



The Use of Micro Additives in Building Gypsum Materials

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Abstract. The paper presents the experimental measurement of the thermal conductivity of the modified gypsum and the influence of added micro additives on this thermal parameter. The polymer and the aerogel are used as additives in the weight fractions 0.5%, 1% and 2% of pure gypsum and the microspheres in the weight fractions 5%, 10% and 15% of gypsum. The water-to-gypsum ratio (w/g) for all specimens was 0.75. For the purpose of measuring of the thermal conductivity λ , a novel non-stationary method was used. Based on the experimental measurements found the gypsum with polymer content resulted in more than 44% lower thermal conductivity in comparison to the specimen without hydroxyethylmethylcellulose as a result of the different porosity of the modified specimens. Decrease in thermal properties, were observed as an effect of microstructure modifications of the gypsum product. The gypsum with aerogel and microspheres content resulted in more than 35% and 42% respectively lower values in comparison to the reference sample without micro additives.

1 Introduction

Modern countries and world economies understand that we have to protect environment. They try to lower greenhouse gas emission, protect waters, soils, reduce noise, recycling, look for an alternative sources of energy and energy efficiency (Ciemnicka et al. 2019; Milošević 2012; Węglorz 2014). Modern construction industry, in which we spend up to 80% of our life, is an important element of our environment and landscape. Ensuring an appropriate state of internal environment is very important when we design and build a building, both in health and comfort of use aspects. For many people, taking care about natural environment is also a priority.

Science and industry are used to reduce thermal losses of internal environment. Different methods allow to decrease demand for energy and its consumption. The subject of energy efficiency is the most important in most of the buildings. Energy efficiency is becoming a standard in modern construction industry.

Different methods of reduction of energy consumption are introduced in the ecological buildings in order to reduce consumption of conventional energy and, as a consequence, to protect environment.

Above goal is achieved mainly through:

- use of energy from alternative sources (renewable),
- use of systems of heat recovery,
- introduction of unconventional methods of obtaining, storing and conversion of energy.

High-tech energy efficient construction industry uses different methods of exchange of solar radiation energy. The basic methods include:

1. Passive solar solutions, which make use of a shape, setting of a building solid to manage available solar energy. It transforms into proper architectural and construction project. Passive systems use and absorb solar radiation from the elements of a building. Proper walls accumulating energy acting as storehouses are used. Heated air (obtained energy) is distributed through channels to the rooms.
2. Active solar solutions, which are usually installation solutions. Photothermal conversion emerges in such systems, that is, conversion of solar radiation energy into thermal energy or photovoltaic conversion, that is, conversion into electric energy.
3. Construction-material-installation solutions aiming at applying other unconventional methods of obtaining energy contained in natural environment, for example, using heat pumps and unconventional methods of its storing in the soil, stone deposits, substances with a low temperature of phase changes. Modern solutions may include: systems of heat recovery, controlling conditions of internal environment microclimate, measurements of energy consumption, non-classic constructions of windows with low values of a coefficient of thermal transmission. Nowadays, very broad field of science within the framework of modern, pro-environmental material solutions is focused on looking for insulations and construction composites with low values of a coefficient of thermal conductivity λ (Ciernicka et al. 2019, Prałat 2015).

Low values of a coefficient of thermal conductivity λ of insulating and construction materials is obtained with the help of an addition or building phase change materials (PCM) in their structure, which are able to absorb, accumulate and release large amount of energy within the range of a phase change temperature. During absorption of energy, temperature of material does not change. The materials used in the articles are inorganic (hydrated salts) and organic compounds (paraffin, fatty acids, ionic liquids).

A new way to lower value of a coefficient λ is to add micro additives to construction materials. It is assumed that adding a polymer has a considerable impact on crystallization of calcium sulphate (gypsum) and on rate and the way of binding water in it.

