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## INFLUENCE OF LITHIUM SILICATE ON MICROSTRUCTURAL AND MECHANICAL PROPERTIES OF AUTOCLAVED SILICATE PRODUCTS

### WPŁYW KRZEMIANU LITU NA MIKROSTRUKTURALNE I MECHANICZNE WŁAŚCIWOŚCI AUTOKLAWIZOWANYCH WYROBÓW SILIKATOWYCH

#### Abstract

As the term „lithium nanotechnology” has become widely known, the application of lithium compounds in the construction industry has grown in popularity. The insertion of lithium silicate into silicate paste enhances the strength of the final product through the reduction of free spaces in the modified silicate structure. In consequence, the silicate paste gets denser as its macro- and microstructural properties improve, since lithium silicate has a beneficial effect both on the chemical reaction with silica and on its rate.

*Keywords: sand-lime silicate, lithium silicate, the C-S-H phase, tobermorite, XRD, SEM, compressive strength, microstructure*

#### Streszczenie

Ostatnie dziesięciolecie są szczególnym przykładem rozwoju technologicznego w przemyśle budowlanym, co jest podyktowane m.in. trwałością wytworzonego materiału oraz sposobem pozyskiwania surowców do jego wytworzenia, a dalej ich zasobami. Rozpowszechnienie pojęcia „nanotechnologia litu” spopularyzowało zastosowanie związków litu w przemyśle budowlanym. Wprowadzenie krzemianu litu do masy silikatowej prowadzi do zwiększenia wytrzymałości wyrobu końcowego przez ograniczenie wolnych przestrzeni w modyfikowanym silikacie. Następuje tym samym zagęszczenie masy silikatowej i poprawa jej właściwości makro- i mikrostrukturalnych, bowiem krzemianu litu korzystnie wpływa na reakcje chemiczne zachodzące z krzemionką oraz ich czas. Wprowadzając domieszki do masy silikatowej, dąży się do tego, aby wyroby te pozostały materiałem ekologicznym.

*Słowa kluczowe: silikat, mikrostruktura, SEM, XRD, silikaty, krzemian lit, C-S-H*

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## 1. Introduction

Silicates are construction materials which provide a suitable interior microclimate with a solid structure. The initial phase of their production involves mixing about 87% of sand, 10% of lime with a 3% of water hydration, which is essential for the proper course of chemical reactions. The mix is then placed in steel silos (reactor tanks), where it is left for two to four hours. Here the process of slaking takes place, accompanied by an increase in temperature to around 60°C. At this stage silica loses its crystalline structure, which in turn facilitates the subsequent formation of products. Next, the silicate mix is directed to the press, in which it is compressed at a pressure of 15–20 MPa, and formed into bricks and blocks of suitable size and shape. Two types of presses are applied: pneumatic and hydraulic. Hydraulic presses with a two-sided press are best for silicate production. In the final phase the compressed elements are placed in autoclaves and subjected to a hardening process which takes place at 203°C and at a pressure of 16 bar (1.6 MPa). During the 6–12 hours of autoclaving the lime reacts chemically with sand and the mixture undergoes the process of recrystallization. In consequence the products obtain very good strength and durability.

For many years scientists have been developing better products or solutions to improve the construction process and to make it more efficient. Combinations of different additions such as pulverized basalt, cement, slag, lime, phosphogypsums, or cements and boron compounds have all been added to silicate paste as modifiers. The effect these different fillers have on the operational properties of the modified substance is examined, taking energy consumption reduction into account, this being another important aspect. The tests also take the serious disadvantage of increasing radioactivity by adding slag or phosphogypsum elements into the modified products into account [1–3].

