

The Analysis of Thermal Properties of Selected Rock Materials by Thermovision Methods

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Abstract

Heat accumulation means denotes the of a material to collect and store inside a specific amount of thermal energy, which can be then returned for a period time from the material. There are many investigations devoted to finding a method to collect heat when there is an excess and to use it when there is a deficit. The parameter determining whether the returned heat long for a term will have an impact on the room temperature, is the time of emission of stored energy. For the specified amount of stored energy, the emission time cannot be too short (in such a case too much heat in the unit time is returned) or too long (in this case a too small amount of heat in the time unit is returned, for example insufficient for heating rooms).

The main aim of this research is to investigate the behavior (during cooling) of natural rock materials. On the basis of research and performed calculations the evaluation of tested materials to serve as the heat accumulator was performed. This analysis would allow them to be applied for the production of components, including precast, working at elevated temperatures, in which the accumulation and transfer of heat is important (eg. housing furnaces and fireplaces).

Keywords: minerals specific heat capacity, heat emission, rocks thermal properties, thermal power, thermovision

Introduction

Nowadays in the techniques the sintered ceramic materials of chamotte type is used as heat accumulators (Cao et al. 2004). Despite the refractory properties and good resistance to temperature changes chamotte is not a good heat accumulator, due to the thermal conductivity and low density. Garbalińska et al. (2011) developed thermal insulation and thermal accumulation of selected wall materials. Moreover Zegardło et al. (2011) made analysis of the thermal properties of concrete made using aggregate from sanitary ceramic wastes.

Another widely used material, especially in the Scandinavian countries is Norwegian "olivine", but the import of this raw material significantly increases the cost of investment (http://www.lkabminerals.com/ Products/Olivine).

For this reason an attempt to assess the suitability of raw materials occurring in Poland in heating techniques and fireplaces was made (Zagorska et al., 2011). During the selection of investigated minerals the availability and economic aspects were taken into account (Giere et al., 2004).

The thermal properties of rock are dependent on the coefficients of thermal conductivity minerals, which build the rock. From a thermodynamic point of view, silicon dioxide has the lowest coefficient of thermal conductivity, so it is the lowest value which is desired. SiO₂ is a bad heat accumulator but its advantage is that it heats up very quickly (e.g. quartz infrared heaters), therefore it can be used both as a protective material, and as a heat propagator to the accumulator (Matveev et al., 2012). In literature, there are several studies on the thermal properities of rocks. Schärli (2001) determined specific heat capacity on rock fragments, then Osako (2010) and Miao (2014) calculated thermal diffusivity, conductivity and heat capacity for several types of rock. Jerman (2011) investigated heat and humidity transfer and accumulation in some industrial materials.

Materials and methods

The authors chose such rocks, which due to their physicomechanical and chemical properties, resulting from mineral composition, can be used as heat accumulators (used e.g. as housing fireplace inserts). Applying these raw materials as heat accumulators is an innovative approach.

Among the relatively numerous documented mineral deposits useful in the mentioned application, only a few are currently mined and if production starts, it will provide opportunities for obtaining raw material.

	÷ 1	1 1		1 1	
Time [min]	Serpentinite A	mphibolite G	abbro	Granodiorite Q	uartzite
1	133,0	129,1	130,7	131,9	124,0
3	120,4	116,8	117,3	119,9	105,8
8	106,4	100,5	102,4	106,0 9	3,7
15 9	1,2	84,5 8	5,1	90,6 8	1,3
25 7	6,5 6	9,9	72,6 7	4,9	67,0
45 5	5,4	52,5 5	2,5	54,6 5	0,1
85 3	7,1	32,8 3	3,3	35,5 3	1,5
145	28,6 2	7,0	26,8 2	8,0	25,4
180	25,0 2	5,0	25,0 2	5,0	25,0

Tab. 1. The results of measuring the surface temperature of materials during heat dissipation. Tab. 1. Wyniki pomiaru temperatur powierzchni materiałów podczas oddawania ciepła.