It is important to have a basic knowledge aiming at finding material constants of aqueous solutions of polymers, such as: viscosity η , thermal conductivity λ or specific heat C_p . Another important aspect is the impact of micro additives on the value of conductivity of prepared construction materials – mainly gypsums (Prałat 2015).

2 Materials

This paper presents the results of measurement of the thermal conductivity λ of modified gypsum. Specimens were modified with the following micro additives: polymer (hydroxymethyl ethyl cellulose), microspheres and aerogel. Measurements were based on a designed, novel experimental set up using the non-stationary method. The composites were characterized by different concentrations of additives. The gypsum sample was modified by additive of polymer and aerogel in different amounts - 0.5, 1.0 and 2.0% and microspheres - 5, 10 and 15% of gypsum.

The material, mechanical and thermal properties of pure gypsum and its components are very well known and described in the literature (Adrien 2016; Karni and Karni 1995; Yu and Brouwers 2012). As a traditional, unmodified building product, it has the thermal conductivity λ , varying in the range of 0.23 to 1.00 W/(m·K), and density $\rho = 1000 \text{ kg/m}^3$ for gypsum boards and blocks. The averaged specific heat is approximately 840 J/(kg·K) (Yu and Brouwers 2012; Heim et al. 2018). The influence of various additives like: aerogels, microspheres and polymers on the thermal conductivity of gypsum is currently not well recognized (Ciemnicka et al. 2019).

Hydroxyethyl methyl cellulose is a nonionic polymer characterized by high viscosity and nontoxic and water-soluble properties. HEMC is one of the cellulose ethers and is widely applied in the building construction sector. It can be used to modify building materials that are made based on any mortars, such as cement or gypsum (Kamsen et al. 2013; Ru et al. 2006, Heim et al. 2018). The particle size of polymer added to gypsum was in the range 150–250 μm .

Nowadays aerogels are one of the best thermal insulation materials. For this work, silica aerogel in the form of particles of fraction 0.7–4.0 mm was used (Garbalińska and Strzałkowski 2016). The granules feature hydrophobic properties and their specific density ranges between 120 and 150 kg/m^3 . They are the only fire resistant materials that offer thermal conductivity values as low as 0.012–0.018 W/(m·K) without the need for vacuum or gas sealed systems (Schiovani 2016). This is achieved by forming the structure in a supercritical drying process. Supercritical drying is performed to replace the liquid in a material with a gas to isolate the solid component from the material without destroying the material's nanostructured pore network of diameter of approximately 20 nm.

Microspheres are light, thin-walled hollow spheres which are by-products of the combustion of pulverized coal at thermal power plants. Due to their properties they are a potentially interesting filler and may be used for cement-based composites production (Pichór 2009). The particle size of microspheres from fly ash, added to gypsum was in the range 50–150 μm . The main chemical constituents in used microspheres: Al_2O_3 (34–38%), Fe_2O_3 (1–3%), SiO_2 (50–60%), CaO (1–4%), MgO (0.2–2%) and TiO_2 (0.5–3%) (Ciemnicka et al. 2019).

In order to present the structure of micro additives, images of the substances used were made by laboratory stereoscopic microscope, with the use of 100x magnification and the Moticam camera, allowing observation of details with a size up to 20 μm (Fig. 1). Because of the visible differences in the structure of the micro additives it was assumed that micro additives will reduce the thermal conductivity of gypsum composites to a different extent.

