Research Article

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Effect of foam glass granules fillers modification of lime-sand products on their microstructure

https://doi.org/10.1515/eng-2019-0038
Received February 12, 2019; accepted May 13, 2019

Abstract: Silicate products are products made exclusively from natural raw materials. A relatively high value of the heat transfer coefficient is still considered a fault. This property adversely affects the thermal insulation of buildings and energy consumption, so you should look for materials with a low heat conduction coefficient. One of the ways of obtaining such products can be the use of light, porous fillers in the mass of lime-sand products. Due to the above, particular attention was paid to white foam glass in the form of granules, which is a product of recycling glass cullet. The research was carried out with a granulate size of 0.25-0.5 mm, share of which in the tested samples ranged from 5 to 30%. The obtained results were referred to the tests carried out on basic (lime-sand) sample.

The aim of the article is to determine the correctness of the formation of selected usable properties of modified lime-sand products, taking into account changes in their microstructure. The article describes the results of volume density and compressive strength tests of basic samples and the samples modified by using the expanded glass granulate as well as the results of their observations by using of SEM and tests of phase composition obtained from XRD.

Keywords: silicate products, glass, tobermorite, calcium silicate hydrates (C-S-H), SEM, XRD.

1 Introduction

Silicate products are products made only of natural raw materials, i.e sand, lime and water, thanks to which obtained products are characterized by very low natural radioactivity and the production technology itself states a mapping of the sandstone formation process in natural conditions [1, 2]. Among many advantages which characterize these products the compressive strength is of particular importance here. The disadvantage of silicate products is the high value of the thermal conductivity coefficient in relation to other building materials. In the aspect of conducted research, this problem is more important because the mandatory regulations rigorously tighten the requirements in the field of thermal insulation and energy consumption of buildings, so you should look for materials with low thermal conductivity both in the aspect of construction and insulation materials. One of the ways of obtaining such products can be the use of light, porous fillers in the mass of lime-sand products.

The a variety of selection of the optimal product available on the market to serve as a filler of materials often becomes a problem that should be solved using decision support methods [3, 4]. In this case, the choice of material that may be a light filler in lime-sand products from a wide range of available on the market raw materials and industrial waste has been made on the basis of multicriterial analysis of their essential characteristics. Thanks to the above, particular attention has been paid to white foam glass granulate being a waste product of recycled glass cullet, which use as a waste material used for production of construction products, can help at the same time to avoid the rising costs associated with environmental damage, as well as to promote the sustainable use of natural resources.

However, we should bear in mind that a reduction in the mass of the product is associated with a decrease in the mechanical strength of final products. This means, that the product obtained in this way will be characterized by properties that are close to properties of autoclaved aerated concrete, as well as for its production will be used only row materials of natural origin (sand and lime) and amorphous silica (the foam glass granulate) - important due to the usage of glass waste in construction industry.

Research on the modifications subject and the reduction of compressive strength of lime-sand bricks is more and more often encountered [5–7]. The modification itself of lime-sand products with recycled glass in various forms [8–11], as well as modification with waste materials [12–15] is already known in literature and practice. The
foamed glass granulates were also tested as an addition to cement mortar [12], and how it contributes to the reduction of density and compressive strength of the product.

Many authors have already studied the change in the microstructure of modified sand-lime specimens [16-18]. Scientific research has not been described so far in terms of hydration reaction on the surface of unreacted quartz grains and foamed glass granulates in autoclaved lime-sand products. This is a very important aspect as during autoclaving, essential chemical reactions occur that determine the phase composition and microstructure of the final compounds in the silicate-calcium autoclaved materials [19, 20]. The OH\(^-\) ions after turning to the liquid phase react with the silicate ions derived from the dissolution of SiO\(_2\) [21]. The result of this reaction is a formation of hydrated calcium silicates, called C-S-H (Calcium Silicate Hydrate) with different ratios of CaO, SiO\(_2\), and H\(_2\)O. They are characterized by a different degree of structure ordering - from amorphous (so-called "C-S-H phase") to crystalline (tobermorite, xonotlite) [22, 23].

