Silicate composites modified with the use of diabase and barite aggregate as an alternative for low-energy construction.

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Abstract. Growing interest in low-energy construction in Poland causes that apart from the use of renewable energy resources to supply power to the buildings, the most modern technological solutions are used, and sand-lime blocks are among them. They are characterized by high level of heat accumulation, high thermal insulation properties, they are a soundproof barrier allowing to maintain the high standard of using the building. Thanks to the use of exclusively natural raw materials for their production, they are also fully ecological. The purpose of the proposed modifications of silicate bricks is to improve physical and chemical properties, thus the performance characteristics, as well as to improve technological process. The article focuses on the optimization of the silicate material composition with the use of diabase and barite aggregate. Compressive strength, water absorption, density with use of pycnometer, porosity and tightness of composites were determined. Microstructure (phases composition) was examined using SEM, EDS and XRD analysis. Silicate components containing 10% of the diabase aggregate and 10% of barite aggregate achieve a compression strength of more than 8 MPa higher than the reference specimen. The use of modifiers at 10% (5% of diabase and 5% of barite) contributes to the improvement of bulk density from 1.821 to 2.189 g/cm³. This approximates the proper design of the material in terms of heat-humidity and reduces energy consumption in buildings.

1. Introduction
Increasing awareness of the possibility to use ecological and energy-efficient solutions in residential construction is the reason for the fact that houses with the NF40 energy standard (energy consumption lower than 40 kWh per 1 sq. m a year) are more and more popular [1]. Thanks to the use of photovoltaic panels, solar collectors, heat pumps and recuperation, the houses that are developed could not, however, reach high parameters of energy efficiency without proper materials that are environmentally friendly and at the same time allowing to reduce the costs of exploitation measurably. This includes the materials serving for making outer and inner walls - sand-lime products, which are also called silicates. These materials are made of only natural raw materials, they do not produce any harmful substances, they are bio-corrosion resistant. Silicates are non-combustible (classification of reaction to fire - A1), they have the highest levels of strength among all building materials and, what is particularly important, they significantly stabilize humidity and temperature in rooms - and this is colloquially called as the best "breathing" walls [2]. An extremely important requirement that should be met by the walls is to ensure properly high thermal inertia of the building. Heat accumulation in the walls is bigger when their mass per unit area is bigger. The use of silicates for making the walls in a building significantly increases the possibility to "store" the heat in the walls during winter and to ensure coolness during summer.
In the recent years, research on the modification of autoclaved sand-lime products has been carried out. Additives used in the conducted research are, among others: plastic additives and recycled materials, polyethylene glycol or landfill leachate. The purpose is to improve the strength of finished materials or to reduce the water absorption. It results from the literature [3] data that the use of a polyethylene glycol from 1% to 5% absorbs about 60% water less than reference specimen and the use of a modifier in an amount of 1% or 5% give similar result in water adsorption test. Specimen containing 1% this kind of liquid characterize improve compressive strength. The addition of recycled plastics to sand-lime products can help to improve their functional properties. Suitably chosen type of polymer and its amount influences the increase in compressive strength, decrease in bulk density and water absorption as well as changes in the microstructure of resulting product. The highest average compressive strength value obtained silicates with HIPS regranulate in an amount of 20%. Specimens in an amount of 30% achieves decrease water absorption of approximately 14.8% (from 16.0% to 1.2 %) [4]. Conducted research allowed that the used landfill leachate contributed to achieving slightly higher compressive strength of modified sand-lime products in comparison to the traditional product (from 20.5 MPa to 21.9 MPa). More significant impact was observed in bulk density and water absorption tests (from 15.40% to 13.43%) [5].

