larger particles a large distance between measuring cell and detector is chosen, so the here appearing small diffraction angles can still be detected very well. With fine and very fine powders, optimal conditions for the measurement of large scattering angles are obtained by selecting a small distance between measurement cell and detector distance. This results in high resolution and sensitivity.

3.3 Measurement of thermal properties

The thermal conductivity and volumetric heat capacity as the main parameters of heat transport and storage were determined using the commercial device ISOMET 104 (Applied Precision, Ltd.), which is equipped with needle probe for soft materials. The measurement is based on the 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. The experiments were done in dependence of different moisture content of researched materials. The dependence of specific heat capacity on moisture content was calculated by the mixing rule given in Eq. (1), where c is the specific heat capacity of moist material [J/kgK], c₀ the specific heat capacity of dry material [J/kgK], c_w the specific heat capacity of water (4181.8 J/m³K), and u is the gravimetric moisture content [kg/kg].

$$c = (c_0 + c_w u) / (1 + u) \tag{1}$$

3.5 Sorption and desorption isotherms

Sorption and desorption isotherms characterize the moisture storage in the hygroscopic moisture range. They express the dependence of the moisture content in the material on the relative humidity of environment. The sorption and desorption isotherms are mostly measured by traditional desiccator method, which is very time consuming method. On this account, dynamic vapor sorption device DVS- Advantage II (Surface Measurement System Ltd.) was used for the measurement of sorption and desorption isotherms in the presented work.

3.6 Electrical properties

Specific resistance, electrical capacity, and impedance were determined in the dependence on different frequency by the use of LCR meter Good Will 821. From the measured data, the values of relative permittivity in the dependence on different frequencies were calculated and results were graphically processed.

4. Results and discussion

Basic physical properties of studied flours are given in Table 1. Figure 1 shows infrared spectra of tested flours, the detail represents bands of amide I and amide II of wheat gluten. We can see that spectra are identical for all measured samples.

Flour	Powder Density (sprinkled)	Powder Density (compacted)	Matrix Density	Initial Moisture Content
		[kg/m ³]		mass [%]
00Extra	715	766	1466	9.6
T650	617	798	1463	10.5
1050	523	774	1474	8.4
RL90	527	611	1475	8.6
WM	781	798	1469	8.0
S	758	774	1454	9.1
GF	698	781	1456	8.3

Table 1: Basic physical properties of studied flours



Figure 1: Infrared spectra of flours.

Results of particle size distribution measurement are given in Figures 2 and 3. We can see that the smooth flours, except T650, have nearly the same particle size distribution. They are milled in comparison with semolina finer, whereas the most roughly milled is graham flour.



Figure 2: Particle size distribution of studied flours – cumulative curve.



Figure 3: Particle size distribution of studied flours – distribution curve.

The obtained results of the dependence of thermal properties on moisture content are given in Figs. 4 and 5. Looking at the results from the quantitative point of view, the highest value of thermal conductivity for dry materials exhibited the whole-meal flours. The results achieved for other materials were very similar each other.



Figure 4: Thermal conductivity of measured flours.



Figure 5: Specific heat capacity of measured flours.

The values of specific heat capacity of studied flours were very different. The lowest specific capacity shows smooth flour noted as 1050, the highest one exhibited smooth flour noted as 00Extra. The effect of moisture on the specific heat capacity was quite remarkable, which is a consequence of the high specific heat capacity of water.



Figure 6: Sorption and desorption isotherms of smooth flours.
Sorption and desorption isotherms measured by dynamic vapor sorption device are graphed in Figures 6 and 7. All the studied materials exhibited high hysteresis, what must be considered within their technological processing. We can observe that smooth flours have possibility to bind quantitatively more water molecules in the comparison with whole-meal flours. While whole-meal flours show broad hysteretic loop contrary to smooth flours.



Figure 7: Sorption and desorption isotherms of whole-meal flours.

Figure 8 shows the dependence of relative permittivity on frequency of tested flour samples.



Figure 8: Dependence of relative permittivity on frequency.

In Figure 8, the relative permittivity curves were approximated by regression equation (2)

$$\varepsilon_r = \varepsilon_{r0} \left(\frac{f}{f_o} \right)^k \tag{2}$$

where *f* [kHz] is frequency, $f_0 = 1$ kHz, r [-] relative permittivity and 0 [-] reference relative permittivity. The relative permittivity of wheat whole-meal flour (WM) was in the range of 2.4-5, while other flours exhibited higher values of relative permittivity, 3.7-7.1. The reason is the structure of flours; bigger particles of flour lead to higher amount of air gaps and reduce touch surfaces between particles. Table 2 represents coefficients of regression equation \mathcal{E}_{r0} and coefficients of determination R².

Flour	\mathcal{E}_{r0}	k	R ²
00Extra, T650 (♠)	5.9745	-0.0857	0.8922
1050 ()	6.1506	-0.0913	0.9217
WM (▲)	3.6683	-0.0996	0.6220
RL90 (*)	5.3260	-0.0579	0.8922
S (■)	6.3550	-0.0920	0.8831
GF (●)	5.3895	-0.0775	0.8886

Table 2: Values of regression equation and determination coefficients

The obtained results of relative permittivity represent valuable information for materials processing, since in the case of powdery and porous materials the mixing equations can be used for calculation of moisture content of material on the basis of measured relative permittivity values. For example Leschnik [11] proposed mixing relationship with the help of water and dry powdery porous material mixture as

$$w = \frac{\sqrt{\varepsilon'} - \sqrt{\varepsilon'_m}}{\sqrt{\varepsilon'_w} - \sqrt{\varepsilon'_m}},$$
(3)

where w is relative moisture content, ε' is final permittivity, ε_w' is permittivity of free water, ε_m' is permittivity of dry material. Thakur and Holmes [12] determined relative permittivity of powdery materials on the basis of particles relative permittivity and particles volume proportion in sample. This model should be used also for samples created as mixture of flour particles and water.

5. Conclusions

The results presented in this paper can find utilization in food industry in such processes where knowledge of physical properties of studied flours is indispensable. They can be applied for instance for the adjustments of drying rate, for the calculations of the economical drying time and for the determination of energetic balances of the drying processes.

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Thermal study of building materials from the church in Pác

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Abstract: Historical bricks from the church in Pác (near Trnava, Slovakia) were investigated by the differential thermal analysis (DTA), thermogravimetry (TG), thermodilatometry (TD), and evolved gas thermal analysis (EGA). We studied fired bricks from Romanesque, Gothic and Baroque parts of the church. It was found that the bricks contained dehydroxylated illitic clay, calcite, feldspar and quartz. Dehydroxylation was fully completed and no rehydroxylation was observed. It could be explained with a protection of the investigated Baroque bricks by a plaster on the masonry. The Romanesque and Gothic pavement bricks were protected from an influence of the atmospheric moisture and CO2 with the Baroque pavement. The surface layers of the bricks absorbed CO2 which escapes at low temperatures (150 – 600 °C). The decomposition of calcite was also observed. Between the temperatures 600 - 800 °C we observed an intensive mass loss (confirmed by the TG), an endothermic minimum in the DTA, an intensive escape of CO2 (found from the EGA), and the contraction of the sample (found from the TD). We estimated the firing temperature to lie between 650 °C and 700 °C.

Keywords: historical brick, thermal analysis, firing

1 Introduction

Historical ceramics has been studied by different thermal analyses for past 40 years. The results of the measurements are most often used for the determination of the firing temperature. In archeology the firing temperature is considered to be the property of the technological level of ancient society [1, 2]. Materials research based on the use of thermal analyses has been applied widely for investigation of historical building ceramics. Most of them exploit TG (thermogravimetry), DTA (differential thermal analysis) and TD (thermodilatometry) [1, 2, 3, 4, 5, 6]. Moreover, we used the evolved gas thermal analysis (EGA). Investigation of the historical building ceramic objects, such as bricks and tiles, helps us to understand the knowledge and skills used to produce them [7].

Thermoanalytical investigations of historical ceramics give useful information about the technology of ceramic manufacturing. The comparison of the results provides the scientists of archeology information needed to draw the corresponding conclusions and arguments [1]. The research of the historical ceramics is also useful for the renovation of historical buildings where damaged material could be replaced with a new one. It could be suitable to assess the durability of applied materials in a specific building [8, 9].

Properties of building ceramics depend on the raw materials and on technological steps, which include forming of the wet ceramic mass, drying of the ceramic pieces and their firing. The dehydroxylation of kaolinite or illite and especially decomposition of calcite play a crucial role in a thermoanalytical investigation of the historical ceramics. The curves of TG, DTA and TD of

the main ceramic constituents (kaolinite, illite, quartz, calcite and feldspar) are known and can be compared to thermoanalytical curves of historical ceramics [4].

The degree of conversion characterizes the phase transformation in clay during firing. If it is measured for a small sample, it depends on the temperature and time, $\alpha = f(T,t)$. In the case of a large ceramic body (e.g. brick), the situation is more complex. Experiments on large cylindrical green samples (Ø80 mm) showed a clear dependence of the degree of conversion on the location of the sample taken for the TG from the cylinder. Consequently, we have $\alpha = f(T,t,r)$, where *r* is the distance of the sample from the axis of rotation [10].

How bricks were fired in the past? Green bricks were prepared from clay and water, then dried and inserted into a field kiln. The process of firing took about 5 - 7 days – it depended on the size of the kiln and the number of bricks in it. The temperature was not measured at that time. Wood was used for heating, so the temperature limit was 700 – 750 °C. We suppose that a similar method was used in the firing of the historical bricks from the church in Pác.

Our study is focused on the analysis of the bricks from Romanesque, Gothic and Baroque parts of the church in Pác. Our aim was to find their approximate original composition and the maximum firing temperature using DTA, TG, TD and EGA.

2. Experimental

The samples were fired bricks taken from a Romanesque, Gothic and Baroque parts of the church located in Pác (near Trnava, Slovakia). We supposed they were made from the raw material excavated from a close local clay pit. The church was originally built in the Romanesque style in 13th, then was partially rebuilt in the Gothic style in 15th century and enlarged in the Baroque style in 1764.

The DTA and TG were performed on the modernized analyzer Derivatograph (Hungary) [11] using a compact sample of $10 \times 10 \times 20$ mm cut from the surface layer of the brick and the heating rate 5 °C/min. A reference compact sample of the same size was made from a pressed powder Al₂O₃. The TD was done on the alumina horizontal dilatometer with the sample $10 \times 10 \times 40$ mm at the heating rate 5 °C/min.

The EGA was done on a powder sample (50 mg) using Setaram LabSys 1600 thermoanalyzer coupled with Pfeiffer Omnistar Mass Spectrometer at a rate 5°C/min up to 1050 °C, in the atmosphere 79 % of Ar + 21 % of O₂ with flow rate of 60 ml/min.

3. Results and discussion

The results of the DTA are illustrated in Figure 1. The first endothermic minimum on the DTA curves, which belongs to the interval of 20 - 300 °C, is typical for porous building clay ceramics, which does not contain glassy phase. The minimum is related to the liberation of the physically bounded water. Consequently, we may assume that the bricks were fired at the temperatures lower than 900 - 1000 °C. An endothermic peak on the DTA curves between 700 and 840 °C is typical for the decomposition of calcite [12], which shows that the maximum firing temperature was in an interval 700 – 840 °C. In the all DTA curves, a small endothermic peak is visible at ~574 °C that confirms a presence of quartz. We observe a typical DTA curve for illite above 800 °C [12, 13, 14] so we conclude that the bricks contained illite as a plastic constituent.



Figure 1: DTA of Romanesque brick (light grey), Gothic bricks (dark grey), and Baroque brick (black).

The results of TG analysis are presented in Figure 2. The first step (20 - 300 °C) belongs to the liberation of the physically bounded water. The second step has a sharp termination at ~840 °C which is a typical feature of the TG curve of calcite decomposition. Between these steps, we observe a gradual decrease of the sample mass. It can be ascribed to the liberation of the absorbed water and constituent water after rehydroxylation. The next source of this mass decrease could be an escape of CO₂ of the organic origin or absorbed CO₂.



Figure 2: TG of Romanesque brick (light grey), Gothic bricks (dark grey), and Baroque brick (black).

The results of TD are depicted in Figure 3. The TD shows the presence of the significant amount of quartz, which corresponds to the small DTA endothermic peak at ~574 °C. The TD measurement also reflects the decomposition of calcite as contraction of the samples.



Figure 3: TD of Romanesque brick (light grey), Gothic bricks (dark grey), and Baroque brick (black).

The mass spectrometry analysis (EGA) gave results showed in Table 1, 2, and 3. In the all cases, we notice a presence of CO_2 that escaped from the samples at low temperatures. When the bricks were taken from the church masonry and the pavement, they were placed in outdoor place. These bricks were used for our analyses after 2 years. It explains a presence of CO_2 in the EGA results at temperatures lower than 600 °C. The origin of this CO_2 is in its absorption and in a burning of the simple organisms (lichen, algae) from the brick surface. The DTA about 300 °C shows a firing of the organic material in the brick. The main amount of CO_2 escapes from the sample between 600 °C and 760 °C that is connected to decomposition of calcite. It is also evident from the TG and DTA results. The presence of the water was confirmed only as physically bounded water. No dehydroxylation as a consequence of the investigated Baroque bricks by a plaster on the masonry. The Romanesque pavement bricks were covered by the Gothic pavement bricks and these bricks were covered by the Baroque pavement. So the all investigated bricks, Romanesque, Gothic and Baroque, were protected from an influence of the atmospheric moisture and CO_2 .

Gas	$\Delta t / ^{\circ}\mathrm{C}$	$T_{peak1} / °C$	$T_{peak2} / °C$	T _{peak3} / °C	$T_{peak4} / °C$
CO_2	50 - 773	106	230	315	750
CO	680 - 760	732	-	-	-
H ₂ O	50 - 225	95	-	-	-

Table 1: The results of EGA for the Romanesque brick

Table 2: The results of EGA for the Gothic brick

gas	$\Delta t / ^{\circ}\mathrm{C}$	T _{peak1} / °C	$T_{peak2} / °C$
CO ₂	175 - 760	290	700
CO	630 - 760	732	-
H ₂ O	30 - 150	95	260-400

gas	$\Delta t / ^{\circ}\mathrm{C}$	T _{peak1} / °C	T _{peak2} / °C	T _{peak3} / °C
CO ₂	160 - 763	225	325	731
СО	651 - 751	732	-	-
H ₂ O	53 - 150	95	-	-

Table 3: The results of EGA for the Baroque brick

According to our results, the original clay, which served for manufacturing of the bricks, was a mixture of illite, quartz and calcite as main minerals. Feldspar is also present in brick clays, so we can assume it as a part of the clay used in the investigated bricks. The feldspar was confirmed in the investigated Romanesque brick by XRD in [15].

4. Conclusions

The historical bricks from the three architectonic periods (Romanesque, Gothic and Baroque) were investigated by the help of thermal analyses DTA, TG, TD and EGA. We found out the original raw clay consisted of illite, quartz, calcite, and feldspar. Dehydroxylation was fully completed and no rehydroxylation was observed.

Since the brick for the analyses were stored in the open air, the surface layers absorbed CO_2 and was also covered with simple organisms. This explains results of the mass spectrometry related to CO_2 at low temperatures. The decomposition of calcite was observed through EGA, TG, TD and DTA and is a direct evidence of the firing temperature which could not be higher than 750 °C.

Taking into account a technical capability of the simple field kilns, we estimated the firing temperature to lie between 650 $^{\circ}$ C and 700 $^{\circ}$ C.

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Thermo-mechanical properties of Be-chalcogenides from density functional theory

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Abstract: Beryllium chalcogenides (BeS, BeSe and BeTe) belonging to group II–VI compound semiconductor family crystallize in the four-fold coordinated zinc-blende structure. They having higher bonding energy and hardness, exhibit unusual electronic, mechanical, thermal, optical properties. These exclusive properties create them very useful for various technological applications including laser diodes, high efficiency photo-detectors. In this paper we have applied the full-potential linear-augmented plane wave (FP-LAPW) method within the frame work of the density functional theory (DFT) for structural, electronic, and thermal properties calculations for Be chalcogenides. For the purpose of exchangecorrelation energy (Exc) determination in Kohn–Sham calculation, the standard generilsed gradient approximation (GGA) formalism has been utilized. Murnaghan's equation of state (EOS) has been used for volume optimization by minimizing the total energy with respect to the unit cell volume. With the knowledge of electronic density of states (DOS) and band structures, mechanical and thermal properties of Be chalcogenides have been estimated.

Keywords: Be-Chalcogenides, electronic properties, mechanical properties, DFT, FP-LAPW.

1. Introduction

The II-VI group beryllium chalcogenides (BeS, BeSe and BeTe) crystallizing in the four-fold coordinated zinc-blende structure have received a considerable attention in the recent years [1–5]. A typical characteristic of these ompounds is that the mass and ionic radius of Be atom is much smaller than the chalcogen (S, Se, and Te) atoms. Unlike other II–VI compounds having partially ionic bond, Be-chalcogenides exhibit a high degree of covalent bond [5-8]. Due to higher bonding energy, Be-chalcogenides exhibit unusual electronic properties characterized by a large band gap and offer potential device applications in technology of green semiconductors lasers. These materials are very promising for the possibility of the application in low dimensional (quantum-well and superlattices) device production [5,8]. The optoelectronic devices based on beryllium chalcogenides have advantage over other II–VI semiconductors due to their high p type doping concentrations and long lifetimes. Incorporation of transition metal ions into beryllium chalcogenide crystal creates dilute magnetic semiconductors commonly used in spintronics applications [9]. Theoretically the structural, electronic, optical and dynamical properties for Zn chalcogenides have also been extensively studied [10-14]. An ab initio approach method was followed for the investigation of the lattice dynamics for ZnO [10]. Linear muffin tin orbital model [11] has been used for analysing the electronic structures of ZnX

compounds. The empirical pseudopotential method has been exploited for the determination of band structure and of the density of states for ZnX binary compound [13].

Comparatively less research has been devoted on the electronic properties study of Bechalcogenides. The objective of this paper is to employ the full-potential linear-augmented plane wave (FP-LAPW) method within the application of the density functional theory (DFT) for the determination of structural, electronic, and optical properties of BeX materials. The exchange-correlation energy (E_{xc}) determination in Kohn–Sham calculation is performed with the standard generilsed gradient approximation (GGA) method. Murnaghan's equation of state (EOS) has been considered for volume optimization by minimizing the total energy with respect to the unit cell volume. Based on electronic propertie determination, elasic, mechanical and thermal properties have been elucidated.