From this group, the deposits were selected and characterized as follows (Figarska-Warchoł et al., 2003; Lubas et al., 2009; Wyszomirski et al. 2000, http://geoportal.pgi.gov.pl/surowce/skalne/kwarcyty_ogniotrwale):

- 1. Serpentinite from Nasławice deposit
- 2. Amphibolite from Ogorzelec deposit
- 3. Gabbro from Braszowice deposit
- 4. Granodiorite from Przedborowa deposit
- 5. Quartzite from Bukowa Góra deposit

The tested samples had a similar volume of approx. 250 cm^3 – because this parameter has crucial importance during the return process of heat. The samples were cut off in the form of blocks with dimensions 10 x 10 x 2,5 cm.

The investigated materials were obtained in the raw state, therefore they were initially presintered at 600°C (duration time 3h). The presintering was applied to eliminate the crystal water from rocks and to prevent futures cracking. Cracking may be caused by the transformation of the sulfide, iron carbonate (and others) at the elevated temperature in stable oxides. This transformation results in a color change of the raw material and relaxation structure. In addition, the rocks containing a large amount of SiO₂ at the elevated temperatures revealed the so-called "quartzose effect" and thus change the polymorphic quartz β , the variation high temperature quartz α at 573°C (Tiskante et al. 2016)

The calculations of basic thermal parameters of materials were performed (J. H. Schön 2015):

1. The amount of heat ΔQ

Taken up by the body during heating or emitted during its cooling is proportional to the product of the mass of the body m and the temperature difference ΔT of the body before and after heat transformation. This rule can be written as (equation 1):

$$\Delta Q = c \cdot m \cdot Dt [J] \tag{1}$$

2. Thermal power P

The measure of thermal energy emission is constituted by thermal power P, which is defined by the relationship (equation 3):

$$E = \Delta Q = c \ m \cdot Dt$$
 the amount of emitted energy [J] (2)

t – the time the emission [s] (10800s for performed experiment)

$$P = E / t - thermal \ power \ [W] \tag{3}$$

The materials accumulating heat used in practical applications should be characterized by a relatively high thermal power.

3. The ability of thermal accumulation b

Another parameter characterizing the material in terms of thermal properties is constituted by heat capacity. Its value b is calculated as the product of the specific heat c and density ρ of the material (equation 4):

$$b = c \bullet \rho \left[J / (m^3 K) \right] \tag{4}$$

Results

The samples were placed in the oven, setting its operating temperature up to 140°C. At this temperature the samples were kept for one hour, then removed from the oven and placed on the ceramic top. The surface temperature of samples was examined using the thermal imaging camera NEC Thermo type Gear G100.

The obtained values are shown in Table 1. The results also shown in Fig. 2.

Thermal imaging camera

The way in which the test materials emitted heat was recorded by thermal imaging camera. The obtained images are shown in Fig. 1.





Amphibolite

Gabbro Granodioryte

Quartzite



Fig.1. Thermal imaging photos of investigated materials Rys. 1. Termowizyjne zdjęcia badanych materiałów



Fig. 2. The surface temperatures of the materials tested during the heat dissipation Rys. 2. Temperatury powierzchni badanych materiałów podczas oddawania ciepła

Oxide	Serpentinite	Amphibolite	Gabbro	Granodiorite	Quartzite
SiO ₂	45,23	43,27	55,90	61,93	98,5
Al ₂ O ₃	4,27	15,73	4,76	16,01	0,8
Fe ₂ O ₃	5,21	10,28	9,65	4,52	0,23
MgO	44,31	8,41	10,91	5,03	0,07
CaO	0,34	13,37	14,77	5,38	-
Na ₂ O	0,40	4,08	2,88	3,92	0,15
K ₂ O	0,04	2,19	0,19	2,61	0,15
TiO ₂	0,20	1,78	0,91	0,58	0,08

Tab. 2. The oxide composition of the samples (main oxides) in % wt Tab. 2. Składy tlenkowe skał (główne tlenki) w % wag

Heat emission

The parameter which determined whether the material returning heat will affect the room temperature in a prolonged time, is the time of emission of stored energy.