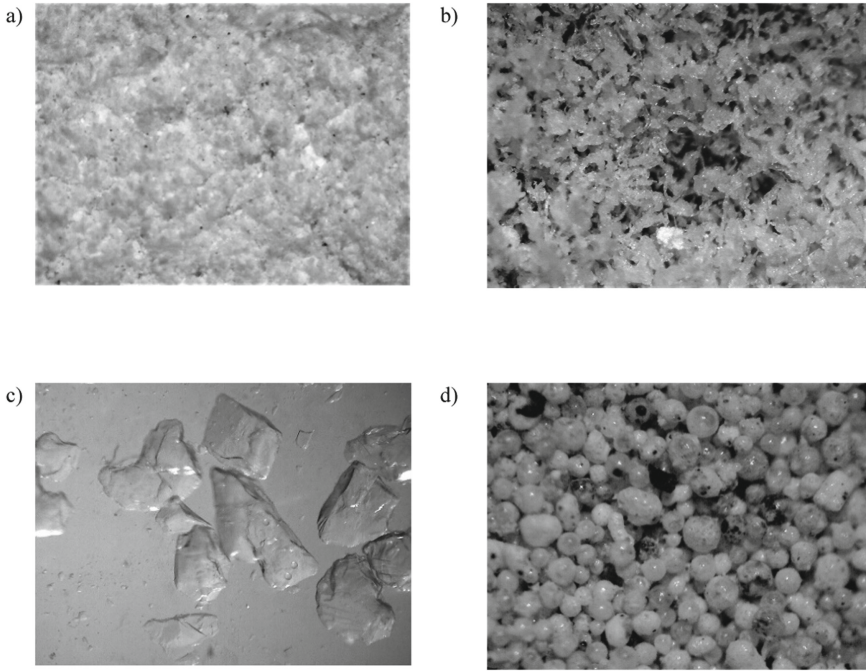


Fig. 1. Microscopic images (magnification x100) of: **a** gypsum, **b** polymer, **c** aerogel, **d** microspheres (Ciernicka 2019)

3 Experimental Set-Up

Presented solution of a device is an elaboration of so called linear thermal probe with constant disbursement. Idea of device consists in the placement inside material, constant source of heat powered by constant electric current in such a way that giving off stream of heat is constant.

Theoretical bases of “hot wire” method gave Van der Held and Van Drunen (Van der Held and Van Drunen 1949). A field temperature describes Fourier Eq. (1), where ϑ means relative temperature, r radius and t time:

$$c_p \rho \frac{\partial \vartheta}{\partial t} = \lambda \left(\frac{\partial^2 \vartheta}{\partial r^2} + \frac{1}{r} \frac{\partial \vartheta}{\partial r} \right) \quad (1)$$

Pace of heating up the wire depends on properties of the centre in which it can be found. With an assumption of negligible small diameter of heating wire $2r$ in relation to its length L , and with following boundary conditions are obtained general solutions (2):

- initial condition: $t = 0, r: \vartheta = \vartheta_0 = 0$
- boundary conditions: $t \geq 0, r = \infty: \vartheta = \vartheta_\infty = 0$

$$r \rightarrow 0, q = -2\pi r \lambda (\partial \vartheta / \partial r)_{r \rightarrow 0} = \text{const.}$$

$$\vartheta = \frac{q}{4\pi\lambda} \int_x^\infty \frac{1}{x} \exp(-x) dx = \frac{q}{4\pi\lambda} \left(-C - \ln x + \frac{x}{1 \cdot 1!} - \frac{x^2}{2 \cdot 2!} + \dots \right) \quad (2)$$

where:

$$x = r^2 / (4at),$$

$$C = 0,5772 - \text{Euler constant,}$$

$$a = \lambda / (c_p \rho) - \text{coefficient of thermal diffusion,}$$

$$q = Q/L - \text{power unit of heating wire.}$$

For very small values x , a value of integral can be written down as $-C - \ln x$, and then Eq. (2) takes the form (3):

$$\vartheta = \frac{q}{4\pi\lambda} \left(\ln \frac{4at}{r_0^2} - 0,5772 \right) \quad (3)$$

Carrying out two measurements of T in moments t_1 and t_2 value of coefficient of thermal conductivity can be determined from dependencies (4):

$$\lambda = \frac{Q}{4\pi L} \cdot \frac{\ln \frac{t_2}{t_1}}{T_2 - T_1} = \frac{q}{4\pi} \cdot \frac{\ln \frac{t_2}{t_1}}{T_2 - T_1} \quad (4)$$

where:

Q – quantity of heat emitted by the source of heat, W;

L – length of heating element, m;

t – time, s;

T – temperature of heating element, °C.