2. Computational details

The structural, electronic and thermal properties of the compound BeX have been studied in the frame work of the full potential linearized augmented plane wave plus local orbitals (FP-LAPW+*l*o) with Wien2k code [15]. The generalized gradient approximation (GGA) parameterized by Perdew, Burke and Ernzerhof (PBE) [16] has been used. By optimization of the total energy with respect to the unit cell volume using Murnaghan's equation of state [17], equilibrium structural parameters are estimated. The calculations were performed with *R*_{MTkmax} = 7, to accomplish energy eigen value convergence, where R_{MT} is the smallest radius of the muffin-tin (MT) spheres and k_{max} is the maximum value of the wave vector. The maximum value of the angular momentum l_{max} is taken as 10 for the wave function expansion inside the atomic spheres. The k-points used in the computational work are taken as 10×10×10 Monkhorst–Pack model [18] in the irreducible Brillouin zone (BZ) of the zinc-blende structure. The iteration procedure is continued with total energy and charge convergence to 0.0001Ry and 0.001e, respectively.

3. Structural properties

The zinc-blende BeX has a cubic symmetry as shown in Figure 1. The Zn atom is located at the origin and the X atom is located at (1/4, 1/4, 1/4). The space group is *F*-43*M*. The ground-state properties are obtained by minimization of the total energy with respect to the unit-cell volume by fitting the results to the Murnaghan's equation of state [17]:

$$E_{T}(V) = \left[\frac{B_{0}V}{B_{0}'} \frac{(V_{0}/V)^{B_{0}'}}{B_{0}'-1} + 1\right] + E_{0} - \frac{V_{o}B_{o}}{B_{0}'-1}$$
(1)

The minimization of the total energy with unit-cell volume for BeS as example is shown in Figure 2.



Figure 1: Crystal structure of the zinc-blende BeX (X = S, Se, Te). The violet ball is Be atom and the yellow ball is X atom.



Figure 2: Configuration energy with unit-cell volume variation for BeS. For simulation Murnaghan's equation of state has been considered. Different fitting parameters are shown in Table 1

In Table 1, the results of bulk modulus B₀, its pressure derivative B₀' and the equilibrium lattice constant a_0 , for the ZB structure of the binary BeX at zero pressure is presented. The calculated lattice parameters are compared with other reported theoretical and experimental data. For BeS, BeSe and BeTe, the energy minimisation occurs for $a_0 = 4.882$, 5.183, and 5.668 Å, which agree well with the experimental values of 4.87, 5.14, and 5.62 Å. Hence well defined stucrural properties is sufficient for further study of electronic and optical properties.

Compound	nd Fitting Parameters Lattice Constant a ₀ (Å)		A)		
	B ₀ (GPa)	Bo'	Present	Othe	ers
				Exp.	Theo.
BeS	92.99	3.82	4.882	4.87 [22]	4.82 [19]
					4.75 [20]
					4.83 [21]
BeSe	75.62	3.78	5.183	5.14 [23]	5.12 [19]
					5.04 [20]
					5.13 [21]
BeTe	56.36	3.74	5.668	5.62 [24]	5.57 [19]
					5.53 [20]
					5.58 [21]

*Table 1: Calculated bulk modulus B*₀ (*GPa*), its pressure derivative B₀' and lattice constant a₀ (Å) of BeX along with the available theoretical and experimental data.

4. Electronic properties

Figure 3 shows the calculated band structure at equilibrium for BeS as a prototype since the band profiles are quit similar for all three compounds, with little differentiation. The overall

bands are in quite good agreement with other theoretical results [19-24]. The valence band maximum and conduction band minimum in each member of BeX appears at different q point.



Figure 3: (Left): Electron energy band of BeS. (Right): electron density of states of BeS.

Thus the energy gap is indirect between the top of the valence band and the bottom of conduction band. The X atom p bands shift up in energy starting from the sulphide to the telluride as a consequence of increase of the lattice parameters, as observed in other II-VI compounds too [25]. The fact that the calculated band gap is underestimated in comparison with experiments results is due to the simple form of GGA which is not able to account the quasiparticle self energy [26]. In Figure 3, the density of states (DOS) for BeS is shown. DOS in the other member of BeX is very similar with small difference. The density of states (DOS) for BeS is shown in Figure 3. It is similar to that of BeSe and BeTe. The first structure in the total DOS is centered at around -12.52 eV, -12.47 eV and -11.38 eV for BeS, BeSe and BeTe respectively. This structure arises from the chalcogen s states and it corresponds to the lowest lying band with the dispersion in the region around the Γ point in the Brillouin zone. The next structures appear between -5 eV and 0 eV for all BeX compounds. It is an attribute of Be d states and chalcogen p states and occupy largest number of states. These structures spread widely in the energy range of -5 eV and zero contributing to the upper Valence Band. Above the Fermi level the DOS originate mainly from the s and p states of Be partially mixed with little of chalcogen d states. Band width of valence band as determined from the width of the peaks in DOS dispersion below Fermi level equal to 14.02 eV, 14.34 eV, 12.73 eV for BeS, BeSe and BeTe, respectively. The results showing valence band width minimum for BeTe, clearly indicate that the wave function for BeTe is more localized than that for BeS.

5. Mechanical properties

The elastic constants of BeX compounds have been determined using the method developed by Charpin incorporated in WIEN2k code [27]. By applying appropriate lattice distortions in a cubic lattice, three independent elastic constants C₁₁, C₁₂, and C₄₄ are determined. The following three equations are considered for the calculation of the elastic constants.

$$B_{0} = (C_{11} + 2C_{12})/3 , \Delta E_{rhomb} = \frac{1}{6} (C_{11} + 2C_{12} + 4C_{44}) V_{0} \delta^{2} , \Delta E_{tetra} = 6 (C_{11} - C_{12}) V_{0} \delta^{2}$$
(2)

Second equation is related to the variation of strain energy (ΔE_{rhomb}) versus volume-conserving rhombohedral strain (δ). Third equation is related to the variation of strain energy (ΔE_{tetra}) versus volume conserving tetragonal strain (δ). The calculated elastic constants for the zincblende BeX are displayed in Table 2.

	C11	C12	C44
BeS	111	71	69
BeSe	91	63	59
ВеТе	79	48	41

Table 2: Calculated values of elastic constants (Cij in GPa) at equilibrium for BeX compound.

The elastic constants decrease in magnitude with increase in lattice dimension from S to Te, due to cohesive energy decreases with the nearest-neighbour distance [28]. The mechanical stability in a cubic crystal requires the elastic constants satisfying the conditions as, $C_{11} - C_{12} > 0$, $C_{44} > 0$, $C_{11} + 2C_{12} > 0$, $C_{12} < B_0 < C_{11}$. The elastic constants in Table 2 obey these conditions. Values of elastic constants are used to determine Bulk modulus, B₀, Young's modulus, Y, Isotropic shear modulus, G and Poisson ratio, σ based on the following explicit expressions [29, 30],

$$G = (G_{\rm V} + G_{\rm R})/2, \ G_{\rm V} = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \ G_{\rm R} = \frac{5C_{44}(C_{11} - C_{12})}{4C_{44} + 3(C_{11} - C_{12})}$$
(3)

The expressions for the Young's modulus and Poisson's ratio are given by

$$Y = \frac{9GB}{G+3B}, \ \sigma = \frac{3B-2G}{6B+2G}$$
(4)

Table 3 displays the calculated values of elastic modulus. Ductility of the material can be chara-

	G	Bo/G	C12-C44	Y	σ
	(GPa)		(GPa)	(GPa)	
BeS	41.88662	2.15152	1.88	108.8	0.299
BeSe	33.41409	2.16735	3.93	86.88	0.3
ВеТе	27.48057	2.19755	7.57	71.584	0.302

Table 3: Calculated values of elastic modulus (in GPa) for BeX

cterised by B₀/G ratio [31]. The B₀/G ratio for all BeX are greater than 1.75 (see Table 3) which reveals that the compounds are ductile in nature. The highest value of B₀/G ratio is 2.19 for BeTe representing it most ductile among all the BeX compounds. With increase in positive Cauchy pressure (C₁₂–C₄₄), compound is likely to form metallic bond. As depicted in Tabe 3, the BeTe has a highest positive Cauchy pressure resulting strong metallic bonding (ductility) in it as compared to other compounds. The highest value of Y occurs for BeS demonstrating to be more covalent in nature as compare to other BeX compounds. Value of Poisson's ratio (σ), as a measure of compressibility for BeX compounds are between 0.29 and 0.30 which predict that all the compounds are compressible.

6. Calculation of Debye temperature

The Debye temperature (θ_D) is considered as a fundamental parameter for many physical properties of solids, such as specific heat, elastic constants, and melting temperature. Once we have determined the elastic constants, we may obtain the Debye temperature (θ_D) by using the average sound velocity V_m by the equation, [32, 33]

$$\theta_D = \frac{h}{k_B} \left[\frac{3n}{4\pi} \left(\frac{N_A \rho}{M} \right) \right]^{1/3} V_m , \qquad (5)$$

Where N_A is Avogadro's number, M is the molecular weight, ρ is the density. The average sound velocity (V_m) is given by [29, 31]

$$\mathbf{v}_{\mathrm{m}} = \left[\frac{1}{3}\left(\frac{2}{\mathbf{v}_{\mathrm{t}}^{3}} + \frac{1}{\mathbf{v}_{\mathrm{l}}^{3}}\right)\right]^{-1/3}, \ \mathbf{v}_{\mathrm{t}} = \sqrt{\frac{C_{44} - \frac{1}{5}\left(2C_{44} + C_{12} - C_{11}\right)}{\rho}}, \ \mathbf{v}_{\mathrm{t}} = \sqrt{\frac{C_{11} + \frac{2}{5}\left(2C_{44} + C_{12} - C_{11}\right)}{\rho}}$$
(6)

Where v_t and v_l are the transverse and longitudinal sound velocities. We have calculated density, the sound velocities and Debye temperatures by using the calculated elastic constants, which are given in Table 4.

	ρ	Vt	\mathbf{V}_l	Vm	θ_D
	(Kg/m^3)	(m/s)	(m/s)	(m/s)	(K)
BeS	4110	3465	6041	3849	424
BeSe	5260	2789	4908	3101	326
BeTe	5650	2318	4178	2582	252

Table 4: Calculated sound velocities and Debye temperatures for BeX compounds

7. Conclusion

The electronic, elastic and thermal properties of Be-chalcogenides (BeTe, BeSe and BeTe) have been studied with FP-LAPW + *l*o method in the framework of density functional theory. The quantities such as band structure, elastic constant, and Debye temperature were obtained. The generalized gradient approximation (GGA) was considered for the exchange and correlation effects calculations. The elastic constants maintain all conditions to be satisfied for mechanical stability of the compound. The profound ductility in BeX compound was observed with the increase in chalcogen atomic number. The band structure of all Be-chalcogenides confirms the indirect energy gap between the top of the valence band and the bottom of conduction band.

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Estimation of Thermal Conductivity of Composites Reinforced with Conductive Particle Fillers – Models and Numerical Study

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Abstract: The effective thermal conductivities of fiber and particle reinforced composite materials are calculated by numerical method using finite element analysis software. Different filler concentrations, arrangements and geometries are examined. The results are compared with the results obtained from theoretical models. Numerical analysis study is conducted in three dimensional. Three dimensional models are used for particle fillers having the geometries of sphere and cube. Concentration ratios are chosen 5%, 25% and 45%. Furthermore, effective thermal conductivities are found for 4 different kf / km ratios such as 10, 100, 1000 and 10000. Effect of changing quantity of fillers in the matrix is also investigated that the number of fillers in the matrix is to be as 1, 8 and 27. Effective thermal conductivities found from numerical analyses are compared with those found from theoretical models. It is found that Hamilton and Crosser, Lewis and Nielsen, Meredith and Tobias and Russell's models showed close results to numerical analysis results.

Keywords: Polymer-matrix composites, Thermal properties, Finite element analysis

1. Introduction

Increasing required for composite materials with better properties to come across new demand or to change existing materials. The determination of thermal properties of composite materials is significant importance in new design and many applications. Practically, determining the thermal conductivity of composite materials is essential in many industrial processes. If the thermal conductivities of materials aren't recognized, don't decide the fields of temperature of composite materials. The thermal conductivity of composite materials are depend on geometry, size, distribution of filler materials, the thermal conductivity of matrix and filler materials, contact between filler materials [1,2]. There are numerous theoretical, ampirical, as well as numerical methods to predict effective thermal conductivity of composites, each of these methods have certain assumptions, therefore they may be applicable for certain specific cases and ranges.

The scope of this study is to determine the effective thermal conductivities of composite materials by numerical analysis (ANSYS) and to investigate their proximity relations with the theoretical models that have been developed for prediction of thermal conductivities of composites. To determine the factors that affect the thermal properties of composites, numerous models have been examined in this work. Shape (cube and spherical), size(% 5, 25, 45) and distribution factors have been considered and all efforts have been made by leaning these factors.

2. Theoretical Thermal Conductivity Models

Among these models, series, parallel and geometric mean models are taken notice for the simplest cases. These models are followed by [1]

Series Model:
$$k_e = \frac{\kappa_f \kappa_m}{k_m \phi + k_f (1 - \phi)}$$
 (1)

Parallel Model :
$$k_e = k_f \emptyset + k_m (1 - \emptyset)$$
 (2)

Geometric Model :
$$k_e = k_f^{\emptyset} + k_m^{(1-\emptyset)}$$
 (3)

Cheng and Vacon was accepted that filler materials are discontunuous phase which has parabolic distribution. And study was started by Tsao's possibility model. Results of studies, Cheng and Vachon improved a model for spherical particles and fiber filled composites. In two phase composite materials, Tsao consants were evaluated, an expression depending on volumetric fraction of filler materials in closed-form was obtained. This model are given by [3]

if
$$k_m > k_f$$
 $\frac{1}{ke} = \frac{2}{\sqrt{C(k_f - k_m)[k_m + B(k_f - k_m)]}} \tan^{-1} \frac{B}{2} \sqrt{\frac{C(k_f - k_m)}{k_m + B(k_f - k_m)}} + \frac{1 - B}{k_m}$ (4)

if
$$k_f > k_m$$
 $\frac{1}{ke} = \frac{1}{\sqrt{C(k_f - k_m)[k_m + B(k_f - k_m)]}} \ln \frac{\sqrt{k_m + B(k_f - k_m)} + \frac{B}{2}\sqrt{C(k_f - k_m)}}{\sqrt{k_m + B(k_f - k_m)} - \frac{B}{2}\sqrt{C(k_f - k_m)}} + \frac{1 - B}{k_m}$ (5)

where $B = \sqrt{3\emptyset/2}$, $C = -4\sqrt{2/3\emptyset}$

Lewis ans Nielsen uses an elastic moduli analogy. Lewis and Neilsen arranged the Haplind-Tsai equations so as to contain geometrical particle shape and orentation of packing in two phase system. Obtained form equations [4]

$$k_{e} = k_{m} \left[\frac{1 + AB\phi}{1 - B\phi\Psi} \right], \tag{6}$$

where $B = \frac{k_f/k_m - 1}{k_f/k_m + A}$, $\Psi = 1 + \left(\frac{1 - \emptyset_m}{\emptyset_m^2}\right) \emptyset$

A and \mathcal{O}_m depends on shape and orentation of filler materials. \mathcal{O}_m maximum packing fraction of the filler materials. This means the correct volume of partical partition to the volume look like taking up when packed to their maximum dimension. The values of A and \mathcal{O}_m for many geometric shapes and orentation are given in Table1 and Table 2.

Type of filler material phase	Direction of heat flow	Α
Cubes	Any	2.00
Spheres	Any	1.50
Aggregates of Spheres	Any	3.00
Randomly oriented rods		
Aspect ratio=2	Any	1.58
Aspect ratio=4	Any	2.08
Aspect ratio=6	Any	2.80
Aspect ratio=10	Any	4.93
Aspect ratio=15	Any	8.38
Uniaxially oriented fibers	Perpendicular to fibers	2L/D (L:length, D:Diameter)
Uniaxially oriented fibers	Parallel to fibers	0.50

Table 1: Value of A for various systems

Shape of particle	Type of packing	Øm
Spheres	Hexagonal close	0.7405
Spheres	Face centered cubic	0.7405
Spheres	Body centered cubic	0.6000
Spheres	Simple cubic	0.5240
Spheres	Random close	0.6370
Rods or fibers	Uniaxial hexagonal close	0.9070
Rods or fibers	Uniaxial simple cubic	0.7850
Rods or fibers	Uniaxial random	0.8200
Rods or fibers	Three dimensional random	0.5200

Table 2: Value of $Ø_m$ for various systems (Kumlutaş and Tavman, 2003; Durmaz, 2004;5]

Using potential theory, Maxwell derived an expression for conductivity of randomly dispersed and non-interaction homogenous spheres in homogenous medium. Maxwell model is not used in many systems because this model is derived for non-interacting spheres. This expression is followed by [5]

$$k_{e} = k_{m} \frac{k_{f} + 2k_{m} + 2\emptyset(k_{f} - k_{m})}{k_{f} + 2k_{m} - \emptyset(k_{f} - k_{m})}.$$
(7)

Lord Rayleigh took into account thermal interaction among particles, and developed Maxwell's solution. The equation for a cubic array was given [5]:

$$k_e = k_m \left[\frac{\frac{2k_m + k_f}{k_m - k_f} - 2\phi - 0.525 \left(\frac{3k_m - 3k_f}{4k_m + 3k_f}\right) \phi^{\frac{10}{3}}}{\frac{2k_m + k_f}{k_m - k_f} + 2\phi - 0.525 \left(\frac{3k_m - 3k_f}{4k_m + 4k_f}\right) \phi^{\frac{10}{3}}} \right].$$
(8)

If Ø is small enough, the final term may be neglected and equations return to Maxwell's equation.

Meredith and Tobias modified Maxwell's Model by thinking infinite count of small fillers addition to a two phase uniform mixture. Meredith and Tobias Model is given by [7]

$$\mathbf{k}_{e} = \mathbf{k}_{m} \left[\frac{\frac{2\mathbf{k}_{m} + \mathbf{k}_{f}}{\mathbf{k}_{m} - \mathbf{k}_{f}} - 2\emptyset + 0.409 \left(\frac{6\mathbf{k}_{m} + 3\mathbf{k}_{f}}{4\mathbf{k}_{m} + 3\mathbf{k}_{f}}\right) \emptyset^{\frac{1}{3}} - 2.133 \left(\frac{3\mathbf{k}_{m} - 3\mathbf{k}_{f}}{4\mathbf{k}_{m} + 3\mathbf{k}_{f}}\right) \emptyset^{\frac{1}{3}}}{\frac{2\mathbf{k}_{m} + \mathbf{k}_{f}}{\mathbf{k}_{m} - \mathbf{k}_{f}} + 2\emptyset + 0.409 \left(\frac{6\mathbf{k}_{m} + 3\mathbf{k}_{f}}{4\mathbf{k}_{m} + 3\mathbf{k}_{f}}\right) \emptyset^{\frac{2}{3}} - 0.906 \left(\frac{3\mathbf{k}_{m} - 3\mathbf{k}_{f}}{4\mathbf{k}_{m} + 4\mathbf{k}_{f}}\right) \emptyset^{\frac{1}{3}}} \right].$$
(9)

Hamilton and Crosser defined followed equation for the thermal conductivity of twocomponent mixture [8]:

$$k_{e} = k_{m} \frac{k_{f} + (n-1)k_{m} - (n-1)\phi(k_{m} - k_{f})}{k_{f} + (n-1)k_{m} + \phi(k_{m} - k_{f})},$$
(10)

where n is an empirical constant(=3 for spheres).