To the silicates, there are also added aggregates of different grain size e.g. basalt, barite. These aggregates are characterized by very high compressive strength. However, they have to fulfill a number of standards and requirements that guarantee the longevity of formed on building materials aggregates and their safety of use. Modification of sand-lime products with basalt aggregate resulted in a threefold increase in compressive strength, reduced water absorption from 16% to 9 % relative to weight, and increased the density of the modified product [6,7]. In the production of silicates, the use of barite aggregates with a grain size of 0-2 mm resulted in a significant increase in compressive strength to 44.9 MPa with a 20% aggregate contribution and to increase the bulk density of the silicate bricks [8].

The main influence on the optimal strength of sand-lime products is that of the type of the used raw materials, the composition of production mixture, the way of raw material preparation, the autoclaving process and the moisture content. The density of the products also has an influence on the improvement of strength. Gross dry density of silicate bricks is usually within the range of 1900÷2400 kg/m³ [9]. In this article, the combination of diabase and barite aggregate was used. Diabase aggregate has been obtained from the Niedźwiedzia Skała mine, located in Małopolska province. Diabase, in terms of mineral composition and origin, belongs to the group of gabras and basalt. It is characterised by good performance properties. Aiming at obtaining a proper grain-size curve for sand-lime products, barite aggregate (BaSO₄) was used alongside diabase aggregate. The purpose of the combination of these two aggregates was to reduce the lime used in basic composition of material mixture. The main purpose of this article is to find an answer to the questions: Will diabase and barite aggregate have a positive influence on the properties of sand-lime products? Will the use of diabase and barite aggregate combination have an influence on the improvement of thermal insulation properties or thermal capacity?

2. Experimental
Specimens of 40 x 40 x 160 mm were made in industrial conditions. A precise L/S (Lime/Sand) molar ratio is not known. Theoretically, the content of quicklime, the quality of which meets the requirements determined in PN-EN 459-1[10] standard, is within the range of 7-8%. On the other hand, the amount of quartz sand is between 92% and 93%. In the experiment, a finished sand-lime mixture obtained from Silicate Production Plant in Ludynia was replaced by diabase (grain size 0-2 mm) and barite aggregate mixture. In this experiment 4 series of 3 specimens were produced. The specimens marked by the R symbol is a reference specimens. The specimens marked by the 1 symbol contains 5% of the modifier (2.5% of diabase aggregate and 2.5% of barite aggregate). Number 2 is with the amount of 10% of the modifier (5% of diabase aggregate and 5% of barite aggregate). Specimens 3 contains 20% of the modifier. Table 1 shows proportioning by weight of particular components. It should be noted that the dry components were mixed with 5% of water in relation to the total weight of the product. The reported results are averaged. Technological process of specimens is presented in the following way:
measured components of sand-lime mixture with diabase and barite aggregate were manually mixed with water, the mass was put in steel molds, the specimens were pressed with the force of 25 MPa, the specimens underwent the autoclaving process for 8 hours (it means: 1 h heating + 6 h autoclaving + 1 h cooling). The temperature of hydrothermal treatment of the products is around 200°C, the pressure 1.6 MPa.

Table 1. Components of sand-lime specimens.

| Symbols | sand + lime [g] | diabase [g] | barite [g] | water [g] |
|---------|----------------|-------------|------------|-----------|
| R       | 1800           | -           | -          | 90        |
| 1       | 1710           | 45          | 45         | 90        |
| 2       | 1620           | 90          | 90         | 90        |
| 3       | 1440           | 180         | 180        | 90        |

3. Testing methods
Experimental specimens were tested for physical and chemical parameters. In accordance with the standard [11], the absorbability of the tested products was determined. Thanks to the test of specific density conducted with the use of pycnometry, the tightness and porosity of the tested silicates was calculated.

After 21 days of the autoclaving process, the compressive strength of silicate products was tested in laboratory conditions, using a hydraulic press (Tecnost KC 300).

Photos of the internal structure were made to observe hydrated calcium silicate morphology using scanning electron microscope (SEM-type Quanta 250 FEG) and EDS analysis. The analysis of the composition was carried out with the X-ray diffraction method (XRD). Powdered specimens of silicates were tested in an Empyrean diffractometer of the PAN analytical company, with the use of Cu X-ray tube, within the range of angles 20 from 5 to 55°. The quality analysis of diffractograms was conducted on the basis of ICDD PDF-2 database.