It is commonly accepted, that the phase C-S-H has layered structure, close to structure of hydrated calcium silicate - tobermorite, and the gels produced by mixing of calcium and silica in water are characterized by C/S ratios between 0,7 and 1,5 [24, 25].

Texture of C-S-H having low grade of ordering consists of isomeric forms stating homogenous sponge-like mass, and respectively to the growth of ordering may develop as lamellar forms (foils) as well as laminar, tubular or fibre forms. There is a lot of classifications of C-S-H phase [26–32], mainly due to the CaO/SiO\(_2\) ratio (C/S ratio), that changes in line with temperature and depends on the grade of saturation of liquid phase by calcium ions [22].

The most known classification is the one described by Taylor, who distinguished two types of the C-S-H phase: C-S-H (I) having the ratio C/S < 1,5 – similar to tobermorite and C-S-H (II) with C/S > 1,5 similar to jennite [31, 33].

In the further research on the C-S-H structure, Diamond distinguished four morphological types of the phase: C-S-H I in the structure of fibre, C-S-H II in the structure of grid, called also honeycomb, that corresponds to the phase C-S-H (I) distinguished by Taylor, C-S-H III that creates isometric particles or braided and interlocked thin foils between themselves, C-S-H IV creating spherical agglomerates (concentrations), distinguished in the electron microscope research as closely packed gel [22, 34].

It should be taken into account that by introducing additives (fillers), new ions are often introduced into the sand-lime mixture, the quantity and quality of which have a significant impact on the formation of both crystalline and amorphous C-S-H phase as well as new phases not found in traditional products [18, 21]. Therefore, from the point of view of the conducted research, an important aspect is also the change in the microstructure of these products expressed in the degree of crystallization of the forming phases, as well as the range of formation of semicrystals. In view of the above, the aim of this article is to determine the correctness of development of selected functional properties of modified lime-sand products, taking into account changes in their microstructure. The results of observations of microstructure with the usage of SEM that are presented in this article were confirmed by the tests of phase composition obtained from XRD.

## 2 Materials and method

Specimens in the form of 40 \(\times\) 40 \(\times\) 160 mm beams were prepared for testing. The mass of the specimen was a silicate mixture (lime-sand), which consists of sand - silica and hydrated lime. The molar ratio of the starting mass is CaO/SiO\(_2\) (C/S) = 0.09. The morphology of the sand grains used to make the specimens was presented by means of an image from the scanning electron microscope (Fig. 1). The characteristics of burned lime used in this study are presented in the Table 1.

![Grain morphology (SEM picture x500)](image)

In order to make beams corresponding to the specimens, the lime-sand mixture was made with water in an amount of 6% by weight, in relation to the mass of the mixture. So the resulting mass was formed into small beams,
Table 1: Characteristics of burned lime

| CaO+MgO | MgO | CO₂ | SO₃ |
|---------|-----|-----|-----|
| [%]     | [%] | [%] | [%] |
| 94.72   | 0.97| 1.47| 0.18|

compressed with a force of to 20 MPa and subjected to 8-hour autoclavage at 203°C.

For the modification of the basic specimens, the foam glass granulate size 0.25-0.5 mm was used. The structure of the grain surface of the granulate as well as its cross-section is represented by the SEM image (Fig. 2). For the granulated product used, the EDS analysis presented in Table 2 was performed.

The specimens of lime-sand products modified by foam glass granulate were made of a mass composed of a lime-sand mixture in the amount of 95-70% and an appropriate amount of filler 5-30% with a measuring step every 5% by weight. The resulting modified mixture was prepared with water share of 6% by weight, in relation to the mass of the specimen, and then subjected to forming and autoclaving in the same way as to obtain traditional specimen.

Physical properties, i.e. compressive strength and volume density were determined in accordance with the methods described in standards. Before the research commencement the prepared samples had been cured during 28 days in the temperature of 18°C and relative humidity of ~60%, to obtain the air-dry state.