Russell obtained one of the first models by using the electrical analogy. Assuming that the filler particul is isolated cubes of same size distributed in matrix material and isothermal lines are planes, he obtained an thermal conductivity model for composite by series parallel network [9].

$$k_{e} = k_{m} \left[\frac{\varphi_{3}^{2} + \frac{k_{m}}{k_{f}} \left(1 - \varphi_{3}^{2} \right)}{\varphi_{3}^{2} - \varphi + \frac{k_{m}}{k_{f}} \left(1 + \varphi - \varphi_{3}^{2} \right)} \right].$$
(11)

Springer and Tsai supposed a cylindrical model fibers has square distribution in the matrix material and developed a semi-theoritical model. The analogy among unidirection composite

and thermal conductivity problem response to heat transfer and shera loading. The predict of the thermal conductivity is on basis of this in the direction normal to the fibers [2].

$$k_{e} = k_{m} \left[1 - 2\sqrt{\frac{\emptyset}{\pi}} + \frac{1}{B} \left(\pi - \frac{4}{\sqrt{1 - \left(B^{2}\frac{\emptyset}{\pi}\right)}} \tan^{-1} \left(\frac{\sqrt{1 - \left(B^{2}\frac{\emptyset}{\pi}\right)}}{1 + B\sqrt{\frac{\emptyset}{\pi}}} \right) \right) \right], \tag{12}$$

$$\text{re } B = 2 \left(\frac{k_{m}}{k_{\epsilon}} - 1 \right).$$

wher

Given equation was developed by Basschirow and Selenew for spherical of particles and two phases which are isotropic [10].

$$k_{e} = k_{m} \left[1 - \frac{a^{2}\pi}{4} + \frac{a\pi p}{2} \left(1 - \frac{p}{a} \ln \left(1 + \frac{a}{p} \right) \right) \right],$$
(13)
where $p = \frac{k_{f}}{k_{m} - k_{f}}$ and $a = \left(\frac{6\emptyset}{\pi}\right)^{1/3}$.

Zehner and Schlünder developed a model depended on heat flow model ,which is a one dimension, for conduction along a packed bed of spherical particles, the supposed particles included point connection in heat flow direction [11]

$$k_{e} = k_{f} \left[1 - (1 - \emptyset)^{0.5} + \frac{2(1 - \emptyset)^{0.5}}{1 - KB} \left[\frac{(1 - K)B}{(1 - KB)^{2}} ln \left(\frac{1}{K} B \right) - \frac{B + 1}{2} - \frac{B - 1}{1 - KB} \right] \right],$$
(14)

where $K = \frac{\kappa_f}{k_m}$ and $B = 1.25 \left(\frac{1-\varphi}{\phi}\right)$

Woodside and Messmer offered a model being a mixture of series and parallel distributions. They used the electrical conductivity analogy of an aggregate of conductive particles saturated with conducting electrolyte, to derive a modified resistor equation to predict the effective thermal conductivity of poros media [12].

$$k_{e} = \frac{ak_{m}k_{f}}{k_{m}(1-d)+dk_{f}} + ck_{f},$$
(15)

where $c = \emptyset - 0.03$, a = 1 - c and $d = \frac{1 - \psi}{a}$.

The signification for "c" is determined by exercising the experimental result of Stephenson and Woodside for a cubic pack of spheres model at a concentration of 47.6%.

Bruggemann devised an alternative means of extending Maxwell's model by considering an infinite number of small additions to a homogeneous mixture of the two phases. For a twophase system containing a uniformly shaped second phase dispersion, Bruggemann obtained

$$1 - \emptyset = \left[\frac{\mathbf{k}_{\mathrm{f}} - \mathbf{k}_{\mathrm{e}}}{\mathbf{k}_{\mathrm{f}} - \mathbf{k}_{\mathrm{m}}}\right] \left[\frac{\mathbf{k}_{\mathrm{m}}}{\mathbf{k}_{\mathrm{e}}}\right]^{\frac{1}{\mathrm{X}} + 1},\tag{16}$$

where X is a shape factor for the discontinuous phase: X is 2 for spheres, 1 for cylinders oriented perpendicular to heat flow, $1/\beta$ for oriented ellipsoids, where $\beta = R \frac{\frac{1}{x}}{\frac{1}{y} + \frac{1}{z}}$, x is the ellipsoidal axis parallel to heat flow, y and z are the other two ellipsoid axes, and R is a surface roughness factor (≈1).

3. Numerical Analysis

Using the finite - element program ANSYS, thermal analysis was carried out for the conductive heat transfer. In order to make a thermal analysis, three dimensional models have been used to simulate the microstructure of composite materials for various filler concentrations at various k_f/k_m . The three-dimensional models used to simulate fiber filled composites are cubes in a cube lattice array and spheres in a cube lattice array, (Figure1 a,b).



Figure 1: Three-dimensional (a), (b) models, Boundary conditions (c)

In the numerical analysis of the heat conduction problem, the temperatures at the nodes along the surfaces ABCD and EFGH (Figure 1.c) are prescribed as T_1 and T_2 . The other surfaces paralleled to the direction of the heat flow are all assumed adiabatic. The temperatures at the nodes in the interior region and on the adiabatic boundaries are unknown. These temperatures are obtained with the finite-element program package ANSYS. Effective thermal conductivity of the composites is calculated by using the results of the thermal analysis. For an elementary three-dimensional cell with the dimensions of L_x (along the x axis) and L_y (along the y axis), and L_z (along the z axis), the thermal conductivity is calculated using the following relation:

$$k_{c} \frac{\Delta T_{cell}}{L_{z}} = \frac{1}{S} \sum_{i} \sum_{j} k_{ij} x_{i} y_{j} \left(\frac{\partial T_{ij}}{\partial z} \right)$$
(16)
with $s_{ij} = x_{i} y_{j}$ and $\sum_{i} \sum_{j} s_{ij} = S$

4. Results

3-D model analyses are based on the following criterions: 2 different filler shapes: sphere and cube; 3 different concentration ratios : Φ =5%, 25% and 45%; 4 different thermal conductivity ratios of filler and matrix : k_f/k_m =10, 100, 1000, 10000; 3 different arrangement forms : 1, 8 and 27 pieces of fillers. Maximum concentration ratio was selected to shown the example results.

As the concentration of filler material increases, isotherm lines are getting deflecting rapidly. At maximum concentration ratio, maximum deflection is seen. (see Figure 2.(a) and (b)). If we compare the isotherms on models with both sphere and cube fillers, we can easily figure that isotherms of sphere fillers are wavier than those of cube fillers. k_f / k_m ratio is also be effective on

amount of deflection of isotherm lines. Increasing k_f / k_m ratio makes the isotherm lines deflect more. The area of maximum heat flux on the surface is wider in the cube filler model than that in the sphere filler model (Figure 3 (a) and (b)).



Figure 2: Temperature distribution over a) 27 piece-sphere-fillers b) 27 piece-cube-fillers model for Φ =45% and k_f/k_m =10



Figure 3: Total heat flux a) 27 piece-sphere-fillers b) 27 piece-cube-fillers model for $\Phi = 45\%$ and $k_{f}/k_{m}=10$

Figure 4, effect of concentration ratio and k_f / k_m on k_e / k_m ratio of both sphere and cube filler models are illustrated. Increasing concentration ratio makes the effective thermal conductivity ratio values higher due to increasing thermal bridges along the path of the heat flow. One can easily conclude from Figure 4 that the effective thermal conductivities of the sphere filler models are higher than those of the cube filler models. As we look at the figure, one can see that 8 and 27 pieces of filler arrangement have not made too much difference in results. In all of the figures, curves of the 1, 8 and 27 piece-fillers models are close each other for either cube or sphere filler shapes. That is because entire arrangement forms are symmetrical and homogeneously dispersed into the matrix material. At 5% and 25% concentration ratio, effective thermal conductivities of sphere filler models are higher than those of cube filler model. But at 45% concentration ratio, vice versa is seen. This can only be explained with that surface of the sphere filler is closer to the boundary surface of the matrix rather than surface of the cube at $\Phi=45\%$. This phenomenon allows the heat flow fast along the z direction.

Cube & Sphere-Particle-Fillers for Φ=45%



Figure 4: Effective thermal conductivity plot of cube and sphere particle fillers at Φ =45% *for various arrangement forms.*



Figure 5: $k_e / k_m vs. k_f / k_m$ graph of sphere filler model for $\Phi = 45\%$

Fifteen different theoretical thermal conductivity models have been investigated in this study. "Hamilton and Crosser's Theoretical Model" is one of the closest models to the numerical analysis. Furthermore, "Lewis and Nielsen's Semi-Theoretical Model" is close at 5% and 25% concentration ratios as well. At highest concentration ratio (Φ =45%), "Meredith and Tobias's Theoretical Model" and "Russell's Theoretical Model" approach to numerical analysis for 3-D models.

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The influence of fibre reinforcement on mechanical and thermo-physical properties of composite materials

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Abstract: The measurements of the most important physical parameters of fire protection plaster boards are presented in the article. Measurements were done at two types of board materials SX6-B (reinforcement with basalt fibres) and SX6 (without fibres). All measurements were done by nondestructive methods on cooled specimens which had been stressed by temperature in rank up to 1000 °C. Thermal conductivity, thermal diffusivity and specific heat capacity were measured by apparatus ISOMET in dependence on temperature. From mechanical properties was measured modulus of elasticity by two methods. The first was resonant method and the second was ultrasonic method for measuring speed of wave spreading. By comparison of results was discussed influence of reinforcement on thermal and mechanical properties of fire protection lining boards.

Keywords: Plaster boards, thermal conductivity, modulus of elasticity, elongation

1. Introduction

In the material engineering is nowadays important trend to develop materials with aimed properties. It is possible by using composites materials where are added other ingredients into basic matrix, which improved its properties. For fire protection of lining boards Research Institute of Building Materials (VUSTAH) in Brno developed material which has basic matrix based on modified gypsum (with improved thermal properties – marked as SX6). For improving mechanical properties is added fibres reinforcement, basalt fibres – marked SX6-B.

For appraisal of the influence of reinforcement on physical parameters were measured thermal and mechanical parameters. At first on specimens which were burned at specific temperatures for material SX6 and then for material SX6-B.

From thermal-physical qualities were measured thermal conductivity and thermal diffusivity and specific heat conductivity and bulk density. From mechanical properties was measured modulus of elasticity. And stability of material was controlled by thermal expansion coefficient and relative loss in mass.

Composition of materials: SX6 – gypsum of firm Gypstrend – Kobeřice Water ratio: 0.328 Additives: Retardant GK Peramin 30 Lightening the mixture: 5% of weight Experlit EP 150

SX6 - B – reinforced by fibres: 3% of weight Baseltex 6 (basalt)

2. The measurement of thermal-technical material parameters

On the delivered material specimens of materials SX6-B and SX6 was done measurement by methodology used for testing board materials in the past years [1, 2]. The measurement was

done on specimens which had been stressed by temperature. After cooling the weight was measured with scales and with apparatus ISOMET were measured thermal conductivity and thermal diffusivity and specific heat capacity.

As an example of chart processing and graphical processing measured results there are presented measurements done on the specimens of material SX6 (The Charter I. – processing of measurement thermo-physical parameters and Figure 1. and 2., where is plot thermal conductivity in dependence on temperature of both materials).

Detailed processing including all graphic dependences is in records at the Department of Materials Engineering and Chemistry of Czech Technical University in Prague - Faculty of Civil Engineering.

3. The measurement of mechanical properties

There was used apparatus for measuring of modulus of elasticity by resonance method and ultrasonic method for measuring speed of wave spreading. It is necessary to remind that at high temperatures the specimens were often destroyed (decomposed) so it wasn't possible to do the measurement. Another finding is that resonant method is more exact because during measuring the speed of ultrasonic wave spreading was influenced by absorbing contact gel and the results were misrepresented.







Figure 2: Thermal conductivity of material SX6-B



Figure 3: Modulus of elasticity dependent on temperature of material SX6



Figure 4: Modulus of elasticity dependent on temperature of material SX6-B

4. The measurement of dilatation

Thermal expansion in dependence on temperature is possible to find out by measuring relative expansion for set temperatures (the most suitable by 100 °C up to 1000 °C) and this measured values plot into figure in dependence on temperature. By analytical express of this function we can determine its derivation for each temperature it means thermal expansion α_t for each temperature.

The measurement was done on special dilatometer [3]. The principle of measurement is that the end of specimen, which is placed in kiln, is connected by contact stick with indicator of length that is placed out of kiln. Into dilatometer is placed the specimen and then the temperature is rising up to 1000 °C and the length changes of specimen are observed. From these values it is possible easily calculate thermal expansion.

Because materials structure doesn't have to be stable the measurement was repeated after cooling specimens. The burned specimen didn't change in length which would arise from structure instability.

In the Figures 5 to 8 are plot dependence of elongation on temperature for the first and the second measurement of both tested materials. Detailed records of measurement and calculation are at the Department of Materials Engineering and Chemistry of Czech Technical University in Prague - Faculty of Civil Engineering.



Figure 6: Elongation of material SX6 – the second measurement





Figure 7: Elongation of material SX6 - B - the *first measurement*

Figure 8: Elongation of material SX6 – B – the second measurement

5. Discussion

Thermal-technical parameters

The measurements show that thermal-technical parameters are influenced by reinforcement only at higher temperatures (circa above 300 °C). At the temperatures up to 200 °C thermal conductivity of both materials is 0.2 W/m.K with decreasing trend, which is probably caused with drying. Then is possible observe increasing which is more intensive on the material without reinforcement.

Mechanical parameters

By comparison of results of modulus of elasticity it is obvious that results of both used methods (resonant method and measuring speed of wave spreading) are comparable.

Also it is visible that non-dried specimens have higher values (mainly at lower temperatures). And finally there is evident the influence of reinforcement on modulus of elasticity. Meanwhile material without reinforcement has the beginning modulus of elasticity higher than with reinforcement, but its value decreases quite fast, the material with reinforcement has modulus of elasticity relatively stable not depending on temperature. Dilatation

From graphical processing of measuring dilatation is evident, that for range of high temperatures is dimension stability very bad. During the first heating (circa up to temperature 110 °C) happens slight increasing of elongation. By exceeding temperature (circa 110 °C) break point occurs and material start to shrinking.

It is caused both by loosing free water and also by transforming calcium sulphate dihydrate into calcium sulphate hemi-hydrate (CaSO₄ \cdot 1/2H₂O). Loss of crystalline water causes shrinking. This transformation is finished at the temperature of 350 – 400 °C. Other increasing of temperature led to transformation calcium sulphate hemi-hydrate to calcium sulphate anhydrate (CaSO₄). Its slow change causes that dimensions don't change a lot. Natural dilatation is compensated by shrinking. At the temperature above 600 °C radical change comes and that's why massive shrinking occurs.

All the described changes were measure by the first heating of both observed materials. The evident different is in intensity of changes. Material SX6 changes in its length much more significantly then material SX6 – B (with fibres reinforcement). It means that the reinforcement made of basalt fibres reinforces the material and this way increases its structural stability. Changes in length of the material without reinforcement were measured by three times bigger.

What is interesting that the measurement was repeated shrinking nearly disappeared. Although it was possible to expected measurement that gypsum will absorb crystal water from humidity. This change happens probably slow and therefore during the repeated measurement only increase of elongation occurred. So the influence of reinforcement wasn't evident.

6. Conclusion

Compared both measurements it is possible to say that basic component of composite material based on modify gypsum (improved with fibre reinforcement) brings advantages for which this material developed. It means better thermal properties, mechanical properties and for better volume stability of material at high temperatures.

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A simple equipment for the evaluation of thermal conductivity of powdery materials at high temperature and in vacuum

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Abstract: The standard approach for the evaluation of thermal conductivity of thermal insulation of powdery materials makes use of the ball-shape stationary equipment. However, at the temperature up to 800°C, for some special materials even up to 1200°C, moreover in vacuum, needed in the design of the high-temperature underground thermal storage, strong requirements to the resistance of the ball vessel, to the thermal contraction of applied materials, as well as to all temperature sensors, make all measurements difficult and expensive. This paper presents the original simplified measurement equipment with the cylindrical vessel. The analysis of validity of obtained results refers to the measurement validity, comparable with the classical one, utilizing the ball-shape equipment.

Keywords: Heat conduction, inverse problems, powder materials, high-temperature material testing.

1. Introduction

The most frequently used approach to the evaluation of thermal conductivity of building materials is the so-called plate method where the crucial data are the amount of thermal flux running through the tested specimen, related to some planar area, and the specimen thickness. The thermal conductivity, coming from the temperature difference from two heated plates, is usually assigned to the average temperature from both plates, generating the stationary thermal gradient, as discussed in [6] (including more advanced non-stationary measurement configurations, too) and [2], p. 109. This approach is incorporated as the basic one into most European, U.S. and other technical standards. However, the plate method brings serious difficulties or cannot be performed at all in the case of some building materials, namely the powdery ones that do not create any insulation layer with constant thickness. Moreover, due to the particle size and localization, their compression, etc., additional processes of thermal transport, as convection and radiation, can be non-negligible – cf. [3], p. 115.

The well-known remedy is the utilization of the Nusselt's ball-shape equipment. Material particles are located in a layer between two spheres. As well as in the plate method, the temperature difference from both surfaces (spherical here), together with the controlled heat flux, is needed for the evaluation of thermal conductivity. From the point of technical design, the Nusselt's equipment consists of two balls with the same centre. The surface of the inner one, made from copper sheet, includes a ceramic element with an electric heating coil, distributing the heat flux uniformly on the surface, and a thermocouple for the detection of temperature. The surface of the outer one, also from copper sheet, must be supplied by holes, needed for filling of the free space between both surfaces by the exactly known mass of tested materials (by weighting); the uniform material compaction is needed. The generated heat is transferred through such specimen to the outer surface and consequently to the environment; thus no additional compensation elements are needed. A wattmeter is used for the evaluation of

electrical energy, similarly to the plate method. Figure 1 shows a representative example of such equipment.

An alternative approach, known as the van Rinsum's one, assumes that the insulation material is fixed on the electrically heated inner tube where the electric power (from the stabilized source) is detected, as well as the temperature, simultaneously with the temperature on the outer material surface. Both approaches rely on the (seemingly simple) identification of thermal conductivity from two values of temperature and one value of heat flux, although the spherical or cylindrical geometrical configurations make such evaluation more complicated as in the plate method; for more details see [4]. However, strong requirements to the resistance of the vessel, to the thermal contraction of applied materials, as well as to all temperature sensors, make all measurements difficult and expensive.



Figure 1: Ball-shape measurement equipment at the Technical University in Lulea (Sweden).

As a part of the project of a high-temperature thermal container, it was necessary to identify the thermal conductivity of certain classes of powdery materials with prescribed compaction for the usual design temperature up to 800°C, in some cases even up to 1200°C, both in natural environment and in vacuum. The drawbacks of standard methods motivated the development of an original measurement equipment, supplied by a non-trivial computational approach, presented in this paper.