Despite the fact the samples are of and are in the same temperature conditions after the removal from the oven they have different temperatures. Five minutes after the end of annealing granodiorite has the highest temperature $(133^{\circ}C)$ and - quartzite the lowest $(124^{\circ}C)$. After 30 minutes the sample granodiorite still was the warmest $(82^{\circ}C)$ and the temperature decreases with time for this the sample were the lowest. The quartzite sample cools down the fastest. The analysis of decreases of temperatures during further cooling confirms this pattern. Granodiorite is hot for the longest period of time, while quartzite cools down the fastest. This is due to the mineral composition and density of the tested materials. After 180 minutes all samples reach the ambient temperature of $25^{\circ}C$.

The oxide composition of the samples and the ability of heat accumulation.

Theoretical specific heat capacity for particular samples was calculated using the data from the chem-

ical analysis and the tabulated values of heat capacity for the individual oxides (Table 2). The oxides which exhibit good and very good thermal conductivity are oxides of iron, aluminum and magnesium. The calculation results are presented in Tables 3–6.

The investigated materials are characterized by similar values of the theoretical specific heat capacity – the highest value was observed for quartzite i.e. 73.71 J/gK, and the lowest in the case of amphibolite 60.68 J/gK. It should be noted that the specific heat values refer to a mass unit 1g, and thermal analysis were performed for the samples of the same volume 250 cm³. This parameter has been included in further calculations.

The chosen thermal parameters (ΔQ , P, b) for particular samples were calculated according to the obtained results. The results are presented in Table 6.

Analyzing the results it can be noticed that the highest thermal power is revealed by a serpentine sample (5.97 in) lower – granodiorite sample (5.69 W). The lowest thermal power is revealed by a sample of quartzite (4.61 W). Maximum values of thermal conductive oxides is observed in the case of serpentinite and granodiorites (wherein the composition of granodiorites is much less stable). These materials are good

Ovida	Cp	Molar mass	Ci
Oxide	[J/mol·K]	[g/mol]	$[J/g \cdot K]$
SiO ₂	44,60	60,08	742
Al ₂ O ₃	79,03	101,96	775
Fe ₂ O ₃	104,6	159,69	655
MgO	37,24	40,30	924
CaO	42,05	56,08	750
Na2O	69,12	61,98	1115
K ₂ O	72,00	94,20	764
TiO ₂	55,08	79,88	690

Tab. 3. Specific heat capacity of individual oxides Tab. 3. Wartości ciepła właściwego poszczególnych tlenków

Tab. 4. Values of calculated specific heat capacity according to the oxide weight [J/g·K] Tab. 4. Wartości ciepła właściwego badanych surowców obliczone w zależności od udziału wagowego tlenku [J/kg·K]

Oxide	Serpentinite	Amphibolite	Gabbro	Granodiorite	Quartzite
SiO ₂	335,6	321,1	414,8	459,5	730,9
Al ₂ O ₃	33,1	121,9	36,9	124,1	6,2
Fe ₂ O ₃	34,1	67,3	63,2	29,6	1,5
MgO	409,4	77,2	100,8	46,5	0,6
CaO	2,5	100,3	110,8	40,4	-
Na ₂ O	4,5	45,9	32,1	43,7	1,7
K ₂ O	0,3	16,7	1,4	19,9	1,1
TiO ₂	1,4	12,28	6,3	4,00	0,5
Σ	820,9	762,7	766,3	767,7	742,5

Tab. 5. Selected physical parameters of the investigated materials Tab. 5. Wybrane parametry fizyczne badanych materiałów

Sample	Mass [g]	V [cm ³]	Density [g/cm ³]	ΔT [°C]
Serpentinite	727		2,91	108
Amphibolite	750		3,00	104
Gabbro	737	250	2,95	106
Granodiorite	755		3,02	106
Quartzite	677		2,71	99

heat accumulators (confirmed by the thermal imaging camera analysis) and can be successfully used in heating technologies.