Quantity of heat Q emitted by heating element is equal to quantity of heat seized by studied material in a unit of time, with an assumption of lack of losses and omission of heat accumulation in heating element (Heim et al. 2016):

$$Q = U \cdot I \quad (5)$$

where:

U – current voltage, A;

I – current strength, V.

For the purpose of conductivity measurements, an improved “hot wire” method was used. The “hot wire” method, based on transient heat exchange, belongs to one of the most interesting methods because of its simplicity, accuracy and ease of implementation. It involves placing the heating wire inside the tested material and measuring its temperature as a function of time. The idea of the experiment assumes placing in the material a source of heat, supplied with electric current in such a way that the heat flow emitted in time is constant. The measurement takes place under the heating conditions

of the material indirectly by determining the rate of heating. In the $T-\ln(t)$ coordinates system, after the transitional period, the dependence takes on a linear character (Van der Held and Van Drunen 1949, Heim et al. 2016).

For the purpose of measuring the thermal conductivity λ a computer-controlled experimental stand was used described in detail in (Heim et al. 2016, Prałat et al. 2019). The basic element was a gypsum specimen measuring $50 \times 50 \times 305$ mm, containing an axially placed Kanthal resistance wire heater with a diameter of 0.2 mm. A miniature resistance temperature sensor type Pt100 has been permanently attached to the heater. A characteristic feature of platinum resistance sensors is the increase of their resistance as a function of temperature. In a small temperature range, this increase can be treated as linear (Heim et al. 2016, Prałat et al. 2019).

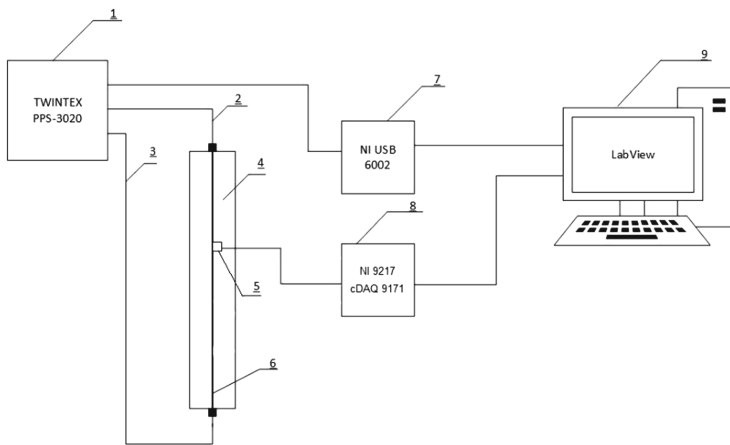


Fig. 2. Experimental set up for measurement of thermal conductivity by “hot wire” method: 1 – adjustable power supply of direct current, 2 and 3 – power cables, 4 – tested specimen, 5 – sensor Pt100, 6 – hot wire, 7 – data recorder, 8 – input module of the resistance temperature sensor, 9 – computer (Prałat et al. 2019)

The temperature sensor was connected with the measuring module NI-9217 produced by National Instruments, which was then connected to the intermediary module cDAQ 9171 transmitting the encoded temperature signal to computer controlling the process. The measuring module NI-9217 can operate in two modes: sampling with high resolution or high frequency sampling (Fig. 2). The dedicated software in the LabView was written for the operation of the measurements procedure. The software made it possible to set the voltage and the current supply limitation, and indirectly heating power, to read the actual parameters, as well as write them to a computer disk. The program also enabled the selection of required power and data logging time sequences (Prałat et al. 2019).