2. Measurement equipment

The new equipment, prepared in the Laboratory of Building Physics at the Faculty of Civil Engineering of Brno University of Technology (FCE BUT), was designed to determine relatively low values of thermal conductivity. All its parts are non-expensive and can be completed easily. The steel cylindrical container of the diameter 101 mm and the wall thickness 5 mm is supplied by the fixed steel bottom and the demountable top. The top involves ceramic elements, made from brick clay, hiding both all wires to thermocouples and all wires feeding the ceramic

heating element, which has the diameter and the height 50 mm. This element involves the heater source, made from constantan spiral wire. The stabilized power supply is guaranteed thanks to the 4-wire plug in; the resulting temperature increase is then approximately 30 K.



Figure 2: New measurement equipment at FCE BUT – temperature 700°C, standard air pressure.



Figure 3: Control of the thermal process from Figure 2.

All measurements are performed in the kiln at the required temperature, e.g. (as in the following example) 700°C, under the condition of (nearly) stationary heat transfer: during the time period 600 s the change of temperature recorded at the inner ceramic heater cannot be greater than 0.2 K. For the comparison, the temperature is recorded on the vessel cover, too.

Certain small variation of temperature of the cover is caused by the activity of the kiln regulator.

Figure 2 shows the kilt with the announced measurement equipment at FCE BUT. Figure 3 demonstrates the remote control of the corresponding quasi-stationary thermal process. The thermal conductivity is expected to be a function of temperature, thus the experiment is rather slow, with the duty to stabilize temperature at all levels of interest. The additional local temperature increase, caused by electrical heating, is assumed to cause only negligible changes of heat conductivity, as well as the (sufficiently small) non-stationary effects and other thermal processes.

3. Computational tools

The equation of heat conduction, coming from the classical thermodynamical principle of conservation of energy, supplied by the linearized Fourier constitutive law, can be written, under the assumption of a priori knowledge of the thermal conductivity λ and the heat capacity per unit mass κ (functions of temperature in general) in the standard form

$$\kappa (T(x,t)) \partial T(x,t) / \partial t - \nabla \cdot (\lambda(T(x,t)) \nabla T(x,t)) = 0 \text{ for all } x \in \Omega \text{ and any } t \in I$$
(1)

where *t* denotes the time from the time interval *I*, usually starting from zero, and ∇ the Hamilton operator (vector of partial derivatives) related to Cartesian space coordinates *x* = (*x*₁, *x*₂, *x*₃) from some domain Ω in the 3-dimensional Euclidean space *R*³. This equation must be supplied by some initial condition of the type

$$T(x,0) = T_0(x) \text{ for all } x \in \Omega$$
(2)

and some boundary conditions of the Neumann type

$$\lambda(T(x,t)) \nabla T(x,t) \cdot v(x) + q(x,t) = 0 \text{ for all } x \in \Gamma \text{ and any } t \in I$$
(3)

together with some boundary conditions of the Dirichlet type

$$T(x,t) = T_*(x,t) \text{ for all } x \in \Theta \text{ and any } t \in I;$$
(4)

here the disjoint sets Γ and Θ must cover the boundary $\partial \Omega$ of Ω in R^3 , ν means the unit normal vector on the boundary of presribed (usually outward) orientation and all needed values of temperatures T_0 , T_* and heat fluxes q must be known in advance. Moreover, the heat transfer at material interfaces is assumed to satisfy the boundary conditions similar to (3)

$$\lambda(T(x,t)) \nabla T(x,t) \cdot v(x) = \lambda(T(x,t)) \nabla T(x,t) \cdot v(x) \quad 0 \text{ for all } x \in \Gamma \text{ and any } t \in I$$
(5)

where the lower dot index refers to temperatures from the neighbour layer.

Since the functions λ and κ are not available for a specimen (only for remaining material layers), some non-negligible intersection of Γ and Θ must exist to compensate this lack of data. In our very special measurement configuration this can be explained such that Θ covers both surfaces with temperature sensors, whereas Γ represents only that one with the controlled heat flux. The radial symmetry of the equipment offers the conversion of the whole mathematical description to the cylindrical coordinates; nevertheless, to be able to study the effects of presence of both type of wires going through the top of the vessel, we shall come out from the original formulation (1). Thanks to the very special experimental setting, we are able to neglect the first additive term in (1) with another material characteristic κ and consequently remove (2) at all

and consider λ to be constant for a chosen temperature level; then (3) and (4), taking (5) into account, are over-determined boundary conditions in the sense of [5], p. 259, to the elliptic partial differential equation (1). Let us notice that, unlike the direct problem (with known material characteristics) where the Lax-Milgram theorem and standard finite element techniques are available, the existence and uniqueness of solution, as well as the convergence of numerical approximations, is not trivial here; for more details see [7]. Nevertheless, the resulting least-square based optimization problem can be handled as the limit case of particular problems with step-by-step improved values of λ , with the help of ANSYS software package.

To understand the basic idea of least-square optimization, applied to our computational problem, let us sketch the ANSYS-supported algorithm in some more details. Let us assume that all material layers are (from the macro-structural point of view) homogeneous and isotropic, thus λ can be expressed for some integer *m* (number of testing equipment material layers, except the specimen) as a (*m*+1)-valued simple function with values λ_0 , λ_1 , ..., λ_m , with just one real unknown parameter λ_0 (referring to the specimen). Considering $\Upsilon = \Theta \setminus \Gamma$, let us suppose that T_* from (4) can be extended from Υ to Ω (thanks to an appropriate regularity assumption) such that the Green-Ostrogradkiĭ theorem converts, under the above discussed simplifications, for a fixed time $t \in I$, (1) with respect to (3) and (5) to its (formally very simple) variational form

$$(\nabla \tau, \lambda \nabla T) = \langle \tau, q \rangle + (\nabla \tau, \lambda \nabla T_*), \qquad (6)$$

making use of scalar products in the standard Lebesgue spaces: [.,.] in $L^2(\Omega)^{3\times 3}$ and $\langle .,. \rangle$ in $L^2(\Upsilon)$, later also [.,.] in $L^2(\Theta \cap \Gamma)$, and arbitrary test functions from the Sobolev space $W^{1,2}(\Omega)$ zerovalued on Θ ; the unknown temperature T has to be find in $W^{1,2}(\Omega)$ again. Let Λ be a set of all admissible values of λ_0 . Then (6) generates a set of its solutions, depending on just one parameter $\lambda_0 \in \Lambda$. Introducing the function

$$F(\lambda_0) = [T(\lambda_0) - T_*, T(\lambda_0) - T_*], \qquad (7)$$

we can finally seek for the minimizer λ_0 of *F* belonging to Λ . Since $T(\lambda_0) \approx T_*$ is expected (the exact equality is not realistic), $T(\lambda_0)$ contains certain stochastic information on the dispersion of identification results.



Figure 4: Geometrical input data, prepared for ANSYS: wire model (left image), solid model (right image).






Figure 6: Distribution of temperature gradients.



Figure 7: Distribution of heat fluxes.

4. Illustrative example

For illustration, we shall pay attention one measurement time step at the global temperature 700°C. The geometrical problem description for the ANSYS pre-processor is shown on Figure 4: due to expected periodicity, thanks to the location of above discussed wires through the top of the vessel, only one segment of the vessel can be considered.

Moreover, some reasonable value of λ (typically that from the previous temperature level) must be supplied to start the optimization procedure. Figures 5, 6 and 7 demonstrate its outputs. Whereas Figure 5 shows the distribution of T(x) (the time variable is omitted here), Figure 6 shows the Euclidean lengths of gradients $\nabla T(x)$ and Figure 7 those of $-\lambda \nabla T(x)$; λ is taken as constant inside one measurement step.

However, Figures 5, 6 and refer to particular results for one special material. Unlike them, Figure 8 shows the complete dependencies $\lambda(T)$ received for two quite different insulation materials: perlite and aerogel. Whereas aerogel preserves its thermal conductivity up to high temperature, the thermal conductivity of perlity increases substantially. The a posteriori analysis of the identification results shows a comparable validity with the results obtained from the ball-shape equipment by Figure 1.



Figure 8: Computed values $\lambda(T)$ (vertical axis, in W/(m.K)) depending on T (horizontal axis, in °C).

5. Conclusions

The alternative non-expensive measurement device, presented in this paper, at least under standard air pressure, gives reasonable values of thermal conductivity at high temperatures, at least under normal air pressure. The modification of the equipment for the measurement in vacuum is still in progress; however, it is required for the development of the high-temperature underground thermal storage, as a part of the Czech-Swedish project of the development of heat production and storage system, based on fibre optics.

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Determination of material parameters necessary for computational modeling of hygrothermal performance of historical buildings

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Abstract: For the determination of hygrothermal performance of historical buildings, methods of computational modeling are often applied in building practice and research. In this way, the time development of moisture and temperature fields can be obtained. This information can be then used for the identification of weak areas of investigated structures and possible future damage. The accuracy of calculated data is, however, critically dependent on the availability of all input parameters. In this paper, the measurements of such necessary parameters of several building stones are presented.

Keywords: historical buildings, hygrothermal performance, computational models, input parameters, measurement

1. Introduction

Understanding the hygrothermal behavior of historical buildings exposed to various environments represents a first step in avoiding damage or the undue heat loss from constructions. It also creates a basis for constitutive models for porous materials whose timedependent properties, such as shrinkage, creep, strength, etc., are strongly affected by the moisture and temperature fields. Their prediction is a very important task when preserving historical bridges and buildings, and insulating existing buildings or their parts.

The damage assessment of historical masonry due to the negative effects of moisture and temperature can be done most effectively by means of mathematical and computational modeling. In this way, the time development of moisture and temperature fields can be obtained which is a crucial for a proper assessment of possible future damage; the moisture and temperature values can be assigned to the mechanical properties, thus to the risk of consequent damage.

In the modeling of coupled moisture, heat and momentum transport in historical masonry, there are two types of input parameters which have to be known in advance. The first are initial and boundary conditions. Initial conditions can be determined using on site and subsequent laboratory analysis of moisture and temperature fields in the historical masonry walls. Boundary conditions are of two types. The first of them are meteorological data for temperatures, relative humidities, rainfall and solar radiation, possibly also concentration of acid-forming gases in the atmosphere. This type of data can be obtained from meteorologists in the form of so-called TRY (Test Reference Year) data which present certain average values over a sufficiently long time period. The second type of boundary conditions involves moisture content (possibly also salt concentration) in the underground soil close to the studied building. These data can be obtained again by on site analysis.

The second type of input parameters is represented by hygric, thermal, and mechanical properties which appear in the complex hygro-thermo-mechanical models. These parameters

can be determined by laboratory methods. Samples for the determination of material parameters can be obtained most easily from the walls of the analyzed historical building. If this is not possible, masonry stone samples can be taken from the original quarries which are usually known for a particular building. In the case of brick masonry, similar bricks can be found.

In this paper, basic physical properties, pore distribution, mechanical, hygric and thermal properties of several types of building stones which are used in reconstructions of historical buildings on the Czech territory, namely several types of sandstone and argillite, are investigated. The main aim of the presented work is to obtain sufficiently wide set of input data for the computational damage assessment of historical masonry.

2. Materials

Three types of sandstone coming from different quarries in the Czech Republic are analyzed together with one type of argillite. Many historical buildings in Czech Republic were built using several kinds of sandstone. Siliceous raw-grained sandstone was usually used for historical architectural constructions (walls, portals, window frames) for its strength. Ornamental parts of the architecture (gothic flowers, romantic shells) and sculptures (from the Romanesque period up to now) were made of fine-grained calcite-argillaceous sandstone. The studied sandstones originate from the quarries Mšené-lázně (it will be denoted as PM in what follows), Božanov (PB), and Hořice (PH). They are formed by suboval quartz clasts, tourmaline, epidote, muscovite and zircone. Also argillite was very popular material in historical architecture. It was used for sacral as well as for secular buildings, flagstone pavements, roof slabs, and facing. The studied argillite (it will be denoted as O) is coming from quarry Džbán. Its main constituents are illite, calcite, minerals on the basis of SiO₂ having granularity 0.3 – 0.15 mm, feldspar, and mica. Rigid materials form 40 - 60% of its volume.

3. Experimental methods

3.1 Basic physical properties

The bulk density ρ_b [kgm⁻³], open porosity Ψ [%] and matrix density ρ_{mat} [kgm⁻³] were determined by the water vacuum saturation method [1]. Each the specimens having a size of 40 x 40 x 20 mm was dried in a drier to remove majority of the physically bound water. After that the samples were placed into the desiccator with deaired water. During three hours air was evacuated with vacuum pump from the desiccator. The samples were then kept under water not less than 24 hours.

Characterization of pore structure was performed by mercury intrusion porosimetry. The experiments were carried out using the instruments PASCAL 140 and 440 (Thermo Scientific). The range of applied pressure corresponded to the pore diameters of 3 nm to 1000 μ m. The specimens with a volume of about 1 cm³ were used in the tests.

3.2 Mechanical properties

The measurement of bending strength was done on $40 \times 40 \times 160$ mm prisms. The experiment was performed as a common three-point bending test using a VEB WPM Leipzig device. The distance of the supporting cylinders was 100 mm. The bending strength was calculated

according to the standard evaluation procedure. Compressive strength was determined on the halves of the specimens left over after the bending test. It was calculated as the ratio of the ultimate force and the load area.

3.3 Water transport properties

The liquid water transport was characterized by two different methods. In the first one, the water absorption coefficient *A* [kg m⁻² s^{-1/2}] and apparent moisture diffusivity $[m^2 s^{-1}]$ were determined by a free water intake experiment [2]. The specimen was water- and vapor-proof insulated on four lateral sides and the face side was immersed 1 mm under the water level. Constant water level in the tank was achieved by a Mariotte bottle with two capillary tubes. The balances allowed continuous recording the increase of specimen's mass. The water absorption coefficient of each specimen was calculated from the linear part of the dependence of the increase of tested sample's mass on the square root of time. Then, the apparent moisture diffusivity was calculated using the saturated moisture content and water absorption coefficient [3]. The measurement was done on the samples with the dimensions of 40 x 40 x 20 mm.

In the second method, the moisture dependent moisture diffusivity was determined using an inverse analysis of measured moisture profiles. The experiment was realized in the form of horizontal suction of liquid water into dry materials. The sample size for moisture profiles measurement was 20 x 40 x 300 mm and the samples were on all lateral sides insulated by epoxy resin to ensure 1-D moisture transport. The moisture content measurements were done by capacitance technique using capacitance device [4] having low-voltage supply that drives an oscillator of 400 kHz working frequency. It has a constant output voltage feeding a circuit where the measuring capacitor (with the analyzed moist sample as dielectric) is connected in series with a resistance. The obtained moisture profiles were then analyzed using solution of the inverse problem of moisture diffusion. For this purpose, the Boltzmann-Matano method [5] was used.

3.4 Water vapor transport properties

The dry cup and wet cup methods were employed in the measurements of water vapor transport parameters [1]. The water vapor diffusion permeability δ [s], water vapor diffusion coefficient D [m²s⁻¹] and water vapor diffusion resistance factor μ [-] were determined. The circular samples had diameter of 95 mm and thickness of 20 mm.

3.5 Sorption isotherms

Water adsorption and desorption isotherms were determined using the desiccators method [1]. The measurement was done on the samples with the dimensions of $40 \times 40 \times 10$ mm.

3.6 Thermal properties

Thermal conductivity λ [W m⁻¹ K⁻¹] and specific heat capacity *c* [J kg⁻¹ K⁻¹], were measured using the commercial device ISOMET 2104 (Applied Precision, Ltd.). 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. The measurement was done on the samples with the dimensions of 70 x 70 x 70 mm.

4. Experimental results and discussion

4.1 Basic physical properties

Basic physical properties of the analyzed stones are presented in Table 1. The lowest bulk density and highest open porosity had argillite, the highest bulk density and lowest open porosity showed sandstone Božanov. The other two sandstones were in between these two extremes, Mšené sandstone being closer to argillite and Hořice sandstone closer to Božanov sandstone. The matrix densities of all three sandstones were similar, the Mšené sandstone with the highest Qmat differed only by about 2-3% from the others. This reflected their similar composition. Argillite, on the other hand, had the matrix density about 12-15% lower than the sandstones.

Material	Q	Qmat	ψ
	[kg m ⁻³]	[kg m ⁻³]	[%]
PM	1807	2627	31.0
РВ	2154	2566	16.1
PH	2004	2556	21.6
0	1353	2235	39.4

Table 1: Basic physical properties of building stones



Figure 1: Pore size distribution of building stones

The pore distribution of sandstones and argillite was very different (Figure 1). While the sandstones had a majority of pores in the range of 10-100 μ m, argillite exhibited the major peak between 0.1 μ m and 1 μ m.

4.2 Mechanical properties

Table 2 shows that the highest compressive and bending strength had Božanov sandstone which corresponded with its lowest open porosity (Table 1). The lowest compressive strength exhibited argillite with the highest total porosity but the lowest bending strength had Mšené sandstone with the highest amount of big pores with the radii between 10 μ m and 100 μ m. Thus, while for the compressive strength the main factor was the total porosity, for the bending strength crack formation in the system of big pores was most important.

Material	Compressive strength	Bending strength
	[MPa]	[MPa]
РМ	21.7	2.2
РВ	53.1	5.8
PH	27.0	5.5
0	15.9	4.4

Table 2: Mechanical properties of building stones

4.3 Water transport properties

Apparent moisture diffusivity and water absorption coefficient are presented in Table 3. The fastest liquid water transport exhibited Mšené sandstone. The other building stoned transported water in a much slower way; their apparent moisture diffusivity exhibited values about three orders of magnitude lower. This was in basic accordance with the open porosity (Table 1) and pore distribution (Figure 1) data.

Material	А		
	[kg m ⁻² s ^{-1/2}]	$[m^2 s^{-1}]$	
PM	0.8841	1.24E-05	
РВ	0.0254	2.50E-08	
PH	0.0433	4.14E-08	
0	0.0959	5.29E-08	

Table 3: Water transport properties of building stones

The moisture diffusivity as a function of moisture content is shown in Figure 2. While the highest moisture diffusivity in the whole range of moisture content had Mšené sandstone, the lowest values achieved argillite. This was in a good qualitative agreement with their pore distribution. The high amount of capillary pores in the range of 10 - 100 μ m (Figure 1) was clearly responsible for the very fast water transport in Mšené sandstone. Argillite with the majority of pores in the 0.1 - 1 μ m range, on the other hand, did not have good prerequisites for

such a fast liquid water transport although its total porosity was higher than of Mšené sandstone. The other two sandstones exhibited liquid moisture transport capabilities closer to Mšené sandstone than to argillite. In this case, the relatively high amount of big pores in the 10 - 100 μ m range was clearly the decisive factor.