Summary

Serpentine is characterized by high density, mainly due to the presence of pyroxene, and magnetite. The value of its thermal conductivity coefficient is also high, as a result of high compactness of this rock and its grain size and shape. Therefore, serpentines should absorb and dissipate the heat at a constant level for a relatively long period of time, which was confirmed /by laboratory tests. The preferred feature of these rocks consists in also the disordered structure which causes the heat to be conducted in all directions equally. Simultaneously, at the same time it provides uniform heating and cooling of the stone. Granodiorite, particularly in its fine-crystalline form, is concise and resistant to mechanical factors. It is characterized by a high thermal conductivity. The isotropy arrangement of components ensures uniform conditions for heating and cooling of the stone. No harmful ingredients are released during heating up to the high temperature of the rock. Substantial variations in the chemical composition of the raw material constitute the downside.

Amphibolite and gabbro show average values of thermal power and the ability of heat accumulation.

Quartzite rock is almost monomineral. It contains more than 90% of very small grains of quartz (0,17-0,20 mm). They have sharp-edged contours and thus mesh with each other. This results in very good chemical resistance and corrosion of this material, which is important when using quartzite as a protective lining. It is the fastest heating raw material.

Sample	$\Delta Q [J]$	<i>P</i> [W]	$h[I/(m^{3}K)]$	
Sample	for V=2.	50 cm ³	$b [\mathbf{y}(\mathbf{m} \mathbf{x})]$	
Serpentinite	64454	5,97	2389	
Amphibolite	59491	5,51	2288	
Gabbro	59862	5,54	2261	
Granodiorite	61439	5,69	2318	
Quartzite	49765	4,61	2012	

Tab. 6. Selected thermal parameters of investigated materials Tab. 6. Wybrane parametry cieplne badanych materiałów

Conclusions

1. Factors influencing the value of the volumetric heat capacity of the materials consist in their mineral composition, since this capacity is the sum of the volumetric heat capacity of individual components. Raw materials containing natural minerals in their composition with a higher volumetric heat capacity will have better thermal energy storage capacity.

2. A good solution would be to use two raw materials simultaneously, i. e. a promoter of heat and accumulator. As a promoter of heat, and the protective material it is proposed to use quartzite, in the form of thin plates, directly adjacent to the heat radiator steel.

3. The parameters which determine the possibility of using the material to accumulate heat in practical applications are: a. volumetric heat capacity

b. the amount of heat energy, which the material is able to receive and to accumulate in a unit of its volume,

c. thermal power, describing the material ability to return accumulated energy in a specific time.

4. An important factor in determining the ability of accumulation of the material is the maximum temperature for which the material can be heated to exceed this temperature result in disintegration of the raw material.

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Analiza właściwości cieplnych wybranych surowców naturalnych, na podstawie badań wykorzystujących metody termowizyjne

Akumulacja ciepła oznacza zdolność materiału do gromadzenia i magazynowania w jego wnętrzu określonej porcji energii cieplnej, która następnie może być przez pewien okres czasu przez ten materiał oddawana. Szuka się więc sposobów gromadzenia ciepła wtedy, gdy jest jego nadmiar oraz wykorzystania, gdy występuje deficyt. Parametrem, decydującym o tym czy oddający ciepło materiał w sposób długotrwały będzie oddziaływał na temperaturę pomieszczenia, jest czas oddawania (emisji) zgromadzonej energii. Przy danej ilości zgromadzonej energii, czas jej emisji nie może być zbyt krótki (wtedy w jednostce czasu oddawane są zbyt duże ilości ciepła) ani zbyt długi (wtedy w jednostce czasu oddawane są zbyt małe ilości ciepła, niewystarczające np. do ogrzania pomieszczenia).

W niniejszej pracy zrelacjonowano eksperyment polegający na badaniu zachowania się, podczas studzenia, naturalnych surowców mineralnych. Na tej podstawie badań oraz wykonanych obliczeń oceniono jego zdolność do akumulacji cieplnej. Pozwoliłoby to na stosowanie ich do wytwarzania elementów, w tym prefabrykatów, pracujących w podwyższonych temperaturach, gdzie jest istotna akumulacja i oddawanie ciepła (np. obudowy palenisk i komików)

Słowa kluczowe: ciepło właściwe minerałów, emisja ciepła, termiczne właściwości skał, moc cieplna, termowizja