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Section: Environmental protection

The impact of barium sulfate on the microstructural and mechanical properties of autoclaved silicate products

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Abstract

Last decades are a special example of the technical and technological development in the construction industry, what is dictated among others by the durability of produced materials and the way of acquiring raw materials for producing etc., and farther by their storing. Moreover, in recent years particular attention has been paid to the naturalness and also harmlessness of materials applied in the construction industry with regard to the protection of people and environment. A protection against the ionizing radiation is also an important aspect due to the harmfulness of radio-elements appearing in nature with the various activity and to the risk of the breakdown of nuclear power plants.
Silicates are obtained from a mixture of ground quartz sand and calx with a small amount of water. They emerge as a result of the hydrothermal treatment conducted under high pressure and at a specified temperature (app. 203 °C).
Addition of barium aggregate to the silicate mass leads to increase in endurance features of the final product by limiting free spaces in modified silicate. Applying the barium aggregate with the grain size 0–2 mm at the production stage also had an effect on the changes in the internal structure of the element and the improvement of its macro- and microstructural properties.
Introduced aggregate led to increase in bulk density of the silicate product.

Keywords: Silicates; barium aggregate; protection; X-ray diffractometry (XRD); Microstructural.

Nomenclature

σ	compressive strength [MPa]
ρ	density (kg/dm^3)
Z	number of electrons in atoms of elements
X_1	percentage content of the barium sulphate in the silicate product
N	standard silicate products
40	silicate blocks with 20% of addition of the barium sulphate
100	silicate blocks with 50% of addition of the barium sulphate
H_x	power of the photon dose equivalent [mSv/h]
K	rate of weakening the radiation beam
X	radiation energy [keV]
SEM	scanning electron microscope
XRD	X-ray diffractometry

1. Theoretical assumptions

Both traditional silicate products and those modified with barium aggregate with the grain size of 2–3 mm have been tested.

For the purposes of the experiments laboratory samples of traditional and modified products were prepared. Under laboratory conditions samples with dimensions of 40×40×160 mm were made. After the laboratory tests solid silicate bricks with dimensions 180×220×250 mm were prepared.

The interpretation of the microstructure was carried on the basis of electron scanning microscopy (SEM-type pyrrol 5400 cooperating with the EDS analyzer) and X-ray diffraction (XRD-Empyrean, PANALYTICAL). Compressive strength test was conducted using a hydraulic press.

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Widely used in science, technology and industry, SEM (Scanning Electron Microscope) was used for quantitative analysis of the elemental composition and elemental distribution in a given area of the sample. The area of the sample was swept by electron probe under voltage of 5–50 eV. On the basis of obtained images the analysis of the microstructure and phase composition of the tested products was possible. The SEM study was preceded by XRD examination, that is X-ray diffraction.

Thesis formulated in accordance with applicable standards (PN-EN 772-9,10,11,13) became the basis to perform the study. For the first thesis the reference point was the question whether the change in mass of silicate product without changing its volume will improve the physical and mechanical properties (i.e. strength) of modified elements [5, 6, 7, 8, 9].

In addition to examined functional properties (i.e. water absorption caused by capillary raising, humidity, bulk density and water absorption) an important aspect turned out to be also another of the physical characteristics, which was the ability of material to weakening ionizing radiation. When using X-ray generators the radiation energy is about 100–120 keV. Therefore, in areas where there are mentioned devices protective screens should be used.

The effectiveness of various materials in weakening of gamma radiation depends on the number of Z elements forming the casing material, which is the number of electrons in the atoms of the elements and the radiation energy. According to [1] with photon energies less than 0.5 MeV, more effective in radiation weakening are these concretes which contain possibly large amount of elements of high Z number (the more effective it is, the lower the radiation energy). With concretes it causes reducing their dimensions and the weight of casing material relative to the casing of lighter concretes. However, at 0.5–5.0 MeV energies the differences in weakening efficiency are proportional to the differences in bulk density of materials [1]. Assumed is thesis that, in the case of silicate products, also at the X-ray energy less than 0,5 MeV, the weakening efficiency depends on the bulk density of the product.