The volume density tests were conducted in accordance with the standard PN-EN 772:13:2001 [38]. To perform the tests beams were used which had been prepared in a way described above, dimensions of the beams (length, height and width) enabled to determine the volume of samples. Then the beams were dried in circulation drier at the temperature of 105°C until the constant mass and afterwards they were weighted. The obtained results enabled for calculating of volume density value for each of item subjected to the test, according to the following equation:

\[ \rho_u = \frac{m_{dry}}{V_g} \text{[kg/m}^3\text{]} \]

where: \( \rho_u \) – volume density, [kg/m\(^3\)]; \( m_{dry} \) – mass of dried sample, [kg]; \( V_g \) – volume of sample, [m\(^3\)].

The test of volume density in each case was conducted at 5-times repetition of the measurement. As a result the arithmetic average value of calculated results was taken.

The compression strength check was conducted according to the guidance determined in the applicable standard [39], at the usage of Tecnotest KC 300 press. Samples of the face surface of 40×160 mm were placed on the test- ing machine plate coaxially with the center of the route of testing plate having dimensions of 62.5×40.0 mm, and then were compressed in a steady way until the sample damage. The result of individual test states the quotient of maximal registered load that was obtained and the area of loaded surface. As a final result of the check the arithmetic average value of 6 obtained measurements was taken.

A scanning electron microscope with an EDS analyzer was used to observe the microstructure. The measurements were conducted on not coated by spraying samples under the conditions of low vacuum (water vapor pressure corresponded to 30 Pa). The test was conducted on the fractures (pieces) of traditional and modified silicate samples.

The phase content of obtained samples was determined at the usage of X-ray diffractometer (XRD) of PAN-analytical company, model name: Empyrean. The quantity share of particular phases was determined according to Rietveld method. The measurements were conducted with the usage of monochromatic radiation of wave length corresponding to copper emission line Kα (CuKα = 1.54178Å), with angles range 5-50° at a scale of 2θ. The results were developed on the basis of ICDD database (The International Centre for Diffraction Data). The test was executed on traditional samples and on 2 samples containing foam glass granulate in the amount of 5 and 20%.

The obtained and presented results of tests performed on basic specimens are a reference to the results of tests obtained on modified specimens.

3 Results and discussion

The results of the conducted volume density tests of the basic lime-sand specimens as well as specimens modified with foamed glass granulate of a fraction of 0.25-0.5 mm are presented on the graph (Figure 3), which shows the shape and form of the curve describing the relationship between the volume density and the use of foam glass granulate of the fraction of 0.25-0.5 mm in the mass of the specimen.

For the obtained test results, the shape and form of the curve describing the relationship between compressive strength and the share of foamed glass granulate of the fraction of 0.25-0.5 mm in the mass of the specimen were also determined (Figure 4).

The microanalysis performed in points 1 and 2 (Figure 5) indicated the presence of products of C / S molar ratio equal to 1.28 (point 1) and 1.59 (point 2), which are the characteristics for phases CSH (I) and CSH (II) accord-
Figure 2: Expanded foam glass granulate - SEM pictures (x250) a) granulate surface, b) cross-section of the granulate

Table 2: EDS analysis (foam glass granulate)

| Spectrum name | The content of individual elements, [%] | Sum [%] |
|---------------|----------------------------------------|--------|
| O Na Mg Al Si K Ca | | 100 |
| a (surface) | 37.07 10.24 1.48 2.04 39.95 0.97 8.25 | |
| b (pore surface) | 50.9 9.79 1.34 1.65 31.26 0.54 4.52 | |

Figure 3: Influence of the content of foamed glass granules of the fraction of 0.25-0.5 mm in the mass of sample on the volume density of final product

In specimens modified by foam glass granulate, large amounts of output component is present observed as less hydrated products - phases of C-S-H system, in relation to specimens with basic composition. The surface of the sand grain is covered with the C-S-H phase having the structure of crystals in the form of elongated metal strip (Figure 6).

The similar microstructure and type, however smaller in size, were observed on the outer walls of the foam glass granulate (Figure 7). This phase is basically of a C-S-H output phase with disordered and less developed compact structure. The observations carried out show that this phase is dominant in specimens modified by foam glass granulate and its level of formation decreases with the participation of granulate.