Thermal conductivity measurements are interdependent measurements, also called simultaneous measurements, because the measurement and recording of all measured values were carried out under the same conditions. The estimation of measurement

error of thermal conductivity was calculated for gypsum specimens after 35 days of maturation and drying. The uncertainty assessment is based on a theory that assumes that measurement error is random and therefore subject to relevant statistics. In this case, the final measurement error is determined mainly by “evaluation of measurement uncertainty type B” of the measuring instruments used, methodology or random errors. It can be assumed that random and methodical errors are very small and can be neglected. Therefore, the uncertainty of the final measurement will be affected by measurement errors of the instruments. The uncertainty assessment is the ratio of the error margin of the instrument to the measured value and decreases with the increase of this value. The relative uncertainty of the complex, independent, random measurement of the thermal conductivity of gypsum was calculated from Eq. (6) (Heim 2016):

$$\frac{u(\lambda)}{\lambda} = \sqrt{\delta(U)^2 + \delta(I)^2 + \delta(l)^2 + \left[\frac{\delta(t_1)}{\ln t_1}\right]^2 + \left[\frac{\delta(t_2)}{\ln t_2}\right]^2 + \delta(T_1)^2 + \delta(T_2)^2} = 0.861\% \quad (6)$$

where: δU - uncertainty of voltage measurement on the heating wire, δI - uncertainty in measuring the intensity of the current flowing through the heating wire, δl - uncertainty in measuring the length of the heating wire, δt_1 - uncertainty of time measurement t_1 , δt_2 - uncertainty of time measurement t_2 , δT_1 - uncertainty of temperature measurement T_1 , δT_2 - uncertainty of temperature measurement T_2 .

4 Results

Specimens were conditioned in temperatures of $20 \div 22$ °C and $RH = 40 \pm 1\%$ for 28 days. After this time they were dried at a temperature of 65 °C for 7 days. During the experiment, thermal conductivity values on the specimens were determined successively at 1, 3, 7, 21, 28 and 35 days after they were made. At the same time, the values of density of gypsum blocks were determined.

Bulk density was determined as a ratio of mass and volume of the gypsum specimens. Total porosity p was calculated based on bulk density with reference to the density of the structure (7).

$$p = \left(1 - \frac{\rho}{\rho_g}\right) \cdot 100\% \quad (7)$$

The obtained values of bulk density and total porosity are presented in Table 1. The specific density of tested specimens was assumed $\rho_g = 2,350$ kg/m³.

When measuring the thermal conductivity based on “hot wire” method, a low heating power of 0.2 W was used. For all gypsum specimens tested, graphs of the dependencies $T - T_0 = f(\ln(t))$ were made and the slope S for the latter was determined. Figure 3 shows the graphs for the gypsum without micro additives.

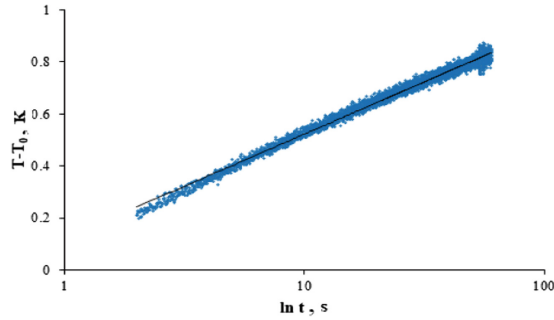


Fig. 3. Sample graph of the temperature change of the heating wire of the gypsum specimen as a function of the natural logarithm of time

Table 1. Bulk density ρ , porosity p and thermal conductivity λ of gypsum specimens after 35 days of maturing.