Figure 2: Moisture diffusivity of building stones as a function of moisture content

A comparison of liquid water transport properties in Table 3 and Figure 2 shows that the apparent moisture diffusivity was (except for Mšené sandstone in the range of highest moisture content) lower than the moisture diffusivity determined as a function of moisture content. The main reason was the very different character of both methods. While the free water intake experiment can be considered only a tool for getting estimated moisture diffusivity values which should serve just for orientation purposes [2], the method based on the inverse analysis of moisture profiles is more rigorous; thus the latter is supposed to give higher-accuracy results [6]. Another factor that could influence the obtained results was that in the free water intake experiment the water transport was realized in vertical direction, while the moisture profiles were measured in an experiment with horizontal water transport. Thus, the effect of gravity could lead to slowing down water transport in the pores with the highest radii. This may partially explain the relatively high differences between the results obtained by both methods for Hořice sandstone and Božanov sandstone, in particular.

4.4 Water vapor transport properties

The water vapor diffusion resistance factor of all analyzed building stones (Table 4) was very low which can partially explain their successful use in historical buildings having traditionally no horizontal waterproof insulation, contrary to the contemporary structures. The moisture content in the walls of historical buildings could thus be moderated by the easy water vapor removal during the warm periods of the year. The values of the water vapor transport parameters were in a qualitative agreement with the total porosity (Table 1). Contrary to the liquid water transport, the total pore volume is a more important factor for water vapor transport than the pore size distribution [6].

	5/50%			97/50%			
Material		D			D		
	[s]	$[m^2s^{-1}]$	[-]	[s]	$[m^2s^{-1}]$	[-]	
PM	2.41E-11	3.32E-06	6.98	3.11E-11	4.28E-06	5.49	
РВ	1.27E-11	1.74E-06	13.38	3.08E-11	4.23E-06	7.18	
PH	1.55E-11	2.13E-06	11.59	3.07E-11	4.22E-06	5.77	
0	2.96E-11	4.06E-06	5.66	8.92E-11	1.23E-05	1.91	

Table 4: Water vapor transport properties of building stones

The measured data revealed that the values of water vapor diffusion coefficient corresponding to the lower values of relative humidity (5/50 %) were always lower than those for higher relative humidity values (97/50 %). This is related to the partial transport of capillary condensed water in the wet-cup arrangement [6].

4.5 Sorption isotherms

Figure 3 shows the measured adsorption (lower curves) and desorption (upper curves) isotherms. The highest overall water vapor adsorption capacity exhibited argillite. This was in accordance with its highest porosity (Table 1) and highest amount of small pores (Figure 1) having high specific surface. The lowest water vapor adsorption showed Božanov sandstone with the lowest porosity and very low amount of small pores. The other two sandstones were in between, Mšené sandstone being closer to argillite and Hořice sandstone closer to Božanov sandstone.

In the range of lower relative humidity up to 0.7, the highest capability of water vapor adsorption presented Mšené sandstone. This can be explained by a different adsorption mechanism in Mšené sandstone as compared to argillite. At very low relative humidity, the molecules of water are bound in one layer to the surface of pores by hydrogen bonds or van der Waals forces [6]. The significance of this phase of sorption was manifested by the relatively fast moisture increase in the initial region of the adsorption isotherm of Mšené sandstone which provided, apparently, a high amount of possible sites for bonding water vapor molecules. Once all surfaces of pores are covered by one layer of molecules, further layers begin to be formed, typically 2-3 at maximum [6]. This phase is characterized by the linear part of the isotherm; for Mšené sandstone the increase of adsorbed water vapor was here already less remarkable than for argillite. The final phase is the phase of capillary condensation, which can be expressed for a single capillary by the Kelvin equation [6]. Here, the amount of small pores up to 50 nm was clearly the decisive factor (Figure 1).

It should be noted that the differences in adsorption and desorption isotherms were for Mšené sandstone and argillite relatively high. This indicated a considerable amount of "bottleneck" pores.



Figure 3: Sorption isotherms of building stones

4.6 Thermal properties

Figure 4 shows that the dependence of thermal conductivity of studied building stones on moisture content was very significant; up to 100% increase of thermal conductivity was observed for water saturated specimens as compared with the dry state.



Figure 4: Thermal conductivity of building stones

The specific heat capacity increased considerably with increasing moisture content (Figure 5) which was related to the high specific heat capacity of water.



Figure 5: Specific heat capacity of building stones

6. Conclusions

For the determination of hygrothermal performance of historical buildings, methods of computational modeling are often applied in building practice and research. In this way, the time development of moisture and temperature fields can be obtained. This information can be then used for the identification of weak areas of investigated structures and possible future damage. On the basis of hygrothermal analysis coupled with mechanical models, the risk analysis of buildings and inbuilt materials can be done as well. However, in practical application of computational modeling, one must take into account the accuracy of calculated data which is critically dependent on the availability of all input parameters.

The experiments presented in this paper provided information on the basic physical properties, mechanical, hygric, and thermal properties of four building stones which were frequently used on the territory of the Czech Republic in medieval rimes. The obtained data revealed very significant differences in measured properties of the particular materials which underlined the necessity of such kind of experimental analysis before the materials' application.

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Temperature dependence of thermal parameters of building materials

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Abstract: The paper deals with new method of study of temperature dependence of thermal diffusivity a, thermal conductivity λ , and specific heat c. We assume that in the future this method can be used for characterization of thermal properties of materials used in building industry. The new method of measurement of thermal properties was based on increasing and decreasing step-wise and ramp-wise methods. The thermal parameters were determined from transient responses to heat power input with the application of multi-regression analysis. The dependences of thermal parameters together with heat source quality parameter s (or heat source fractal dimension D) and heat losses parameter R on time were calculated for different reference temperature for interval from 20 °C to 50 °C. All results were extrapolated to fractal dimension of ideal planar heat source (D = 2). The extrapolated values for model material (PMMA) correlate for 20 °C with table thermal parameters published in literature. Measured parameters of PMMA were compared and practicability of the new method of thermal properties measurement of solids was demonstrated. This method based on step-wise and ramp-wise can be used for study of other materials and give new information about temperature dependences of their thermal parameters.

Keywords: transient method, fractal model of heat transport, thermal diffusivity, thermal conductivity, specific heat

1. Introduction

Study of thermal parameters especially of building materials, which in this article will be discussed is the basis for the characterization of the materials and determines their next use. The dependences of thermal parameters of characterized materials on temperature have, of course, significant importance. Therefore, we deal with improving measurement methods that will provide accurate and reproducible results of the measured materials.

The general aim of this article is the study of thermal dependence of thermal parameters of materials. Currently, research on thermal parameters of various substances involved in many researchers used different methods that have different results. Based on previous experience, we decided to use and improve the measurement of thermal properties [1] and their dependence on temperature using transient pulse and step-wise methods [2], [3]. So far, we and also another researchers have used these methods separated, Bezjak a Zvizdič [4] for the determination of thermal conductivity of insulators, Bauer, Laing and Tamme have used this methods for characterization of sodium nitrate as a phase change material [5], Wu and Morrell have studied thermal expansion in thermal conductivity of insulators with hot-plate method [6] and Jensen & col. have dealt with thermal conductivity measurements with transient methods [7]. Currently we have proposed a new method that combines both ones and allows determining all of the thermal parameters of the studied materials together.

This new method enables due to short jump increases of power to determine all of the thermal parameters such as with using the pulse transient or step-wise method. This method is actually a combination of step-wise and ramp-wise method. The current study of thermal parameters of substances indicate that the results may be issued in several ways to achieve correct and reproducible results, some to determine the thermal parameters of materials use the differential scanning calorimetry (DSC) [8], [9], others are more inclined to transient methods. That depends on the way of evaluation and presentation of results. Currently, we are using our new method of evaluation process of the results of transient methods and DSC too.

Carslaw and Jaeger derived precisely the response to a unit of heat pulse delivered to the ideal planar heat source and infinite lossless sample, per integration this method was extended to the step-wise. The results of measurement of other configurations are discussed as well.

Application of fractals, the Carslaw and Jaeger theory [10] was generalized and can thus be used for the characterization of any type of heat source (point, linear, planar, volume, respectively generally fractal heat source) [11] for a step-wise increases of the supplied heat, if the sample has finite dimensions (heat losses are included).

In this paper, the results are extended to a ramp-wise method. There are derived thermal responses to a linear increase of power supplied to the system of the sample (ramp-wise). In the next part, there is a general derivation of the responses to step-wise heating and then from that derivation the pulse response of a linearly increasing power of heat.

In the experimental part the knowledge is applied – the new combined method of small heat increases – a ramp formed by step-wise increases.

To determine the thermal parameters the multi-parameter linear regression is used, which allows us identification of thermal parameters (diffusivity and thermal conductivity, specific heat, heat loss, but mainly fractal dimension of the heat source for which results have been found).

To allow comparison the results were re-calculated to the dimension of the ideal planar heat source.

2. Models of heat transfer

2.1 Ideal fractal Dirac Pulse Model

The dependence of the temperature change on time for a simple fractal model after a Dirac pulse of heat supply prom surface heat source can be derived with using of the term [12]

$$\Delta T(t) = \frac{Q}{c_{\rm p}\rho} (4\pi at)^{-s} \exp\left(-\frac{h^2}{4at}\right),\tag{1}$$

where $Q = P\Delta t$ means total pulse heat energy (*P* is a power of heat source, Δt width of the pulse), c_P is specific heat, *a* is thermal diffusivity and *t* is time and s = (E - D)/2 is heat source quality parameter. The special case for planar heat source (E = 3, D = 2) is [1, 3]

$$\Delta T(t) = \frac{Q}{c_{\rm p}\rho\sqrt{4\pi at}} \exp\left(-\frac{h^2}{4at}\right).$$
(2)

2.2 Ideal fractal Step-Wise Model

The thermal response for this model can be derived by integration of Eq. (1), assuming that the heat power P is constant. The dependence of temperature change on the time can be for planar heat source in this case described by

$$\Delta T(t) = \int_{0}^{t} \frac{P(4\pi at)^{-s}}{c_{\rm p}\rho} \exp\left(-\frac{h^2}{4at}\right) dt .$$
(3)

By a simple deriving (integrating per partes) we can get

$$\Delta T(t) = \frac{P (4\pi a t)^{1-s}}{4\pi (1-s)\lambda} \left[\exp\left(-\frac{h^2}{4at}\right) - \left(\frac{h^2}{4at}\right)^{1-s} \Gamma\left(s, \frac{h^2}{4at}\right) \right], \tag{4}$$

At this equation, the $\lambda = c_p \rho a$ is the thermal conductivity. The special case for planar heat source (*E* = 3, *D* = 2) is [1, 3]

$$\Delta T(t) = \frac{P}{2\lambda} \left[\frac{\sqrt{4\pi at}}{\pi} \exp\left(-\frac{h^2}{4at}\right) - h \cdot \operatorname{erfc}\left(\frac{h}{\sqrt{4at}}\right) \right].$$
(5)

 $\operatorname{erfc}(x) = \Gamma(1/2, x^2)/\sqrt{\pi}$ is complementary error function (also called the Gauss error function) and $x = h/\sqrt{4at}$.

2.3 Ideal fractal Ramp-Wise Model

The thermal response for this model can be derived by integration of Eq. (4), assuming that the heat power *P* is linear increased ($dP = P_0 dt = \text{const.}$). The dependence of temperature change on the time can be for planar heat source in this case described by (after neglecting of error function)

$$\Delta T(t) = \int_{0}^{t} \frac{P_0 (4\pi at)^{1-s}}{4\pi (1-s)\lambda} \exp\left(-\frac{h^2}{4at}\right) dt \,.$$
(6)

By a simple deriving (integrating per partes) we can get

$$\Delta T(t) = \frac{P_0 (4\pi at)^{2-s}}{16\pi^2 (1-s)(2-s)\lambda a} \left[\exp\left(-\frac{h^2}{4at}\right) - \left(\frac{h^2}{4at}\right)^{2-s} \Gamma\left(s-1,\frac{h^2}{4at}\right) \right],\tag{7}$$

By a simple deriving (integrating per partes) we can get

$$\Delta T(t) = \frac{P_0}{12a\lambda} \left[\frac{(4\pi at)^{3/2}}{\pi^2} \exp\left(-\frac{h^2}{4at}\right) - h^3 \cdot \operatorname{erfc}\left(\frac{h}{\sqrt{4at}}\right) \right].$$
(8)

2.4 General Fractal Model

The model will be derived from the fractal theory of a physical field published by authors in [13], [14]. The dependence of the temperature ΔT on the radius *r* of space-time for the thermal field [15] can be written for this model as

$$\Delta T(r) = -\frac{\hbar c}{k_{\rm B}} \frac{K r^{D-E+2}}{D \cdot (D-E+2)} \tag{9}$$

where \hbar is the modified Planck constant, *c* is the speed of heat propagation, *k*^B is Boltzmann's constant, and *E*, *D*, *K* are Euclidean and fractal dimension and fractal measure, respectively.

If heat source quality parameter is $\alpha = (D - E + 2)/2$, the size of the space-time vector is rewritten as $r^2 = r_T^2 - c^2(t - t_0)^2$, where r_T is the radius of topological space, t_0 is the time response delay, and $t_T = r_T/c$ is transit time, can be rewritten as

$$\Delta T(t) = -\frac{K\hbar c}{k_{\rm B}} \frac{(2c^2 t_0)^{\alpha}}{2\alpha \left(2\alpha + E - 2\right)} t^{\alpha} \left(1 - \frac{t_0^2 - t_{\rm T}^2}{2t_0 t} - \frac{t}{2t_0}\right)^{\alpha}.$$
(10)

And finally, if we define the absorption coefficient *A*, relaxation time constant $t_{\rm R}$, and diffusion time constant $t_{\rm D}$ as

$$A = -\frac{K\hbar c}{k_{\rm B}} \frac{(2c^2 t_0)^{\alpha}}{2\alpha \left(2\alpha + E - 2\right)}, \ t_{\rm R} = \frac{2 t_0}{\alpha}, \ t_{\rm D} = \frac{\alpha \left(t_0^2 - t_{\rm T}^2\right)}{2t_0}$$
(11)

we can write for the dependence of the change of temperature with on time, the equation,

$$\Delta T(t) = At^{\alpha} \exp\left[-\left(\frac{t_{\rm D}}{t} + \frac{t}{t_{\rm R}}\right)\right].$$
(12)

where $t_{\rm D} = h^2/4a$, $t_{\rm R} = R^2/4a$, $h = c\sqrt{t_0^2 - t_{\rm T}^2}$ is thickness of sample, $R = 2ct_0/\alpha$ is heat losses parameter (larger then radius of sample), and $a = c^2 t_0/2\alpha$ is thermal diffusivity.

Thermal absorption coefficient *A* (see Eq. 4, $\alpha = 1 - s$)

$$A = \frac{P(4\pi a)^{\alpha}}{4\pi\alpha\lambda} = -\frac{K\hbar c}{k_{\rm B}} \frac{\alpha^{\alpha-1}(4\pi a)^{\alpha}}{2\pi^{\alpha} (2\alpha + E - 2)}$$
(13)

depends on arrangement of experiment. For step-wise method (constant heat power) and ideal planar heat contact in 3D space (*E* = 3, *D* = 2) will be $\alpha = (D - E + 2)/2 = 1/2$ will be

$$A = \frac{P\sqrt{4\pi a}}{2\pi\lambda} = -\frac{K\hbar c}{k_{\rm B}}\sqrt{\frac{a}{2}}.$$
(14)

For pulse transient method (constant heat energy, P = Q/t) and ideal planar heat contact in 3D space (E = 3, D = 2) will be $\alpha = (D - E + 2)/2 = 1/2$ and

$$A = \frac{Q}{c_{\rm p}\rho\sqrt{4\pi a}} = -\frac{K\hbar c}{k_{\rm B}}\frac{\sqrt{4\pi a}}{2\sqrt{2\pi}}.$$
(15)

2.5 Method for Evaluation of Transient Measurement

The described method can be used for the determination of the real fractal model parameters, Eq.0 using a regression method applied to

$$\mathbf{y}(t) = \ln \Delta T(t) = \ln A + \alpha \ln t - \frac{t_{\rm D}}{t} - \frac{t}{t_{\rm R}} = m_0 + m_1 x_1 + m_2 x_2 + m_3 x_3 , \qquad (16)$$

where $x_1 = \ln t$, $x_2 = 1/t$, and $x_3 = t$. From the parameters m_0 , m_1 , m_2 , and m_3 the thermophysical and other parameters of the measured system can be calculated: the heat source quality parameter $\alpha = (D - E + 2)/2 = m_1$ (or fractal dimension *D* of heat source in 3D space, E = 3), the heat loss parameter proportional to the measured sample diameter $R = h\sqrt{t_R/t_D} = h/\sqrt{m_2m_3}$, the thermal diffusivity $a = h^2/4t_D = -h^2/4m_2$, and the thermal conductivity $\lambda = P/(4\pi\alpha A) \cdot (4\pi a)^{\alpha} = P/(4\pi m_1 e^{m_0}) \cdot (-\pi h^2/m_2)^{m_1}$. From the last two parameters and the known mass density ρ , the specific heat $c_p = \lambda/(\rho a)$ can be calculated.

2. Experimental

The experiment was set up for combination of step-wise and ramp-wise method of measurement.



Figure 1: Principal of step-wise, ramp-wise and combined way of measurement

The principal is shown on Figure 1. It is necessary to choose optimal value of power, pulse width and reference temperature. All these parameters influence measurement and results. The aim of this paper is to characterize this effect of pulse parameters to values of thermal parameters of measured materials. There were studied effects of the change of reference temperature, pulse width, value of power and direction of measurement (heating and cooling) to the shape of responses and to values of set parameters: thermal absorption coefficient, relaxation time constant, diffusion time constant and also the character of heat source.

Heat is spread in the three dimensional space (E = 3) from the heat source, which can has ideal thermal contact with its surrounding (point, linear, planar, volume heat source) or real thermal contact with its surrounding, in this case the value of dimension is higher or lower than in ideal case. If we calculate with ideal heat source, we distinguish some shapes of heat sources, see in Table 1.

Type of heat source	Fractal dimension of heat flow	Method of measurement
point	<i>D</i> = 0	hot ball
linear	D = 1	hot wire
planar	<i>D</i> = 2	hot plate
volume	D = 3	microwave

Table 1: The shape of ideal heat source

Character of sample heating we can describe due to some functions, see in Table 2. In the ideal case we can the heating describe according to Carslaw and Jaeger as a Dirac pulse. In the real situation can be realized as a rectangle pulse. Because of the rectangle pulse is used for the measurement.

Table 2: Character	r of sampl	e heating
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Type of heating	Description with function	Coefficient <i>a</i>
Dirac pulse	Dirac function $\delta(t)$	$\alpha = (D - F)/2$
Rectangle pulse	Rectangle function $\Pi(t)$	$\alpha (D L)/2$
Step-wise	Heaviside function <i>H</i> (<i>t</i>)	$\alpha = (D - E + 2)/2$
Ramp-wise	Ramp function <i>R</i> (<i>t</i>)	$\alpha = (D - E + 4)/2$

In the paper there are discussed results of measurement combined of step-wise a ramp-wise method (see on Figure 2). Heating of sample was realized by increasing respectively decreasing of power of heat pulses. Heating respectively cooling was realized relative to the reference temperature T_0 set by thermostat.