Compressive strength of traditional silicate products is about 15–20 MPa, and their bulk density is approximately equal to 1.73 kg/dm^3. Contrary to popular opinion silicates are not 'wet' material, because they absorb up to 8% less water than other building materials for the construction of external and internal walls (silicates absorb 16% of water relative to their weight, whereas other groups of building materials absorb up to 24% of water relatve to their weight).

Silicate products are material formed as a result of hydrothermal treatment (autoclaving). In traditional silicate products, hydrated calcium silicates of varying structure arrangement occur forming among others CSH phase and tobermorite phase with lamellar cross section. The inner structure of silicates has not been fully recognized yet, so studies on its effect on the functional properties of silicate products and the possibilities and directions of their modification are still ongoing [2, 3, 4].

The research was conducted in collaboration with Silicate Production Plant in Ludynia, belonging to the SILIKATY GROUP.

2. Methodology of experimental research

Based on the theoretical assumptions, the aim of the research was the modification of silicate products directed toward improving their microstructural and physico-mechanical properties. In addition, due to the risk caused by radiation, present not only in nuclear power plants, but also in hospitals and medical institutions, the modification of silicate products which main task would be to limit the emission of harmful radiation was attempted. The experiment was performed on solid silicate masonry elements of dimensions 250×180×220 mm, class 15, and also on the modified products, of the same dimensions, but different structure.

Preliminary technical and economic analysis showed that among the various types of additives to improve the physical and mechanical properties (i.e. functional) of products, the best was, among others, is the use of: barite, basalt, hematite, or magnetite. The density of resulting products plays here an important role due to the assumed thesis.

Some of the used aggregates have a high hardness. These materials exhibit durability of up to 8.5 on the Mohs scale, hence their relatively widespread use in the construction industry. Following this division, it was concluded that the hardness of the solids is dependent on the energy of bonds existing in their structure. Therefore, barium aggregate fraction 0–2 mm was chosen to the experimental studies. Silicate mixture was modified with the barium aggregate in an amount of: 5, 10, 20, 30, 40, 50, 60%. So modified silicates were analyzed determining their functional (physico-mechanical) properties and microstructural properties (SEM, XRD). The study determining the level of ionizing radiation was carried out on the following silicates:

- silicate blocks „N" – standard silicates
- silicate blocks „40" – with 20% of addition of the barium sulphate
- silicate blocks „100" – with 50% of addition of the barium sulphate

Measurements of ionizing radiation

In accordance with the adopted methodology of research, the measurement of ionizing radiation on X-ray position was performed using an electrometer UNIDOS with ionisation chamber LS-01.The measured value was Hx [mSv / h] (the power of the photon dose equivalent). The scheme of the measurement system is shown in Figure 1.

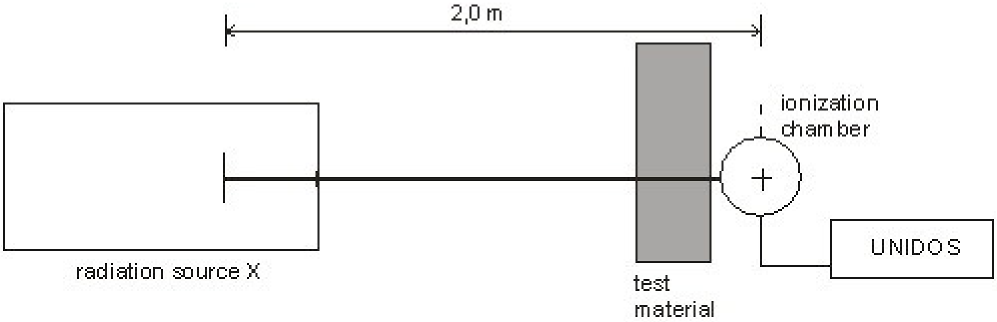

Fig. 1. The scheme of the measurement system

3. Results of experimental research

The first performed test was the compressive strength of modified silicate products measurement. Compressive strength test also helped to determine the optimum composition of the silicate mass with the addition of barium aggregate (barium sulfate $BaSO_4$).