On the inner walls of the foam glass granulate, and thus on the pore walls, a three-dimensional 'honeycomb' structure was composed of a poorly developed C-S-H...
phase. It is noticed that in small pores close to the outer surface of the granulate, this structure forms a layer growing towards the central part of the pore, while in the pores of the large ones in the central part of the granulate, the CSH phase creates irregular spherical clusters in the form of a "honeycomb (Figure 8), corresponding to the phase C-S-H II according to the Diamond classification [34].

During the observation, it was also noticed that with the increasing content of the used granulate, the contribution of the tobermorite phase in the analyzed specimens decreased.

Presented above observations as well as the EDS spectrum indicates, that together with the growth of silica in the output mixture and at the same time together with the decreasing C/S ratio – the C/S ratio in the products of C-S-H phase also decreases, what is analogical to the findings of other authors [35–37]. The confirmation of the upper observations state the results of the X-ray phase analyses (XRD) performed on powdered samples as well as the quantitative analyses obtained according to Rietveld method (table 3). The research indicates, that in the content of traditional sand-lime products occur typical for these products crystal structures, i.e. quartz (SiO₂), calcite (CaCO₃) as well as hydrated calcium silicates in a form of tobermorite 11Å (Ca₅Si₆O₁₆(OH)₂·4H₂O).
The quartz which occurs in the largest quantitative share (79.9%) is here an output product in the mass of tested sample, i.e. it is a sand which is incompletely reacted. It can be caused by too low C/S ratio in the mass of the sample [37]. The calcite occurring in the amount of 12.6% is from the chemical point of view a calcium carbonate stating a product of carbonation processes occurring in hydrothermal conditions. The \( \text{CO}_3^{2-} \) ions content may be related with also undissociated calcium carbonate contained usually in small quantities in a burnt lime [21].

Tobermorite 11Å, occurring in the amount of 7.5% is a characteristic crystal form of hydrated calcium silicate, its presence influences on the improvement of strength properties of the product [22, 31].

On the basis of conducted X-ray analyses (Figure 9) it outcomes that in the content of products modified by addition of foam glass granulate, the main crystal products states quartz (\( \text{SiO}_2 \)) and calcite (\( \text{CaCO}_3 \)). In the analysed samples the highest intensity had reflections generated by quartz that were the most highlighted as peaks at angles of \(-20.9^\circ\) and \(-26.6^\circ\) (2\( \theta \)). Relatively big intensity indicated also the peaks that are characteristic for calcite, focused at \(-39.4^\circ\) (2\( \theta \)).

In any of analysed samples of modified products no distinctive reflections from phase C-S-H were found. The
analyze conducted by Rietveld method indicates (Table 3), that together with the growth of granulate content in the analysed samples the amount of calcite decreases in each of the analysed systems. The analyse did not indicate the presence of tobermorite phase, the existence of which was stated in the referential samples (WP). The confirmation of disappearance of reflections coming from the phase is the enlarged fragment of difractometer diagram from the angles range of and 28-31° (2θ) (Figure 10).

Analysing the obtained results of the tests, it comes to mind, that decreasing share of tobermorite in the modified samples is related to the increasing proportion of granulate, which is the source of amorphous silica – i.e. glass. On this basis, it can be concluded that the used silicate additives of glass do not produce a sufficient number of reinforcements in the contact zones during the autoclaving process, what makes it impossible to increase the compressive strength of the final products.

### 4 Conclusion

1. The addition of foam glass granulate in the mass of lime-sand specimens reduces the volume density of the sand-lime products made on the basis of a traditional lime-sand mixture under traditional autoclaving conditions.
2. The modification of lime-sand products by the application of granulate affects the morphology of the autoclaved specimens obtained.
3. The use of foam glass granulate in the mass of sand-lime specimens causes a weaker formation of microstructure of the C-S-H phases on the surfaces of sand grains and the introduced granulate. The arrangement of the microstructure decreases with the increase of the granulate amount in the mass of the sand-lime specimen.
4. A weaker formation of the specimens microstructure, apart from the reduction of the volume density, has also an effect in reduction of the compressive strength of autoclaved products.

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