Antypina A.S. is one of the few entities to have studied the microstructure of silicate products. The products analysed were prepared on the basis of lime-wollastonite and lime-diatomite mixtures. Antypina dealt with silicates resistant to high temperatures (above 800°C). It also made an attempt to determine the phase structure of products subjected to modifications where various technologies (pressing, vibropressing, air-entrainment, foaming, gassing and hydrothermal treatment at 175°C with a vapour pressure of  $P = 0.8$  MPa and thermal treatment) were all applied. At 700–800°C okenite and xonotlite formed in certain specimens. The tests conducted by Antypina and performed in laboratory conditions were useful with regard to the application, but not viable economically at this stage [4, 5]. In traditional silicate products, the presence of other phases than C-S-H or tobermorite is hindered due to the relatively small amount of lime in the paste. The processes taking place during the autoclaving of silicate materials were first presented in pioneering studies developed by Kalousek and in the illustrative works of Taylor [6, 9–11]. Particular phases are formed in the course of hydrothermal treatment, starting from the C-S-H gel, which emerges at 20°C, to more ordered and better developed structures. Individual phases maintain their own rates of reaction with water. The hydration process takes place within the individual phases which interact with each other as a result of bonds that are formed during the conversion of the liquid phase composition or the gel product absorption on the surface of the grains (eg, sand, lime) [7]. The analysis of various calcium silicates revealed that their composition depends on technological factors. For this reason, a simplified model of hydrated calcium silicates in the form of C-S-H, in which the numeric values between components are omitted, is often used in specialist literature. The application of admixtures in the silicate production process is little known and not very common, although they are easier to dose. An appropriate kind of

admixture should first be added to the lime-sand paste, and then a certain amount of water should be introduced into the mixture in order to achieve the correct viscosity and workability [12, 13].

### The analysis of the silicate paste modifier selection

After the analysis of specialist literature concerning the possibility of modifying the silicate paste with various additions and admixtures, a multicriteria engineering and economic analysis was performed using the „Multidimensional Exploratory Techniques” module found in the STATISTICA 10.0. computer programme.

Table 1

#### Characteristics of silicates applied in silicate paste for engineering-economic analysis in measurable and immeasurable values

Filler (cases)	Criteria (variables, factors)					
	Costs [zł/l]		Ecology	Airtightness		
Lithium silicate	140	4	Environmentally friendly	5	High	5
Aluminium silicate	120	5	neutral	3	Good	3
Potassium silicate	470	2	neutral	3	Medium	2
Sodium silicate	180	4	Moderately balanced	4	Medium	2

The graphic part included a map which showed the location of active variables (cost and ecology) and passive ones (airtightness) – criteria (vectors) and points showing the types of fillers (cases).

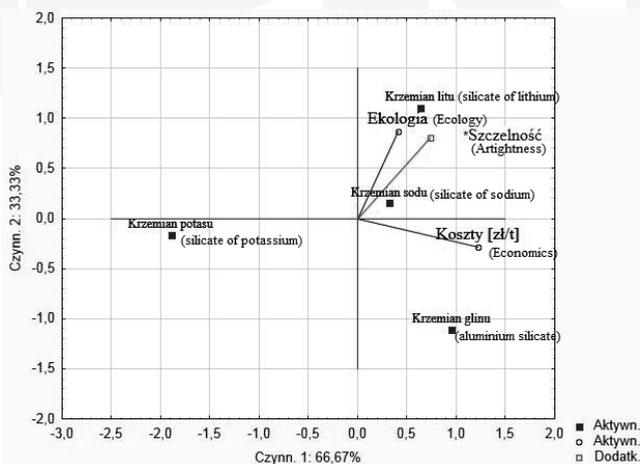


Fig. 1. Cases projection on factor plane

## 2. Methodology of the conducted examination

Laboratory samples of silicate products (traditional ones and those modified with a selected admixture) were made each time an experiment was conducted. Silicate samples measuring 40x40x160 mm were prepared in laboratory conditions.

After the laboratory tests had been performed, full silicate bricks with the dimensions of 180 × 220 × 250 mm were prepared, with the faces of the tested products measuring 40 × 160 mm and 250 × 180 mm. The products were manufactured at the Silicate Production Plant in Ludynia, where the silicate mix for tests and modification was also produced. Compressive strength tests together with the tests determining the bulk density, water absorbability and the absorption caused by the capillary rise were performed in the laboratory of the Kielce University of Technology, whereas the micro structure was tested at the Kielce University of Technology and the University of Science and Technology in Krakow.

### 2.1. Physical-mechanical properties of silicate products

Silicate product compressive strength tests were performed in accordance with guidelines based on applicable standards. The laboratory samples of the silicate products were examined using a press Tecnotest KC 300, while full bricks were tested in a hydraulic press. Compressive strength is the first criterion, to which producers and consumers pay attention when choosing appropriate building materials, therefore it is of crucial importance. Silicate products have a compressive strength in the order of 15–20 MPa. The determination of absorb-ability and water absorption caused by capillary rise of wall elements (i.e. silicate) was performed on the basis of the PN-EN 771-2 and EN 772-11 standards. In simple terms, the concept of absorption caused by capillary rise is a phenomenon associated with transporting the water coming from the ground up a wall. Standard silicates can absorb 16% of water (relative to their weight) due to the absorption caused by the capillary rise. The determination of bulk density of silicate products was made in accordance with the relevant standards in force. Bulk density is the mass of a volume unit of the dried silicate material together with its pores in a natural state. The bulk density of standard silicate is 1.73 kg/dm<sup>3</sup> [16–19].