Physical and mechanical properties of modified sand-lime products were evaluated on the basis of the compressive strength of the samples (σ) and their bulk density (ρ). For this purpose *Statistica* program was used. Mixed factorial (complete) design 71 was carried out (with k = 1), i.e. full 1-factorial experiment. For each value of the input factor six parallel studies were performed.

The methodology of planning the experiment and the results of performed experiments are shown in Table 1.

Table 1. The matrix of experiment planning, the level of factor and test results

№ badania	Factor		Compressive strength [MPa]
	In imaginary cale	In natural scale	σ
	x_1	X_1 (Sb – barium sulfate) [%]	
1	1	5	33,3
2	2	10	36,6
3	3	20	44,9
4	4	30	43,4
5	5	40	42,1
6	6	50	36,9
7	7	60	20,2

The compressive strength of samples is described by regression equation:

$$\sigma = A_0 + A_1\,(Sb) - A_2\,(Sb)^2 \tag{1}$$

From the analysis of the regression Eqn (1) the following conclusions can be drawn:

1) Positive sign of coefficient of factor X1 indicates increased compressive strength with increased percentage content of Sb filler ($BaSO_4$).

The value of regression coefficient gives an idea about this, how much the compressive strength value changes, when the factor is changed by one variance interval.

To determine the optimal X_1 value (Sb-$BaSO_4$, which is the factor that characterizes silicate products compressive strength conditions), full 1-factorial design was carried out. Thanks to this it was possible to obtain the maximum value of the compressive strength of silicate products modified with the barium aggregate (Sb-$BaSO_4$).

Based on the results of experiments carried out for the established magnitude of the percentage content of X1 additive (Sb – 5%; 10%; 20%; 30%; 40%; 50%; 60%), compressive strength (σ) – the use of additive curve was created and shown in Figure 2.

The value of test factor in the optimal point at the maximum compressive strength value (σ).

The study of bulk density was conducted analogously Figure 3.

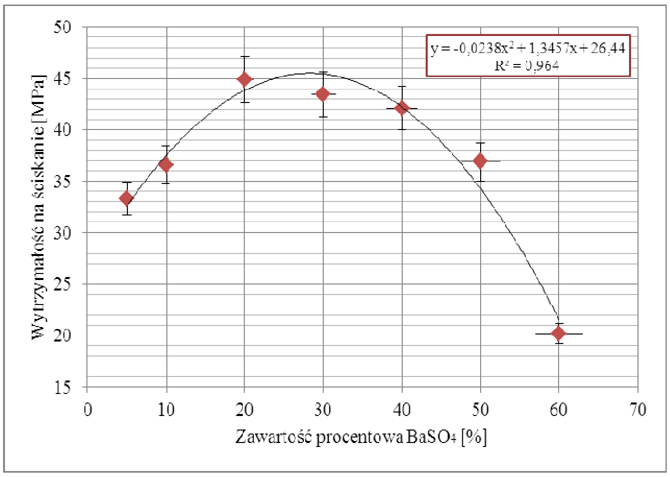

Fig. 2. Compressive strength value depending on the percentage content of barite aggregate ($BaSO_4$)