4. Results and discussion
Figure 1 shows the dependency of the density on the compressive strength. The increase of the amount of diabase and barite additive in raw materials mixture has an influence on the growth of compressive strength of the obtained materials. The highest value was achieved by adding 20% of modifier to the autoclaved materials (10% of diabase aggregate and 10% of barite aggregate). However, regardless of the quantitative composition of raw materials mixture, a higher value of strength in relation to the reference products was obtained in each case. Diabase aggregate is characterised by the strength of 230 MPa, and the larger the amount of this modifier in the specimen is, the higher its strength is. So it can be concluded that diabase aggregate is responsible for the increase of strength in the tested sand-lime products. It is optimal amount in raw materials mixture is 10%. It results from the experimental research carried out by the author that using larger amount of diabase (30, 40, 50 %) has a negative influence on the performance properties of the finished products.

Specimens with the amount of 10% of diabase aggregate and 10% of barite aggregate in proportion to the total mass of the product show the highest value of density, and it is 2.684 g/cm³. The statement known from the literature indicates that the increase of the density is related to the increase of compressive strength and it appears to be reflected in autoclaved sand-lime products modified with the use of diabase and barite aggregate.

The increase of bulk density is connected with the value of thermal conductivity[12]. Taking into consideration the data from Table 2, it can be concluded that the addition of diabase and barite aggregate can have a negative influence on the change of thermal insulation properties.

Specimens 1, 2 and 3 that were tested in terms of absorbability show higher value in relation to the reference specimens. Growth of 2.13% for specimens 1, 2.75% for specimens 2 and 1.92% for specimens 3 was recorded. However, data shown on Figure 2 are within the range between 10% and 16%, characteristic for silicates that are in Grupa Silikaty manufacturer's catalogue [13].
Figure 1. Density dependence on compressive strength.

Interference in the basic composition of the raw materials mixture of autoclaved sand-lime products seems to have positive repercussion, taking into consideration the thermal capacity of the material. It was noted that regardless of the amount of the modifiers, bulk density increases. The higher the bulk density of the silicate is, the higher amount of heat it is able to accumulate [14]. Using 10% of the modifiers (specimens 2) allows to conclude that this product will be characterised by the largest thermal capacity among the tested materials. Thanks to this fact, the interior of the building made of this type of silicate will not heat up excessively and there will be no need to cool it. The accumulated heat in the silicates will be emitted in cold period, and this will reduce the amount of energy needed for heating.

Figure 2. Water absorption for specimens R, 1, 2 and 3.
By analysing the microstructure of sand-lime products that are the basis of this article, it can be stated that there is co-occurrence of two basic products of synthesis taking place in hydrothermal conditions, i.e. C-S-H (Figure 9) and tobermorite occurring in the form of extended plates (Figure 5). EDS analysis revealed the occurrence of the C-S-H phase (what is visible in Figure 7) and confirmed the addition of a barite (Figure 6). The C-S-H phase (Figure 4) is the basic product created at the initial stage of the reaction between ions of calcium and silicon and thanks to its binding properties, it permanently and very efficiently joins particular grains of quartz sand [15]. The replacement of sand-lime mixture with 5% and 10% of filler in the form of two aggregates allowed to notice both semi-crystalline C-S-H phase, as well as tobermorite phase. In specimen 3, with the content of 20% of modifier, the stabilisation of the C-S-H phase was observed. The production of large amount of this phase (Figure 8) has a positive influence on the mechanical properties of the finished product (compressive strength). The changes consisting in the modification of raw materials composition of the production mass thus have an influence on the internal structure of autoclaved products, i.e. on the occurrence and the amount of the created products of the synthesis and the porosity of the product. On the basis of the conducted tests, it can be concluded that the type and size of the aggregate is of significance in the total pores volume. It results from the data that specimens R, 1 and 2 are characterised by comparable total porosity (+-2 %). In the specimens with symbol 2, this value decreased by more than 12% in relation to the reference specimen (Table 2). The conclusion relating to the cause of the occurred decrease can be drawn only when the information about the size of the pores, their distribution and shape is obtained.