Gypsum specimens	λ , W/(m·K)	ρ , kg/m ³	p , %
Gypsum + 0.5% polymer	0.2685	1011	57
Gypsum + 1% polymer	0.2664	1233	48
Gypsum + 2% polymer	0.1948	947	60
Gypsum + 5% microspheres	0.2083	1011	57
Gypsum + 10% microspheres	0.2797	1208	49
Gypsum + 15% microspheres	0.2027	999	57
Gypsum + 0.5% aerogel	0.2481	1026	56
Gypsum + 1% aerogel	0.3261	1206	49
Gypsum + 2% aerogel	0.2266	908	61
Gypsum	0.3465	1309	44

The thermal conductivity of the specimens was calculated using Eq. (8). The density and porosity of all the tested gypsum specimens were determined. The values obtained experimentally are shown in Table 1. In addition, the thermal conductivity of gypsum was compared with the literature data.

$$\lambda = \frac{Q}{4\pi L} \cdot \frac{1}{S} = \frac{q}{4\pi} \cdot \frac{1}{S} \quad (8)$$

Experimental values of thermal conductivity of gypsum specimens with the addition of polymer, aerogel and microspheres were respectively over 44% (with 2% polymer addition), 35% (with 2% aerogel addition) and 42% (with 15% microspheres addition) lower than the reference specimen, made of gypsum without additives.

On this basis, the thermal conductivity change in time diagrams were made (Fig. 4) and in the function of varying density (Fig. 5). It was observed that since the 14th day of the specimens maturation, the thermal conductivity has stabilized.

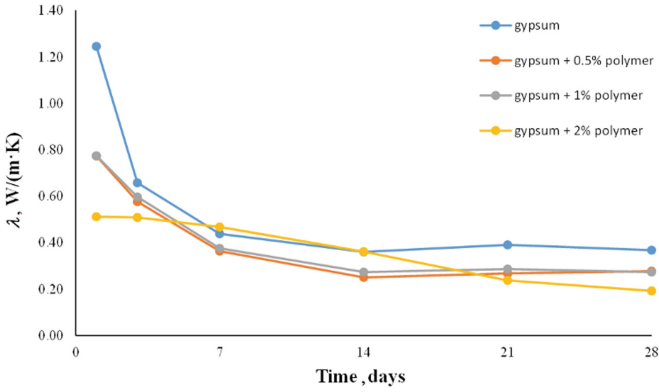


Fig. 4. Changes in thermal conductivity of gypsum specimens during the aging process of pure gypsum and gypsum with micro additives

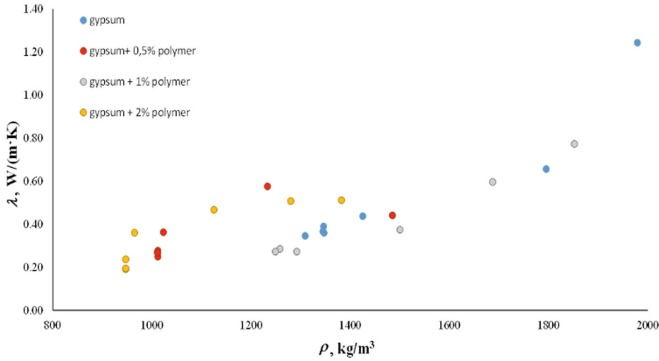


Fig. 5. Graph of the dependence of $\lambda = f(\rho)$ of gypsum specimens with different moisture content

5 Conclusions

The gypsum with polymer content results in more than 44% lower thermal conductivity in comparison to the specimen made of pure gypsum as a result of the different density and total porosity of the material. Experimental values of thermal conductivity of modified gypsum specimens with the addition of aerogel were 35% and microspheres 42% lower than that made of pure gypsum. The analysed gypsum composites with micro additives are thus environmentally friendly materials with improved insulating performance.

The relative uncertainty of the complex, independent, random measurement of the thermal conductivity of gypsum after 35 days aging process was lower than 0.9%. The experimental value of $\lambda = 0.3465 \text{ W/(m·K)}$ of the specimen with the content of pure

gypsum differed from the literature value $\lambda = 0.3537 \text{ W/(m}\cdot\text{K)}$ by 1.0% (PN-EN 12524:2003). It has been confirmed that the novel experimental set up based on “hot wire” method was designed and made properly.

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