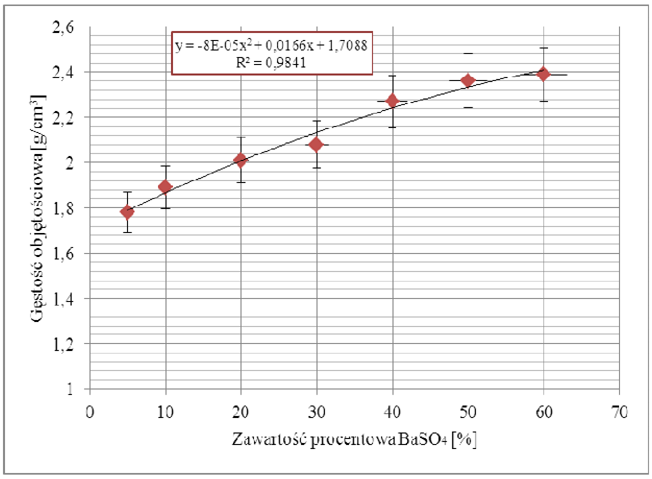

Fig. 3. Bulk density value depending on the percentage content of barite aggregate ($BaSO_4$)

3.1. Measurements of ionizing radiation

The result of measurements of the ionizing radiation of the element is the rate of weakening the X radiation beam. It was denoted by K and this is a quotient of power of the photon dose equivalent $H_{x,0}$.

Table 2. The results of weakening the X radiation beam test performed on the traditional and modified silicate products

Silicate brick	X radiation energy[keV]	Value of Hx,0 [□Sv/h]	Value of Hx [□Sv/h]	Rate of weakening, K
N	100	70,41	2754,2	0,02556
	118	598,66	16098,0	0,03719
40	100	3,41	2754,2	0,00124
	118	34,77	16098,0	0,00216
100	100	2,55	2754,2	0,00093
	118	14,55	16098,0	0,000904

The calculations of the thickness of radiation shield have been done. The required multiplication factor of the weakening the radiation beam was assumed. For the distance from the X-ray source to ionization chamber of L = 1.5 m, with X-ray energy of 100 keV, the required rate of weakening K = 1740, which corresponds to the thickness of ionizing radiation shield equal to 1,5 mm for a plate of lead. The results are shown in Table 3.

Table 3. The results of the calculations of required thickness of radiation shield

Silicate brick	X radiation energy [keV]	Weakening multiplication	Weakening multiplication ratio [σ]	Required thickness of radiation shield, d [mm]
N	100	39	44,6	153
40	100	807	2,16	7,4
100	100	1080	1,6	5,6

3.2. Microstructure of modified silicate products

Introduction of barium aggregate ($BaSO_4$) with grain size of 0–2 mm to silicate mass in the production stage has influenced the internal structure of the element (i.e. the microstructure, especially the phase structure). Beside CSH phase and the tobermotite (Fig. 4) a high strength phase has been created (Fig. 5). CSH phase is clearly amorphous (sometimes spongy) or takes the fibrous form. Tobermorite is characterized by the regular lamellar shape. High strength phase formed during autocalving is present in the form of long fibers with sharp endings, visually resembling needles. Unusual phenomenon was the sedimentation of the components, and more precisely barium sulfate $BaSO_4$, which is present in the product in the form of flakes or so called caramels (unreacted barium, Fig. 4, point 1). Research has shown that barium sulfate does not fill all the voids in silicalite, because of phases present in the product microstructure. In addition, barium sulfate only to a certain point connects to the phases, but after saturation it is only a filler of silicate mass. A high strength phase equated with xonotlite, occurs in the product with various frequency. The compressive strength of the modified product increased by over 60%.