Table 2. Results of the research.

| Symbols | Amount of diabase [%] | Amount of barite [%] | Density [g/cm³] | Bulk density [g/cm³] | Tightness [%] | Porosity [%] |
|---------|-----------------------|----------------------|-----------------|----------------------|--------------|-------------|
| R       | -                     | -                    | 2.587           | 1.821                | 70.39        | 29.61       |
| 1       | 2.5                   | 2.5                  | 2.551           | 1.850                | 72.52        | 27.48       |
| 2       | 5.0                   | 5.0                  | 2.641           | 2.189                | 82.89        | 17.11       |
| 3       | 10.0                  | 10.0                 | 2.684           | 1.910                | 71.16        | 28.84       |

Because of the above fact, it is suggested to develop the research on the porosity of the autoclaved sand-lime products modified with the use of diabase and barite aggregate.

Figure 10 shows diffractograms of three specimens of silicates of different quantity of barite and diabase. On all diffractograms, peaks of quartz are the most clearly distinguished. Its three main peaks were identified (26.64; 20.858; 50.141 °2θ) and a range of minor ones, occurring above 35 °2θ, were also identified. The presence of barite was also proved (25.864; 28.766; 42.952 °2θ), but because of small amount in the specimen, its peaks were significantly less noticeable than the quartz peaks. The intensity of the barite peaks increases along with its amount in the specimen. Plagioclases included in diabase can be responsible for the occurrence of the peaks visible within the range of angles of 27.0÷28.5 °2θ. The use of calcium during the production of silicates proves the presence of the peaks from portlandite on diffractograms (34.101; 18.066 °2θ) and the peak for the angle of 29.4 °2θ which is consistent with the most intense peak of calcite. The calcite in the tested specimens could have occurred as a result of carbonatation of portlandite. Insignificant intensity and the lack of other peaks characteristic for these phases is the result of small quantity of the lime that was used. The intensity of the portlandite and calcite peaks decreases along with the increase of the amount of barite and diabase because they were partially replaced by lime. On the produced diffractograms, no clear peaks that could origin from tobermorite produced as the result of autoclaving process were found.
Figure 3. Microstructure of specimen 1.

Figure 4. Microstructure of specimen 2.

Figure 5. EDS analysis of specimen 3.

Figure 6. EDS analysis of specimen 2. C-S-H phases.

Figure 7. Microstructure of specimen 3.

Figure 8. Microstructure of specimen R.
Figure 9. Diffractograms of silicates: B- barium, C-calcite, Q- quartz, P- portlandite, T- tobermorite.

5. Conclusions
Diabase and barite aggregate modifies the performance properties of autoclaved sand-lime products.

The optimal quantity of the modifier, taking into consideration the compressive strength, is on the level of 20% (10% of diabase aggregate + 10% of barite aggregate). The indicated amount of aggregates in the raw materials mixture allows to obtain the compressive strength which is more than 8 MPa higher in comparison with the reference products.

The observed effect of the improvement of strength characteristics of autoclaved products is not reflected in the microstructure of the tested materials. Regardless of the changing, in the quantitative sense, initial composition of raw materials mixtures, the occurrence of C-S-H phase and small quantities of tobermorite phase is noticed.

The use of 5% of diabase aggregate and 5% of barite aggregate in the mixture has an influence on the improvement of specific density, and simultaneously, on the decrease of total porosity of the products.

The use of the mixture of diabase and barite aggregate as the substitute of sand-lime mixture can contribute to the decrease of lime consumption, without deterioration in the quality of the obtained with their content sand-lime products, and in specific cases, to obtain finished products with more beneficial performance properties.

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