Figure 2: Character of the sample heating and cooling

3.1 Effect of pulse width on PMMA results

The experiment was realized for different initial conditions (steady state) within the temperature interval $T_0 \in \langle 20, 100 \rangle$ °C. The initial temperature was set by thermostat this is the reference temperature for measuring of heat responses by the differentially connected thermocouple. Heating of the sample was realized by planar heat source, which is nickel foil in a film of Kapton with diameter of 3 cm, maximal current was set to the value of 1 A by voltage of 1.7 V. The pulse width and value of increment of power was given by number of steps. Parameters of individual experiments are listed in Table 3 and Table 4. All of the experiments were realized for two reference temperatures 20 a 50 °C.

pulse width (min)	measurement direction	temperature (°C)	power increment (W)	change of temperature (K)	α
15	up + down	20	0.024	0.84	1.29
15	up + down	50	0.023	0.78	1.25
20	up + down	20	0.024	0.85	1.10
30	up + down	50	0.023	0.80	1.11
(0)	up + down	20	0.024	0.86	0.85
60	up + down	_	_	-	_

Table 3: Parameters of individual experiments, pulse number 50

Table 4: Parameters of individual experiments, pulse number 100

pulse width (min)	measurement direction	temperature (°C)	power increment (W)	change of temperature (K)	a
15	up + down	20	0.012	0.44	1.22
15	up + down	50	0.012	0.40	1.36
20	up + down	20	0.012	0.42	1.09
	up + down	50	0.011	0.40	1.12
(0)	up + down	20	0.012	0.42	0.90
60	up + down	-	-	-	_

To characterize effect of pulse width on thermal parameters of measured material there is shown a comparison of results of experiments 4, 5, 6 (see on Table 3) for PMMA. The experiments were arranged at reference temperature $T_0 = 20$ °C, pulse width was set on 15 min, 30 min and 60 min by the same value of power. The typical processes of heating and cooling are shown on Figure 3.



Figure 3: Sample heating and cooling for different pulse width

These results were obtained by reference temperature $T = 20 \,^{\circ}\text{C}$. The required parameters (thermal diffusion coefficient *A*, heat source parameter α , diffusion time constant t_{D} , relaxation time constant t_{R}) were calculated from linear regression.

Parameter α depends on the pulse width. However the extrapolation to the ideal heat source parameters we get the same values. In the Table 3 and Table 4 there are shown the values of

parameter α for the measurement with 50 and 100 pulses. Parameter α depends on proportion of step-wise : ramp-wise. For longer steps (60 min) of the same value of power corresponds parameter α to step-wise function $\alpha = (D - E + 2)/2$. For the short steps (15 min) the value of α approaches to a ramp function $\alpha = (D - E + 4)/2$, see chap. 1.4. Values for the ideal planar heat source we obtain after extrapolation of calculated parameters.

We can see that for results of narrow pulse is the value of α over 1 which corresponds more with ramp function, for the width pulses the value of α approaches more to step-wise character. The narrow pulses are less affected by fluctuations in ambient temperature error (measurement takes 15 minutes), width pulses are affected uncertainty, experiment takes 60 minutes. The individual experiments are carried out under different conditions of temperature of surroundings, suggesting that the shorter the whole experiment, the overall results are less affected by error (see Table 5).

pulse width (min)	To	α(-)	D (-)	$\frac{A_{\alpha}}{(\text{kg.m}^{-2}.s^{-\alpha})}$	t⊳ _α (s)	t _{Rα} (s)
15	20 °C	1.25	3.51	0.026	69.23	3.23.10-9
15	50 °C	1.15	3.29	0.024	58.44	2.47·10 ⁻⁹
20	20 °C	1.10	3.19	0.025	81.08	1.21.10-7
	50 °C	1.08	3.17	0.024	81.82	2.90.10-8
(0	20 °C	0.92	2.84	0.025	85.71	6.44·10 ⁻⁹
60	50 °C	-	-	-	-	-

Table 5: Overview of parameters for individual experiments

This method was based on the recalculation of all parameters to fractal dimension D = 2 using the equation $a = 2a_0/(D - E + 2) = a_0/(1 - s)$. In this case, the evaluation was performed of one hundred data by dragging multi-parametric linear regression (16) through the different positions in time response of change temperature. Number of data used for multi-parametric linear regression was 209 for pulse width 15 min. For the dragging method the number of data was reduced by 10 to 199, the linear regression was performed 10 times. Basic analysis was done for all of the data, by extrapolation of different analysis (the data 1–199, 2 – 200, ..., 10–209) we will get different parameters due to measurement uncertainty. For other pulse width was algorithm modified (439 for pulse width 30 min and 875 for pulse width 60 min) The dependences of all parameters on time were recorded.





Figure 4: Results of approximation of data of individual experiment (number of data 50, reference temperature 20 °C, length of experiment 30 minutes)

The results of extrapolation for PMMA are the yellow coloured points (see on Figure 4). They are listed in Table 6. The green coloured points represent the calculation. As you can see in Table 6 the measured values of PMMA thermal parameters correspond to their tabular values. This way of thermal parameters measurement is apparently applicable to the measurement of thermal parameters of other materials.

pulse width (min)	To	A (kg.m ⁻² .s ^{-1/2})	<i>t</i> ⊳(s)	tr (s)	R (m)	a (mm ² .s ⁻¹)	Cp (kJ.K ⁻¹ .kg ⁻¹)	λ (W.m ⁻¹ .K ⁻¹)
Tabulated values	-	-	-	-	-	0.112	1.45	0.193
45	20 °C	0.026	69.23	3.23.10-9	0.041	0.130	1.92	0.297
15	50 °C	0.024	58.44	2.47.10-9	0.039	0.154	1.67	0.306
20	20 °C	0.025	81.08	1.21.10-7	0.232	0.111	1.98	0.262
30	50 °C	0.024	81.82	2.90.10-8	0.113	0.110	2.27	0.298
	20 °C	0.025	85.71	6.44·10-9	0.052	0.105	2.59	0.325
60	50 °C	_	-	-	-	-	-	-

Table 6: Overview of extrapolated parameters for individual experiments, = 1/2

3.2 Measurement of temperature dependences of PMMA

In the Figure 5 there are listed the temperature dependences of diffusion time extrapolated to an ideal planar heat source, D = 2, $\alpha = 1/2$ for all of the experiments (see Table 6). Long-term experiment (100 × 60 minutes) was carried out only for the reference temperature of 20 °C. From the dependences is clear that the diffusion time (and therefore diffusivity) varies slightly depending on temperature. Best continuity between the two reference temperatures was for 15 minutes, 50 pulses. It is obvious that the reference temperature of 50 °C and 100 pulses experiments are loaded higher noise. For width pulses (dominant step-wise) the errors caused by noise are significant as compared with than for narrow pulses (ramp-wise).



Figure 5: Temperature dependences of diffusion time extrapolated to D = 2, $\alpha = 1/2$

From the dependences (shown on Figure 6) it is evident that these parameters are very close to table values of these parameters for PMMA. Parameter α depends on pulse width, we can see that for results of narrow pulse is the value of α over 1 which corresponds more with ramp function, for the width pulses the value of α approaches more to step-wise character.



Figure 6: Temperature dependences of heat source parameter

This fact is confirmed by the dependence of the coefficient α from the image (see on Figure 6). It is obvious that for narrow pulses is the value of coefficient α higher (for ideal ramp-wise will be α = 1.5, for width pulses is the value of coefficient α smaller than one, for ideal step-wise will be α = 0.5).

From the measurement results, it is clear that for best results, it is advisable to use the shortest possible measurement. It is clear that an extrapolation burdens experiment results smaller error than the implementation of long-term measurements. Power must be sufficient to not show errors and quantization error noise temperature. Based on this consideration, in this article were

presented results of measurement implementing following criteria: measurement duration is 15 or 30 minutes, number of pulses is 50.



Figure 7: Temperature dependences of thermal diffusivity extrapolated to D = 2, $\alpha = 1/2$

Measured values of thermal diffusivity are in good agreement with the table values. On Figure 7 is evident the continuity of the results measured by 20 °C and 50 °C.



Figure 8: Temperature dependences of absorption coefficient extrapolated to D = 2, $\alpha = 1/2$

Absorption coefficient varies linearly (see on Figure 8), it is related to the thermal conductivity. Extrapolated absorption coefficient depends on the power, thermal diffusivity; absorption coefficient depends also on the character of the experiment and the shape of the heat source.



Figure 9: Temperature dependences of thermal conductivity

On Figure 9 there is shown the dependence of thermal conductivity on the temperature. The values of thermal conductivity are slightly higher than the tabulated value for PMMA. This difference is caused by the ration of ramp-wise and step-wise character of measurement.



Figure 10: Temperature dependences of specific heat

The results of temperature dependence of PMMA specific heat are in good agreement with tabulated value. Also on Figure 10 we can see continuity of measurement by different reference temperature. It follows that this new method of measurement of thermal parameters combining ramp-wise and step-wise is useful for measuring thermal parameters and their temperature dependence for other materials.

3. Conclusion

The main aim of this paper was study of thermal parameters of solids by increasing and decreasing step-wise and ramp-wise methods. These two methods were combined and thermal parameters of PMMA were measured by the new method. The thermal parameters were determined from transient responses to heat power input with the application of multiparametric regression analysis. All results was also extrapolated to fractal dimension of ideal planar heat source (D = 2). The extrapolated values for model material (PMMA) correlate for 20 °C with table thermal parameters published in literature. The results show that heat source parameter α depends on character of heating. Parameter α depends on ratio of stepwise : ramp-wise. For width pulses (60 min) of the same value of power corresponds parameter α to step-wise function. For the narrow pulses (15 min) the value of approaches to a ramp function. With the combined ramp-wise method we can obtain correct and reproducible results to characterize the thermal parameters of materials. Testing of this method was performed on PMMA which is model material with tabulated values of thermal parameters. These measurements confirmed that the combined ramp-wise method is suitable for determining the thermal parameters of substances and it is therefore advisable to continue using it for determining the thermal parameters of building materials and other substances. The results show that the measurements carried out at a reference temperature of 20 °C and 50 °C give sufficient information about the behaviour of thermal parameters of the examined substances in the whole interval, results of these two measurements provide sufficient continuity. It was necessary to choose the optimal pulse width and of course power. When the pulse is too narrow the temperature in the sample is saturated not enough. If the pulses are too width or the long measurement period is used the sample is more susceptible to influence of surroundings. According to requirements the preferably measurements of thermal parameters are of the measurement duration of 15 or 30 minutes. Variations in measurements shown in the figures for individual thermal parameters were due to precision measuring instruments.

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Dynamic mechanical analysis of double base solid rocket propellant with addition of soot

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Abstract: The paper deals with Dynamic Mechanical Analysis (DMA) of double base solid rocket propellant (black) [1] of density rho=1.55 g/cm3 at room temperature with addition of soot. Its mechanical properties such as storage modulus (E'), loss modulus (E'') and internal friction $(\tan \delta)$ were measured using Netzsch DMA 242C analyser [2] within temperature range from -120 0C up to +90 0C at 1 K/min of heating rate. Test sample was subjected to the dual cantilever mode with frequency f = 1Hz recommended by the appropriate European standard. A special attention was paid to the problem of a proper selection of the parameters of the analyzer and the sample thickness which were essential to obtain correct DMA results. In addition to this the specific heat of black (with soot) and brown (without soot) double base solid rocket propellants were determined using Netzsch DSC 404 F1 Pegasus apparatus. The results of DSC investigations were obtained by applying our own numerical procedure according to Panas et al [3] in order to take into account the time base drift influence on the specific heat results. To validate the results of DMA measurements polytetrafluoroethylene (PTFE) was used as a reference material [4].

Keywords: DMA, solid rocket propellant, mechanical properties, specific heat

1. Introduction

Double base rocket propellants consist mainly of nitrocellulose (NC) 50-60% and nitroglycerine (NG) 30-39% which deliver energy to the system and other plasticizers, stabilisers, inorganic catalysts. For example, addition of soot and/or oxides or salts of certain metals - modify the course of combustion [5]. For the sake of usage double base rocket propellants belonging to the group of viscoelastic polymeric materials [6] as a fuel of rocket motors it is important to know their thermal and mechanical properties which may affect the proper operation of the rocket engines leading up even to its explosion. Changing of mechanical properties for such materials are caused by physical processes (e.g. migration of plasticizers and humidity), chemical reactions (e.g. oxidative cross linking like decomposition of nitrates to nitrogen oxides) and mechanical processes (e.g. acceleration, rotation, mechanical vibration, fast increase of pressure, etc.) occurring in double base rocket propellants under conditions of their storage and operation. A powerful technique for determination of mechanical properties of rocket propellants such as dynamic storage modulus E' which represents the elastic properties of material, dynamic loss modulus E" which represents the viscous properties of material and $tan(\delta) = (E''/E')$ which represents the damping of material is the dynamic mechanical analysis. In DMA technique the input signal is a sinusoidal oscillating force with a small amplitude of several Newton subjected to the investigated sample. As a result, the sample begins to deform in an oscillating manner generating in-phase and out- of-phase strains (output signal). The difference between the applied stress and the resultant strain is an angle, δ . The storage E' and the loss E" moduli in this experimental technique can be measured as a function of time,

frequency of oscillation and temperature according to a program of investigation set by the user. As one can see, by testing rocket propellant samples using DMA technique let you specify the strength of the material under dynamic loads and its ability to irreversible dissipation and conservation of mechanical energy supplied during the periodic loads. This is of particular interest in order to be able to predict rocket motors behavior during possible operational use. In the relevant literature [6, 7] one can spot information about an influence of individual experimental parameters like heating rate, sample dimensions, used gas and frequency on the DMA results, nevertheless, there is hard to find details about correct execution of the experiment. The purpose of this paper is partially to fill the resulting gap.

2 Experiment description

2.1 DMA experiment

Sample of double base rocket propellant with a small amount of soot with density $\rho = 1.55$ g/cm³ at room temperature were used as an object of DMA investigations within temperature range from -120 °C up to +90 °C. The test specimens were first cut out from a piece of hollow cylinder made of double base solid rocket propellant along its axial direction and then they were ground in by hand using abrasive paper until they reached a rectangular shape. There were four test specimens (S1,...,S4) and one extra specimen made of PTFE treated as a reference material. The test specimens were next subjected to DMA investigations using Netzsch DMA 242C analyser with sample holder 2 x 16 mm in dual cantilever mode. The frequency *f* = 1Hz, recommended by the appropriate European standard, and the heating rate at 1 K/min or 2 K/min were chosen. In table 1 there were given DMA parameters used for experimental research. According to DMA 242C operating instructions [2] the sum of the static and the dynamic forces should be selected in such a way as to not exceed a total value of 8N. However, in case of dual cantilever mode, it is recommended by Netzsch manufacturer to accept the static force as equal to zero. In the last column in table 1 there are also given the assumed values of amplitude of bending of

Specimen	Thickness, width, length / mm	Temp. range / ºC	Heating rate / K/min	Static force /N	Dynamic force / N	Amplitude / µm
S1	4.28, 10.0, 60.0	-120 ÷ +80	2	0	7.5	40.0
S2	2.74, 10.0, 60.0	-120 ÷ +80	2	0	7.5	30.0
S3	1.15, 10.0, 60.0	-120 ÷ +90	1	0	7.5	30.0
S4	1.15, 10.0, 60.0	-120 ÷ +90	1	0	7.5	50.0
PTFE	1.97, 9.7, 60.0	-150 ÷ +150	1	0	7.3	40.0

Table 1: DMA input parameters for dual cantilever mode

sample in (μ m), chosen within the range from 0.01 μ m up to 240 μ m, which should be achieved by the sample during experiment as a result of acting force (dynamic force) on it. Temperature

range of measurements from -120 °C up to +90 °C or from -150 °C up to +150 °C was feasible by using for this purpose the liquid nitrogen.

2.2 DSC experiment

Two kinds of sample of dual base rocket propellant were used for the specific heat measurements using Netzsch DSC 404 F1 Pegasus apparatus. The first sample (black, $m_1 = 51.28$ mg) of dual base rocket propellant involved soot and was taken from the same piece of hollow cylinder as the specimens (S1,...,S4). The other one sample (brown, $m_2 = 46.22$ mg) of dual base rocket propellant didn't contain soot. The temperature characteristic of the specific heat $c_P(T)$ of testing materials using DSC technique was obtained using three-curve procedure, i.e. the base curve, the reference curve using sapphire as a standard material and the curve of investigated material. Temperature range of investigation was from +25 °C up to +55 °C. As an inert gas helium was used. The mass of the reference sapphire was $m_{ref} = 85.04$ mg. The mass of reference crucible was $m_{re} = 273.94$ mg. The temperature program was performed twice in the following way: isothermal at +25 °C for 20 min, heating up to +55°C at 5 K/min, isothermal at +55°C for 20 min, cooling down to +25 °C at 5 K/min, isothermal at +25°C for 20 min. Due to the fact that the commercial software doesn't allow to calculate the specific heat with respect to the base line measured before and just after finishing the measurements it was decided to apply our own procedure according to the formula given in [3]

$$c_{p}(T) = \frac{m_{ref}}{m} \frac{\dot{H}(T) - \dot{H}_{b}(T)}{\dot{H}_{ref}(T) - \dot{H}_{b}(T)} c_{p,ref}(T)$$
(1)

where $\dot{H}_b(T)$, $\dot{H}_{ref}(T)$, $\dot{H}(T)$ stand for the enthalpy fluxes with respect to the base, reference material (sapphire) and the test sample, respectively, m_{ref} and $c_{p,ref}$ is the mass and the specific heat of sapphire, respectively and *m* is the mass of test specimen.