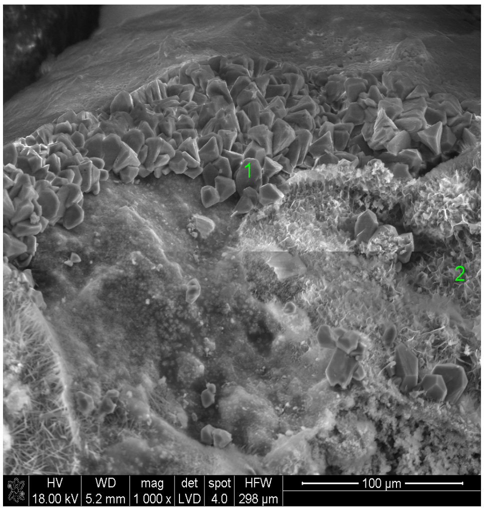

Fig. 4. Microstructure of products modified with barite aggreagte (CSH phase, tobermoeite, unreacted $BaSO_4$

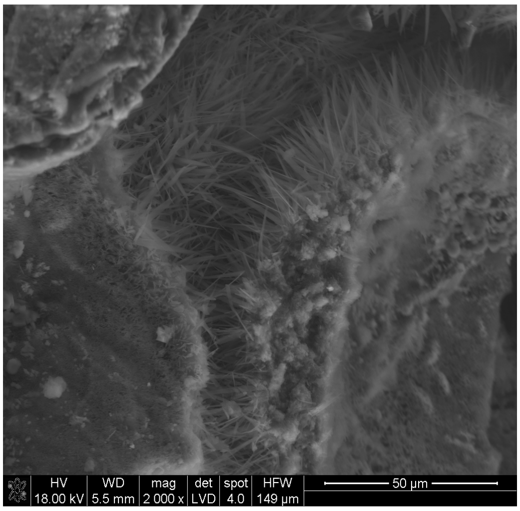

Fig. 5. Compaction of the microstructure of modified product and high strength phases.

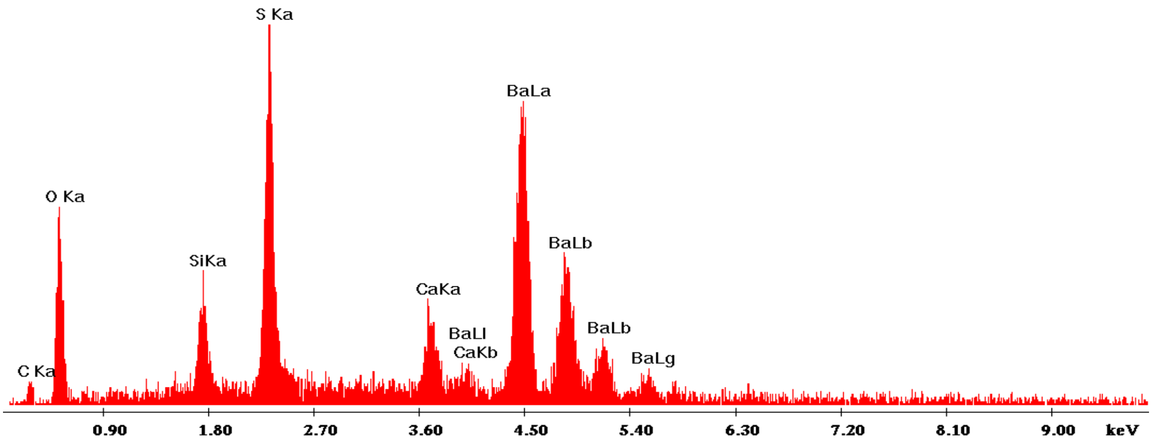

Fig. 6. EDS spectrum of silicate product modified with barite aggregate (BaSO4)

Modified silicate products have been subjected to XRD examination (X-ray diffraction). Performed studies have shown in the microstructure the existence of minerals typical for silicates (Fig. 7), i.e. quartz, which is composed mainly of silicon dioxide, and is a basic component of silicates, aragonite and calcite (multiform varieties of calcium carbonate $CaCO_3$ and products of hydrothermal processes). Calcite and aragonite is a variety of calcium carbonate. The minerals differ from each other by the hardness (calcite has a hardness value of 3 on the Mohs scale, while aragonite 4 on the Mohs scale), and crystallographic system. Aragonite occurs much less frequently than common calcite and has a higher density (2.95 kg/dm^3). Polymorphic forms of calcium carbonate are not present in various states of matter, as some sources claim, but there are various phases that make up the analyzed material. Transitions one variety to another are called phase transitions of the first order and are dependent on the thermal history of the sample. This means that phase transitions do not undergo in strictly defined temperatures (but in a temperature ranges), which in turn means that the compound may exist in two different polymorphic forms at the same temperature. XRD study of the crystalline part of the sample showed the presence of peaks from barite and tobermorite (Fig. 7). These are the qualitative analyzes.

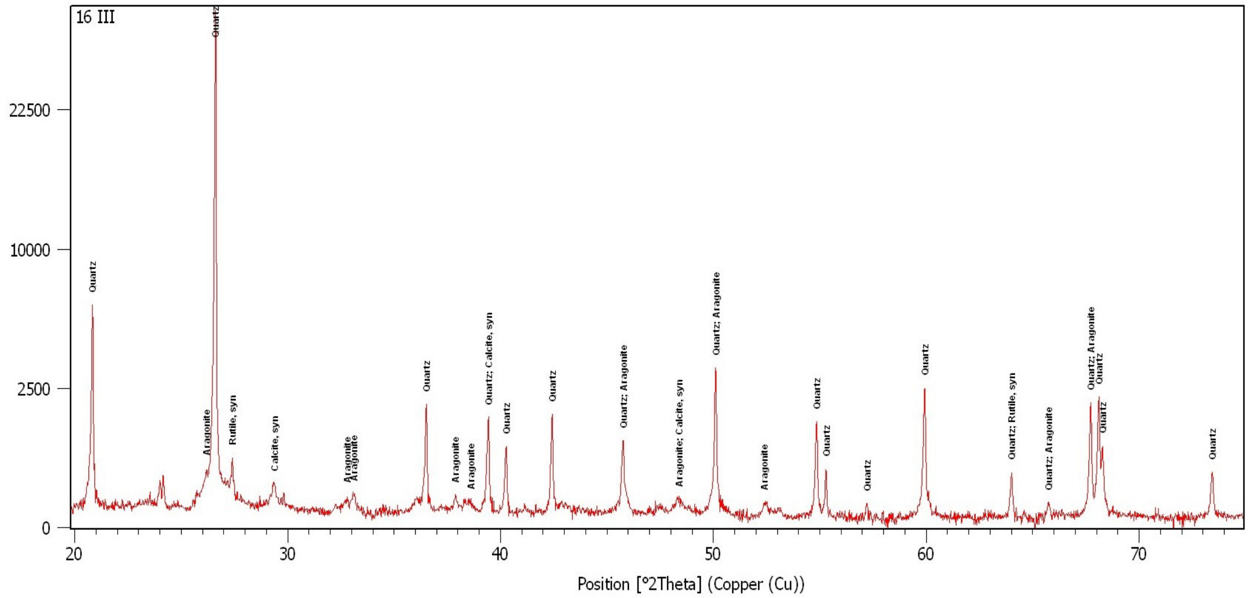

Fig. 7. X-ray diffraction of silicate product

4. Conslusions

On the basis of experimental research it can be concluded, that the assumed thesis has been defended. In the case of silicate products at the X-ray energy less than 0.5 MeV, the efficiency of weakening depends on the bulk density of the product. In the modified product, a high strength phase has also appeared.

Furthermore, introduction of barium sulfate ($BaSO_4$) with the grain size of 0–2 mm to the silicate mass had a positive impact on improving:

- compressive strength of the modified product to the value of 44.9 MPa with 20% share of barium aggregate in the silicate mass.
- bulk density, which average value was equal to 2.2 kg/dm^3, advantageously at 5–40% share of barium aggregate in the silicate mass.
- water absorption and water absorption caused by capillary raising, which in the modified product is limited to 10% relative to the weight of the product at 5–40% of barium aggregate in the silicate mass (from a standard value of 16%).

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