The correlation function for the specific heat of the NBS reference sapphire $c_{p,ref}(T)$, which values are tabulated by Netzsch within temperature range from 273.15K up to 1873.15K, was chosen in the form (determination coefficient $R^2 = 3.959 \cdot 10^{-6}$)

$$c_{p,ref}(T[K]) = a_0 + a_1 T + \frac{a_2}{T^2} + a_3 T^3 + a_4 T^4 + a_5 T^5 + a_6 \ln(T), \ \mathbf{J} \cdot \mathbf{g}^{-1} \mathbf{K}^{-1},$$
(2)

with the coefficients *ai* given in table 2

Table 2: Coefficients for calculating the specific heat of reference sapphire based on Eq. 2

$a_0 = -4.96823635445709$
$a_1 = -1.82630640547086$ E-003
$a_2 = -1.53532615749585E+003$
$a_3 = +7.47063054335224$ E-010
$a_4 = -4.28782054156033\text{E}{-}013$
$a_5 = +7.68617373541201E-017$
$a_6 = +1.10372836726587$

3. Results and discussion

In figure 1 (left part) for each investigated specimen (S1,...S4) there are shown the storage modulus *E'* (in brown), loss modulus *E''* (in red) and tan(δ) (in blue) obtained experimentally using DMA 242C analyser together with dependence of amount of complex total amplitude |A| and dynamic force *F_dyn* on temperature. As one can notice easily in figure 1 specimen S1 of thickness 4.28 mm is too rigid within the temperature range from -120 °C to +58 °C in order to achieve the amplitude of 40 µm. The specimen S2 of thickness 2.74 mm likewise specimen S1 is too rigid within the temperature range from -120 °C. Programmatically established amplitude (30µm for S3 and 50µm for S4) is reached only by the specimens S3 and S4. It can be



Figure 1: Results of DMA investigations vs. sample thickness and DMA input parameters (see Table 1)

seen that, in the entire temperature range DMA test results may be considered reliable only for specimens S3 and S4. In figure 2 the results of storage modulus *E'*, loss modulus *E''* and tan(δ) of double base rocket propellant with soot (specimen S3) are presented. The storage modulus *E'* is dropping dramatically at temperature -57.6 °C (onset temperature) which is caused by the process of softening of this material. The peak on the loss modulus *E''* at -44.2 °C is regarded as the glass transition temperature [8] which is shifted of about 9 K on the right in comparison to the results reported by Mušanić et al [6] (-53.22 °C). The tan(δ) reaches its maximum twice: at -35.3 °C and at +73.0 °C which correspond to the regions of glass transition and the softening one, respectively. In order to verify our own results of DMA investigations of double base propellant the PTFE material which was thoroughly examined by Blumm et al [4] was accepted as a reference one. In figures 3a, 3b there are shown the results of our own DMA investigations in dual cantilever mode of PTFE together with the dependency of complex total amplitude |A| and dynamic force F_dyn on temperature for this material. Comparison of our own results with the DMA results reported by Blumm et al [4] for PTFE material are given i table 3.



Figure 2: Results of DMA investigations in dual cantilever mode of double base rocket propellant (specimen S3)



Figure 3a: Results of our own DMA investigations in dual cantilever mode of PTFE



Figure 3b: PTFE Complex total amplitude /A /and dynamic force F_dyn on temperature

	Storage modulus E'	Loss modulus E''	Tan(δ)
Blumm	Onset, endset: -122.9 ,	Peak: -104.7, +27.8 / ºC	Peak: -100.1, +37.6,
et al [4]	19.2, 39.0, 110.1 / °C		+135.8 / ^o C
Own	Onset, endset: -118.2,	Peak: -105.0, 26.5 / ºC	Peak: -97.4, 29.2,
results	22.5, 38.6, 113.7 / °C		129.1 / ºC

Table 3: Results of DMA investigations of PTFE

As one can see in table 3 all the temperatures important for DMA analysis and obtained experimentally differ little from each other. When comparing figure 7 in [4] with figure 3a it can be seen greater differences in the values of storage and loss moduli. For example the loss modulus at -104.7 °C have values of about 400 MPa [4] and 252 MPa, respectively. The difference of the loss and the storage moduli values may be due to a kind of test material (there are different PTFE materials), dimensions of the specimen (e.g. 2.10mm x 10mm x 55mm – [4]) and the kind of DMA mode (three-point sample bending – [4]). In figure 4 results of the specific heat investigations of black and brown sample of double base propellants using Netzsch DSC 404 F1 Pegasus apparatus and our own procedure are illustrated. As can be easily seen in figure 4 the specific heat values of the black (with soot) and brown (without soot) double base propellants hardly differ from each other within temperature range from +30 °C up to +50 °C during 1st heating. The average value of the specific heat in this temperature range can be accepted as 980 J/kg/K. The results of the specific heat obtained during cooling period were cut off at about 40 °C because the assumed temperature cooling rate at 5 K/min was not possible without possession of suitable cooling system.



Figure 4: Results of the specific heat investigations of black and brown sample of double base propellants using Netzsch DSC 404 F1 Pegasus apparatus and our own procedure

4. Conclusion

In this paper the results of DMA and DSC investigations of double base solid rocket propellant with addition of soot were presented. In addition to this a sample of PTFE was used as a reference material to verify DMA results with the ones reported by Blumm et al in [4]. The main conclusion resulting from the carried out experiments is that the results of the storage and the loss moduli should be given together with the dependency of complex total amplitude |A| and dynamic force F_dyn on temperature. In the case of non-compliance with this condition results of DMA investigations may be subject to large errors. The presented studies are preliminary and will be developed in the near future.

Acknowledgments

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The thermal conductivity and specific heat capacity of soil

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Abstract: The paper deals with the study of thermophysical properties (the thermal conductivity and specific heat capacity) of soil. The thermal conductivity was measured by the hot-wire method and the specific heat capacity by the differential scanning calorimetry. We investigated soil samples which were taken at two different localities of Nitra and drained in a laboratory furnace before the measurement. The thermal conductivity of soil from the two localities was found to be 0.21 W·m-1·K-1 and 0.39 W·m-1·K-1, respectively. The values of the specific heat capacity in the temperature range from -25 °C to 35 °C from the two localities were found to be 0.71 – 0.85 kJ·kg-1·K-1 and 0.78 – 0.89 kJ·kg-1·K-1, respectively.

Keywords: thermal conductivity, specific heat capacity, soil

1 Introduction

The thermal conductivity of a soil depends on the mineralogical composition, texture, and structure of the soil, but mostly on its moisture. If the moisture is too low, the heat is transferred through spot contacts of conductive elements and the air works as a heat isolator. As soon as the aquatic films are created, a rapid growth of contact areas appears and the rate of the thermal conductivity increases with moisture. As the moisture increases, these contact areas grow slowly and at a high moisture the rise of the thermal conductivity is caused only by the reduction of the air capacity [1].

Studies of the thermal conductivity and specific heat capacity in dependence on the moisture and granularity have been already carried out [2-6]. It was found out that the thermal conductivity increased with moisture and that the thermal conductivity was even higher if the soil granularity decreased.

The determination of thermal properties of soil, like the thermal conductivity, the specific heat capacity, and the thermal diffusivity, is important in agriculture, engineering, and geology. Some studies [7] showed that the rates of soil thermal properties were dependent mostly on the volume share of the air in the samples.

The thermal conductivity of the soil is a crucial factor for the draft of a thermal pump system. Thermal pumps are a technology which can be used to heat or to condition houses in an effective and ecological way. The knowledge on the rates of the thermal conductivity is necessary for the analysis and finding of the initial investment, energy saving, and operating power of the system. That is the reason why many works deal with the topic of measuring soil thermal conductivity [8, 9].

The aim of this work was to compare the thermal conductivity and specific heat capacity of soil from two different localities in Nitra, Slovakia, and also to find out if the hot-wire method and determination of the specific heat capacity using the differential scanning calorimetry (DSC) are suitable methods for the investigation of soil samples.
2 Experimental

2.1 Samples

The studied samples of soil came from two localities (one locality was near the kindergarten in Párovce and the other one near the main post office of Nitra) and were processed for the usage in the apparatuses for measurement of powdery samples. At first big impurities (also of organic origin) were removed from the samples and subsequently the soil was grinded. Then the samples were ready for a hot-wire measurement. For the measurement of the specific heat capacity the powder samples of soil were prepared which were suitable for a DSC measurement. Before the measurement the samples were drained in a laboratory furnace.

2.2 Measurement methods

For the determination of the thermal conductivity of soil samples we used the hot-wire method. It is a dynamical method based on the measurement of the temperature increase in the sample at a defined position from a heat source. The linear heat source (a hot wire) affects the volume of the tested material and its power per unit length is constant. Then, the thermal conductivity λ is determined from the relation between the temperature increase ΔT and the logarithm of time *t* [10],

$$\lambda = \frac{q}{4\pi K},\tag{1}$$

where *q* is the power of the linear heat source per unit length and *K* the slope of the linear part of the relation between ΔT and ln *t*. In the ideal case the relation should be linear in the whole time interval, but due to different specific heat capacity, thermal resistance, and finite dimension of samples and heat source nonlinearities may occur at the beginning of the measurement and also after a long time interval. In our calculations only the linear part of the relation is used.



Figure 1: The scheme of an experimental arrangement of the hot-wire method

The samples were placed into a thermally isolated vessel (Figure 1). The linear wire as a hot wire was fitted through the center of vessel. In this case the kanthal wire with a diameter 0.4 mm and powered from a constant DC supply was used. The voltage and current in the wire

was recorded by a voltmeter and an ampere-meter, respectively. The measuring values were used for the calculation of the wire power per unit length.

A temperature sensor was placed in the sample parallel to the hot wire. Since the measurement was performed at room temperature, a thermistor was used as a sensor. The advantage of a thermistor is that the sensitivity for temperature changes in the measuring interval is better than for common thermocouples. Also, the surface of a thermistor is larger than the surface of a thermocouple, and therefore a possible inaccuracy resulting from the sensor location with respect to the grain distribution in the sample is eliminated. As the relation between the resistance R and the thermodynamic temperature T is nonlinear, the Steinhart-Hart equation was used for its description [11],

$$\frac{1}{T} = a + b \ln R + c \left(\ln R \right)^3, \tag{2}$$

where the coefficients *a*, *b*, *c* were determined using the measurement in a separate furnace. The resistance of the thermistor was measured by an ohmmeter, and the time was recorded simultaneously from the beginning of the measurement.

For the determination of the specific heat capacity (c_p) of the samples we used the Differential Scanning Calorimetry (DSC). It is a thermoanalytical method where the differences of power needed for the measured and the reference sample heating are measured in the temperature or time dependence [12].

For the measurements powder samples are usually used. The studied sample and the reference sample are put into pans. The mass of the samples is of order 10⁻⁴ g. An empty pan is usually used as a reference sample. The measuring furnace of a calorimeter is purged with a gas because the combustion gases are often liberated from the samples [13].

For the determination of the specific heat capacity it was needed to measure three DSC curves: the baseline, DSC curve of the studied sample, and DSC curve of the reference sample (which is usually sapphire). The measuring mode must be as follows: isothermal heating – linear heating – isothermal heating. The duration of the isothermal heating is at least 2 min. The isothermal heating is used for the determination of the baseline. Then the relation between the thermal flow and time is measured.

If we subtract the measured values of the sample and the standard from the baseline, we obtain new curves which are without the effect of device. The specific heat capacity of the sample is then calculated as [13]

$$c_{p} = \frac{1}{m} \left(\frac{\partial H}{\partial T} \right)_{p} = \frac{1}{m} \left(\frac{\frac{\partial H}{\partial t}}{\frac{\partial T}{\partial t}} \right)_{p} = \frac{1}{m} \frac{\Delta P}{\beta},$$
(3)

where *m* is the mass of the sample, *H* is the enthalpy of reaction, and ΔP is the difference of the power which is needed for the sample and the reference sample heating.

Our measurements were carried out in aluminum pans with a mass about 40 mg. For the determination of the specific heat capacity we applied the temperature regime from -25 °C to

35 °C with a heating rate 10 °C·min⁻¹, the duration of the isothermal heating was 5 minutes. All experiments were performed using the device Mettler – Toledo DSC822^e.

3 Results and discussion

At first we will discuss the measurement of the thermal conductivity of soil. For each measurement of the thermal conductivity the plots of the relation between the increase of temperature and the logarithm of time was plotted (see Figure 2). Then the plot was fitted by a line whose slope K was derived. From this slope and the power per unit length q the thermal conductivity was calculated using Eq. (1). For the accuracy of the results, the measurement was repeated 5 times for each sample.



Figure 2: The relation between the increase of temperature and logarithm of time for one of the measurements

The result of the thermal conductivity of the soil sample from the locality Kindergarten Párovce was $0.21 \pm 0.01 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, while from the locality Main Post Office it was $0.39 \pm 0.03 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. The rate of inaccuracy occurs because the linear part of the plots was determined empirically. Namely, we proceeded as follows: we selected the beginning and end points of the linear part step by step and then found the best value of the regression coefficient R^2 (the closest value to 1).

The other investigated soil property was the specific heat capacity which was studied by the DSC and our results are given in Figure 3. The specific heat capacity for soil from the locality Kindergarten Párovce increases from 0.71 to 0.85 kJ·kg⁻¹·K⁻¹ in the whole temperature interval (from –25 °C to 35 °C). At the locality Main Post Office the specific heat capacity of soil is lower in the same interval, ranging from 0.78 to 0.89 kJ·kg⁻¹·K⁻¹. The difference between these two localities is about 5 % at temperature –25 °C and 10 % at 35 °C. For the accuracy of the results the measurement of the specific heat capacity was repeated 3 times for each sample and under the same conditions.



Figure 3: The relation between specific heat capacity and temperature of the samples from the two localities (gray line – Main Post Office, black line – Kindergarten Párovce)

4 Conclusions

In this study the thermophysical properties (the thermal conductivity and specific heat capacity) of soil were studied. The thermal conductivity was measured by the hot-wire method and the specific heat capacity by the differential scanning calorimetry. Two different soil samples from two localities of Nitra were investigated. Before the measurement the samples were drained in a laboratory furnace. The thermal conductivity of soil at room temperature from the locality Kindergarten Párovce is 0.21 W·m⁻¹·K⁻¹ and it is lower (by almost 50 %) than from the locality Main Post Office (0.39 W·m⁻¹·K⁻¹). We found out that the hot-wire method using thermistor as a temperature sensor is suitable for the measurement of the thermal conductivity of soil. The values of the specific heat capacity in the temperature range from -25 °C to 35 °C from the two localities were 0.71 – 0.85 kJ·kg⁻¹·K⁻¹ and 0.78 – 0.89 kJ·kg⁻¹·K⁻¹, respectively. The samples in the DSC are very small (around 50 µl), and therefore we can conclude that the DSC method is not really appropriate for the investigation of the specific heat capacity of soil, although the results could be used as yielding approximate values of the specific heat capacity.

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Effect of temperature on evolution of hydration process in different cement pastes

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Abstract: Predicting time evolution of cement hydration process is of strategic importance for the concreting of massive structures. The amount of heat generated during cement hydration depends mostly on the chemical composition of the cement. In general, higher curing temperature, higher cement content and finer cement grains cause an increase of the heat of hydration. If this heat is not rapidly dissipated, a significant rise of the temperature can occur in interior part of a massive concrete structure. This may result in considerable tensile stresses of the surface zone and in material cracking. To determinate the hydration degree evolution, the heat flow calorimetry was applied. The tests were performed by means of the TAM Air isothermal calorimeter, to determine the evolutions in time of hydration degree and its rate. The tests were performed at temperature of 20°C, 30°C and 40°C for the cement pastes made of: CEM I, CEM III and CEM V, with the water – cement ratio of 0,47. The widely used in mathematical modelling of cement hydration process, normalised chemical affinity functions and activation energy of hydration process at different degrees of its advancement, were determined for the analyzed cement pastes.

Keywords: Cement hydration, isothermal calorimetry, activation energy, numerical model of cement hydration process.

1. Introduction

Predicting time evolution of cement hydration process is of strategic importance during designing concreting technology of any massive concrete structure. The amount of heat generated during cement hydration depends mostly on the chemical composition of the cement. In general, higher curing temperature, higher cement content and finer cement grains cause an increase of the heat of hydration. If this heat is not dissipated with a sufficiently high rate, a significant rise of the temperature can occur in an interior part of massive structure. This may result in considerable tensile stresses of the surface zone and even in material cracking.

To determinate the evolution of hydration process and associated heat production isothermal calorimetric technique can be applied. Knowing the amount of heat generated by hydration process over a given time period, the so-called *source function* [1], describing the evolutions in time of hydration degree and its rate, can be determined. This function is widely used in modelling of hygro-thermal performance and strains of concrete at early ages, see e.g. [2].

In this paper the results of isothermal calorimetric tests performed at temperature of 20°C, 30°C, and 40°C for the cement pastes made of: CEM I, CEM II, CEM III and CEM V, with the water – cement ratio of 0.47, are presented. The activation energies of hydration process for the

materials are determined and their applicability for the description of temperature effect on the evolution of hydration is discussed.

2. Mathematical model of cement hydration

The advancement of the hydration process can be described by the so called hydration degree Γ_{hydr} , which is defined as follows [2],

$$\Gamma_{hydr}(t) = \frac{Q_{hydr}(t)}{Q_{hydr\infty}},$$
(1)

where $Q_{hydr}(t)$ is amount of heat released during hydration until time instant *t*, and $Q_{hydr\infty}$ is the total amount of heat released during this process.

The evolution of cement hydration process can be described by the following rate type relationship [2],

$$\dot{\Gamma}_{hydr} = \frac{d\Gamma_{hydr}}{dt} = \tilde{A}_{\Gamma} \left(\Gamma_{hydr} \right) \beta_{\varphi} \left(\varphi \right) \exp \left(-\frac{E_a}{RT} \right)$$
(2)

where $\tilde{A}_{\Gamma}(\Gamma_{hydr})$ is the hydration degree-related, normalized affinity which can be determined from isothermal calorimetric tests or isothermal strength evolution tests, [2]. Function $\beta_{\varphi}(\varphi)$ describes effect of the relative humidity on the hydration rate, *R* is the universal gas constant, *T* the absolute temperature, and E_a is the activation energy, describing effect of temperature on the hydration rate according to the Arrhenius law, commonly used in Thermodynamics. Such an relation is widely used since 1977 when it was originally proposed by Freisleben-Hansen and Pedersen [5].

In equation (2) one assumes that temperature influences the hydration rate in a similar way at different stages of the process advancement. This assumption has been proved to be true for the cement pastes made of CEM I, and here it will be verified for other types of cements.

3. Materials and methods

The calorimetric tests were performed for the cement pastes made of: CEM I 32.5R N/A, CEM II B-S 32.5R, CEM IIIA 32.5 N/A, CEM IIIA 42.5 N and CEM V A/S-V 32.5R, with the water – cement ratio of 0.47. The cement samples were prepared in accordance to the ASTM C 1679-08 standard. To analyse the effect of temperature on the hydration process at different stages of its evolution, the isothermal calorimetric tests were performed at temperature of 20°C, 30°C, 40°C and 50°C. The technique was developed by Woods et al. [1] and has become the standard method specified in many National Standards, e.g. EN 196-8 and ASTM C 186.

The tests were performed by means of the TAM Air isothermal calorimeter. On the basis of the amount of heat supplied in TAM over a given time period (i.e. the time integral of the measured hydration heat rate), the so-called *source function* [1] was determined which has been used for determination of the hydration degree (Eq. 1) and its rate evolutions in time (Eq. 2). The values of activation energy for different degrees of hydration, $E_a|_{\Gamma_{hydr}}$, were determined on the basis of the experimentally determined at

two different temperatures, functions $\dot{\Gamma}_{hydr}(\Gamma_{hydr})$, by means of the following relation,

$$E_{a}\Big|_{\Gamma_{hydr}} = R\left(\frac{1}{T_{0}} - \frac{1}{T}\right)^{-1} \left[\ln \frac{d\Gamma_{hydr}}{dt} \Big|_{\Gamma_{hydr},T} - \ln \frac{d\Gamma_{hydr}}{dt} \Big|_{\Gamma_{hydr},T_{0}} \right],$$
(3)

where T_0 is the reference temperature.

3. Results

Some exemplary results of the isothermal calorimetric tests performed for the considered cement pastes at different temperatures are presented in Figures 1 - 5. Figure 1 shows the time evolutions of heat rate released during hydration of the following cement pastes: CEM I 32,5R N/A, CEM II B-S 32.5R, CEM IIIA 32.5 N/A, CEM IIIA 42.5 N and CEM V A/S-V 32.5R, at temperature of 20°C, 30°C and 40°C.





Figure 1: Heat rate of hydration as a function of time, obtained from the calorimetric tests performed at three different temperatures for the cement pastes: a) CEM I 32,5R N/A, b) CEM II B-S 32.5R,
c) CEM IIIA 32.5 N/A, d) CEM IIIA 42.5 N, e) CEM V A/S-V 32.5R.

Figure 2 presents the exemplary results (for the cement paste CEM I 32,5R N/A) obtained from time integration of the rate curve shown in Figure 1a. Using such results, the evolutions of hydration degree were calculated by means of Eq. (1), see e.g. Figure 3, where the exemplary results for temperature T= 20°C are shown.



Figure 2: Normalized heat of hydration as a function of time, obtained from the calorimetric tests performed at three different temperatures for the cement paste CEM I 32,5R N/A.



Figure 3: Hydration degree as a function of hydration time, obtained from the isothermal calorimetric tests performed at temperature of 20°C for the analyzed cement pastes.



Figure 4: Hydration degree rate as a function of hydration degree, obtained from the isothermal calorimetric tests performed at temperature of 20°C for the analyzed cement pastes.

The latter results were used for determination of the hydration characteristics $\dot{\Gamma}_{hydr}(\Gamma_{hydr})$, given by Eq. (2), necessary for numerical modelling of cement hydration process. The exemplary results of such calculations performed for temperature of 20°C are presented in Figure 4.

Using the above mentioned data for the all considered cement pastes, the activation energies at different hydration degrees were calculated by means of relation (3). The results obtained from the $\dot{\Gamma}_{hydr}(\Gamma_{hydr})$ curves at temperatures: 20°C and 30°C, as well as 20°C and 40°C are presented in Figures 5 a-e.





Figure 5: Activation energy as a function of hydration degree, obtained from the isothermal calorimetric tests performed at temperature of 20°C, 30°C and 40°C for the analyzed cement pastes: a) CEM I 32,5R N/A, b) CEM II B-S 32.5R, c) CEM IIIA 32.5 N/A, d) CEM IIIA 42.5 N, e) CEM V A/S-V 32.5R.

4. Discussion and conclusions

The shape of curves describing evolution of cement hydration process in the analysed cement pastes at the same temperature were visibly different, see Figure 2. Moreover, for the all analysed cement pastes, the shape of curves describing evolution of cement hydration process at temperature 30°C and 40°C were distinctly different than the curves for temperature of 20°C, Figures 1a-e. For this reason, the value of activation energy for a given cement paste is not constant and it depends both on the temperature and the hydration degree, especially for the pastes made of cement with various admixtures (i.e. different than CEM I). For these cements one can observe a delayed reaction, kinetics of which is strongly influenced by temperature. This clearly shows that the Arrhenius type relation with a unique value of activation energy, used for description of temperature effect on the hydration rate should not be used, especially for cements with admixtures, and more research on mathematical modelling of cement hydration process at variable temperature is still needed. It seems that cement hydration should be described as a superposition of several chemical reactions of its components, with different kinetics, and with influence of temperature characterized by different values of activation energies.

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Variations of heat and moisture transport through walls of the St. Martin Cathedral tower in Bratislava

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Abstract: Historic monuments are subject to degradation due to exposition to surrounding meteorological conditions and groundwater. Long term monitoring of the tower of St. Martin Cathedral in Bratislava have been performed under window sill of the belfry in exterior in south orientation in period 19.4.2013 – 15.8.2013. Monitoring has been carried out in plaster and in the masonry in a distance about 10 cm from the wall surface. The thermal conductivity sensors are used for monitoring of the temperature and thermal conductivity. Monitored data are correlated to the meteorological data. Details of various effects will be discussed.

Keywords: Moisture monitoring, Thermal conductivity sensor, Hot-ball method

1. Introduction

Buildings consist of components that have a porous structure. Such objects, in real environments, are attacked by atmospheric moisture, precipitation, wind, solar radiation and groundwater [1]. The absorption and transport of water in porous materials combined with the effects of air/vapour movement through structures are complex processes.

St. Martin Cathedral is the largest and the oldest church in Bratislava. The frame of the tower is built of dimension stones. The space in frame is filled with bricks. Masonry wall thickness of the tower is 1.5 m. Wall surface was originally plastered. During reconstruction works moisture sensors were placed in a depth of up to 60 mm in the bricks and in plaster. Sensors were placed just below the window sill. Moisture sensors based on the principle of measuring the thermal conductivity of porous structures were used. This paper discusses data that were collected during monitoring of temperature – moisture regime of the tower wall in the south orientation in period 19.4.2013 – 15.8.2013.

2. The principle of the moisture sensor

Principle of the moisture sensor is based on the measurement of thermal conductivity of porous structure. The thermal conductivity of porous structure is a function of the matrix and the content of pores, its volume and percolation paths. In real environment, the pores can be filled with air / vapour, water or ice, depending on the thermodynamic state and the surrounding conditions.

We use a hot-ball method for measuring thermophysical properties [2]. The method uses a small ball that generates a transient temperature field in the porous material and simultaneously it measures its own temperature. Then the ball temperature is a measure of the thermal conductivity. One obtains the following working equation of the measuring method [2]:

$$\lambda = \frac{q_0}{4\pi r_b T_m} \tag{1}$$

where q_o is the heat output of the hot-ball having radius r_b and T_m is the stabilized value of the temperature response.



Figure 1: Principle of the hot ball method (left) and the measured signal (right).

A hot-ball sensing element is shown in Figure 2a. The element has been constructed of two components, a heater and a thermistor. Both components are fixed in the ball using epoxy resin. The diameter of the ball ranges from 1.8 mm to 2.3 mm.



Figure 2: Photo of hot-ball sensing element (a) and moisture sensor (b)

Moisture sensor made of a borehole core has a cylindrical shape with a diameter of 20 mm and same length. A small hole is drilled in the axis of the cylinder with a diameter of about 2 mm in order to fix the hot-ball. The hot-ball alone is fixed by epoxy resin. The final form of the moisture sensor is shown in Figure 2a. A RTM-W wireless device (Institute of Physics SAS) is used for monitoring. Device has two independent channels thus it can be connected with two moisture sensors. In practice the moisture sensor is calibrated.

Sensor in the form shown in Figure 2a was fixed at the surface of the wall before plastering. Sensor in the form shown in Figure 2b was placed 60 mm below the wall surface in a drilled hole in tower wall. Wall was composed of bricks, with density around 1800 kg m⁻³, 30% porosity and $\lambda_{dry} = 0.55$ W m⁻¹ K⁻¹. Baumit Bayosan plaster with porosity >45%, thickness around 35 mm and $\lambda_{dry} \sim 0.85$ W m⁻¹ K⁻¹ was used for covering the tower wall.

3. Results and discussion

Monitoring covered the period from 19.4.2013 – 15.8.2013. A large data set was obtained during this period. Figure 3 shows monitored data of both sensors. Scales q/Tm were adjusted to see correlations between the sensors.



Figure 4: Air humidity and precipitation in period 19.4.2013 – 15.8.2013

Two driving forces act during moisture diffusion, namely temperature and moisture gradient. While moisture gradient is formed due to rain precipitation and air moisture, temperature gradient is predominantly formed due to sun radiation. Figure 3 shows moisture variation in plaster and wall. Clear intervals of dry periods by intercomparison of precipitation (Figure 4) and moisture level (Figure 3) can be found where differences in level of moisture in plaster and in wall are significant. Dry periods (no rain) formed moisture gradient that is





Figure 5: Dry period indicated by variation of moisture in the plaster and the wall.



Figure 6: Details of humidity and precipitation in the studied period.



Figure 7: Temperature details in air and plaster during dry period

Level of moisture in plaster is always lower due to drying process (see Figure 5.). Temperature of the plaster is always higher in comparison to air due to radiation of sun (see Figure 7.). Variations in moisture diffusion controlled by temperature are shown in detail in Figure 5. These variations are given by cycle day – night. Variations are significantly higher in wall in comparison to plaster. Plaster has high porosity thus moisture equilibration due to interaction with air is fast.

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Monitoring of temperature-moisture regime in different depth levels of rock mass, Brhlovce dwellings case study

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Abstract: The progressive rock mass deterioration has been induced by the simultaneously action of more exogenous factors. Between the one of the most important factors belongs the temperature and moisture content. The aim of this paper is to evaluate the temperature-moisture regime in different depth levels of the rock mass based on terrain monitoring and also on laboratory research. Monitoring system of the temperature-moisture regime is based on the hot-ball method which has been generally used on measuring of a thermal conductivity. The three moisture probes were implemented into the volcanic rock mass of natural rock dwellings in Brhlovce village. Probes were installed into the 10 cm, 37 cm and 53.5 cm depth of rock mass. The hot-ball sensors had to be laboratory tested and calibrated before the finally embedded of probes into the rock mass. For data evaluation of in situ monitoring of temperature-moisture regime in various depths was used 6 month time period (from April to September 2013) of real time measurements. The measured data obtained from in situ conditions indicate the correlation with the laboratory tested data. Partial results of in situ monitoring point to the difference depth distribution of moisture and temperature in the rock mass. The gradual decrease of moisture with depth was recorded. The measured moisture in the rock mass was influenced not only by temperature changes but also by precipitation recorded with the meteorological station implemented at the measured site.

Keywords: Brhlovce rock dwellings, tuff, hot-ball method, moisture monitoring, thermal conductivity

1. Introduction

The monitoring of temperature-moisture regime of a rock mass is relevant not only from the scientific aspect but it is also important for the protection of historical monuments. The ones of the most important degradation factors of a rock mass, in our case it is the rock dwellings, are the temperature and moisture content. The changing of the moisture content, respectively the oscillation of saturation degree of rock mass, causes the faster degradation of structural bonds inside the rock mass and also mineral changes. The higher humidity contents in pores of rock increases the velocity and depth of the temperature penetration inside the rock mass [1]. Only few authors were devoted to research of temperature-moisture regime in a rock mass as the one of degradation factors in Slovakia. Among current well-known researches belong the follows: [1], [2], [3], [4], [5] and [6].

For the research of the temperature-moisture regime in various depth levels of rock mass has been selected the tuff's mass of rock dwellings museum in Brhlovce village. For the general public the rock dwellings in Brhlovce (Levice district) are relatively well-known, whereas present the unique historical monument from the time of the Turkish invasion in the 16th and

17th Century. Since 1983, the site has been declared as a reservation of folk architecture and has been included to the national list of cultural heritage objects. Dwellings are built in the porous andesite tuff's complex and present the last preserved objects of its kind in Slovakia. Despite of this fact, relatively many of these objects are in privately owned and are abandoned or improperly used. In consequence of influence of several unfavorable factors, the current state of some objects was worsening not only from engineering-geological aspect, but also from geotechnical point of view as well. By one of the negative factors causing the gradual degradation of dwellings is physical weathering of the rock mass. Moisture content inside the rock mass has destructive impact caused by drying and wetting cycles and freezing and thawing processes. An example of degradation of rock mass leaded to the rock terrace collapse in November 2012 is view in Figure 1.



Figure 1: Collapse of rock mass stage (terrace) jeopardized the family house. On the left side is view the state of rock mass before crashed and on the right side is the state of rock mass after the collapse in November 2012.

The temperature-moisture regime is monitored by moisture sensors in connection with RTM electronic unit. Using the hot-ball method there are continually measured the temperature T [°C] of rock mass and moisture content represented by measured values of q/T_m parameter – the amount of heat generated by hot-ball probe and temperature difference of temperature response to the heat pulse. These parameters are characterizing the correlation between the measured thermal conductivity and real moisture content, which is the most important degradation's factor in the process of weathering. The measured parameters (moisture and temperature) of rock mass are correlated with precipitation's data obtained from metrological station installed at the monitored site (in the area of rock dwellings museum). For the research of the moisture change with depth, the three moisture probes were implemented into the rock mass in three different depth levels, exactly in 10 cm, 37 cm and 53.5 cm depth. The Figure 2 illustrates the locality of implemented moisture probes and the meteorological station position and arrangement of measurement apparatus.



Figure 2: Localization of measurement apparatus and meteorological station (left) and the detail of solar RTM and moisture probes implementation's site (right).

2. Principle of hot-ball method and moisture probes

As previously mentioned for the in situ monitoring of temperature and moisture content of rock mass there were used the moisture probes based on the transient hot-ball method (Figure 3, left). The principle of hot-ball method is based on obtaining information of the thermal conductivity λ [W.m⁻¹.K⁻¹] leading to the information about the moisture content. For this purpose it was used the hot-ball sensor (Figure 3, middle part) implemented to the rock's (tuff) sample which has cylinder shape with diameter 32 mm. In a middle of the cylinder was drilled out a hole (diameter 2.5 mm) where the sensor has been inserted. The moisture probes prepared in this way had to be supported by the cage made of nickel wires (Figure 3, right).



Figure 3: Model of hot-ball method (left), small hot-ball sensor installed into the rock's sample (middle) and the final hot-ball probe prepared for the implementation into the rock mass (right).

The small hot-ball sensor generates the heat flow in the form of step-wise function and simultaneously measure the temperature of ball's surface. The temperature response has been recorded up to the temperature stabilization (see the Figure 4). The temperature difference measured before and at the end of the measurement and the total amount of generated heat characterizes the thermal conductivity λ [W.m⁻¹.K⁻¹], equation (1). Thermal conductivity in pore materials is depended on moisture content in pores. Thus the measured q/T_m characterizes the value of thermal conductivity and thus the moisture content.



Figure 4: Example of measurement cycle - measured temperature response for tuff.

Therefore the system was calibrated in the dry and saturated state [5]. On the basis of the temperature response it can be calculated the thermal conductivity according to equation (1), where q means the constant value of the generated heat [W], r_b means the radius of the ball sensor [m] and T_m [°C] is the temperature difference before application of the heat flux and after stabilization response of the temperature [4].

$$\lambda = \frac{q}{4\pi r_b T_m(t \to \infty)} \tag{1}$$

During the stabilization time the head produced by the ball penetrates into a material volume. Penetration depth into the surrounding is less than 20 mm. The one measurement cycle consists of three phases: measurement of initially stabilized temperature, switching on the heating pulse and simultaneously recording the temperature response and after the stabilization of measured temperature the heating is interrupted and temperature stabilization follows.

3. Calibration procedures and the partial results of in situ measurements

The first probe was installed into the rock mass in 10 cm depth in 2011 and other two probes were implemented at April in 2013. The main purpose of the first probe embedded was to initialized measurement and on the base of first results of in situ measurements the other two probes were prepared and subsequently optimized on the terrain conditions. Before the hot-ball probes installed into the rock mass, the probes had to be calibrated in laboratory for the limit values of dry and full saturated state. The first part of paper has been focused on the study of moisture regime of tuff with moisture probe in laboratory conditions.

3.1 Calibration procedures and results

Moisture probes (rock bodies with hot-ball sensor) were calibrated in temperature range from - 20 °C to +22 °C in the climate chamber KD-20-T4.1 in dry and moisture saturated conditions [5]. Results of the experiment are shown in Figure 5. The figure presents the thermal conductivity in limiting values for dry and moisture saturated conditions (red and blue line) during freezing

cycle for three different humidity probes. Measured mean values of thermal conductivity of rock's probes in the given temperature range were of linear dependency on temperature. The test showed that the values of q/T_m in the case of water saturated probes are much higher than dried moisture probes. The difference in the values of the q/T_m between dry and reached water-saturated state also proves on high water absorption of tuff. The real in situ measured data obtained from three different depth levels of rock mass are in between the calibration lines. This experiment was helpful in moisture monitoring in the field research, because values of thermal conductivity were defined in extreme dry and moisture saturated conditions. The temperature dependence of thermal conductivity is negative and linear. Thus we could easily determine the actual moisture in rock mass by using q/T_m parameter. The probe sensitivity should be high enough to register the moisture content change during the moisture process between dry and water saturated state (range from 0 up to 100 % of moisture content). This change is measured as the difference of q/T_m parameter [3].

3.2 Partial results of in situ measurements

Our research is focused on the study of temperature-moisture regime in different depth levels in rock mass mainly. Based on calibration measurements it was possible to present the progress of moisture change inside the rock mass depending on the precipitation and measured temperature changes. To the first part of the results analysis of all three probes were selected data from the six-month monitoring period in the temperature range from 8 °C to 30 °C. The results are shown in Figure 6. The changes of q/T_m and thus the moisture content changes after an installation are more progressive at the beginning period of monitoring (16.04. 2013). During the first month the change of moisture content was about 40 % for 10 days. While the probe installed in 10 cm depth recorded approximately 50 % moisture of rock mass, the other two new probes (probes in 37 cm and 53.5 cm depth) recorded the gradually saturation of rock mass in two steps - 0-10 % moisture and 10-25 %, respectively 10 - 40 %, which characterized the adaptation of probes to the natural condition of mass. The gradual saturation of humidity probes without the rainfall is documented during the first month of measurement.

After 2.5 months of real time monitoring the probe embedded in 37 cm depth level in rock mass was interrupted and had to be repaired. Despite of this, during the continual measuring of the all probes, the several precipitation days were recorded which have been reflected on the measured moisture of rock mass with some time retardation. Regarding the short monitored period is not possible to affirm accurately whether the rock mass is evenly saturated or the degree of saturation of rock mass decreases with the depth as demonstrated by the following graph (Figure 6).



Figure 5: Calibration of hot-ball probes in dry and water saturated conditions for measurement course of the change of q/T^m *with temperature change in the tuff's rock mass.*



Figure 6: Monitoring of temperature-moisture regime in different depth levels of rock mass with used hotball probes and precipitation station.

4. Conclusions

The main aim of the monitoring is to understand the weathering process of rock dwellings; whether the influence of moisture and temperature in interaction with other natural conditions could be presented as one of the trigger mechanisms of rock mass deterioration. The paper presents the measured data from real time in situ monitoring of temperature and thermal conductivity of rock mass in different depth levels. The present partial results indicate the quite good correlation between the laboratory tested data and data obtained from in situ conditions (Figure 5). The resulting data obtained from the six month time period of continual monitoring point to the difference in depth distribution of moisture and temperature in rock mass. There were recorded the gradual decreases of moisture with depth. The measured moisture in rock mass was influenced not only by the temperature but also by the precipitation recorded with the metrological station (Figure 5). Using the spatial and depth differentiation of long-term measurements of selected physical parameters in rock mass, it will be possible to determine the distribution of moisture in the rock mass more precisely.

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