### 2.2. Microstructural properties of the autoclaved products

The interpretation of the microstructure was performed on the basis of scanning electron microscopy (SEM), using a Quanta 250 FEG microscope manufactured by FEI and an IROL 5400 scanning electron microscope cooperating with the EDS analyzer. The widely used ( in science, technology and industry) SEM was applied for quantitative analysis of the elemental composition and distribution of elements in both the point and a given area of the examined sample.

The photographs above (Fig. 2, 3) shows the micro structure of traditional silicate products.

The C-S-H and the tobermorite phases are dominant in the sample, although they occur in different areas of the sample and with different intensity. The C-S-H phase seen in the picture (Fig. 2) adopts the spongy form, and its width is usually 3.34 μm (over 5000×). Tobermorite in the traditional silicate took its typical form of long, slender and fairly regular plates. The EDS spectrum (Fig. 3), i.e. the elemental composition of the examined sample shows the

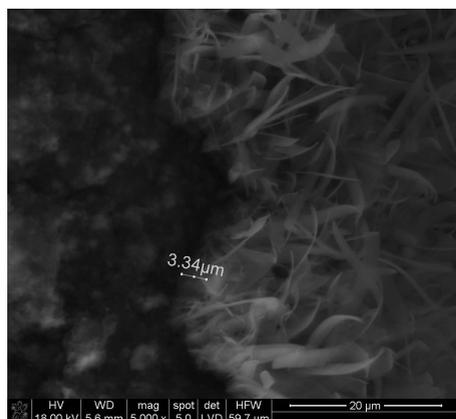


Fig. 2. The microstructure of traditional silicate

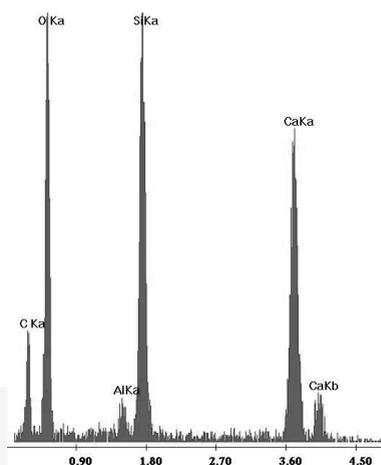


Fig. 3. EDS of traditional silicate

presence of elements such as Ca, Si, O, C (from dusting the sample with carbon), and Al (obtaining a substrate for the production of a product). Aluminum has a beneficial effect on the transition phase, e.g. the C-S-H into tobermorite or tobermorite into xonotlite.

The structural X-ray (XRD) both in the chemistry sensu stricto and in the construction chemistry is a method that allows for the accurate determination of the structures chemical compounds forming the analyzed crystals. Its advantage is the ability to accurately determine, with almost absolute certainty, the chemical structure of the compounds included in the composition of the tested material, permitting the construction of their real spatial model. In traditional silicates this study showed the presence of tobermorite in the structure of the product.

### 3. The results of the conducted research

Tests for examining compressive strength and bulk density were carried out on the basis of a multi-criteria engineering and economic analysis, with a simultaneous determination of the optimum composition of the silicate paste with the addition of lithium silicate in the form of a solution. Physical-mechanical properties of silicate products were evaluated with regard to compressive strength and bulk density. A fractional plan (complete)  $4^1$  (at  $k = 1$ ), i.e. full one-factorial experiment. Six parallel tests were performed for each value of the assumed factor. The methodology for planning the experiment and the results of the experiments are shown in table 2.

From the analysis it can be concluded that a positive coefficient sign next to the  $X1$  factor, indicates the compressive strength rising with an increase in the percentage of the  $Li$  filler. The value of the regression coefficient provides a clue to the extent in which the compressive strength value (and bulk density value) will change if the factor changes by one variance interval. A full one-factorial experiment is conducted to determine the optimum size of the  $X1$  ( $Li$ ) value, (the factor defining the conditions of compressive strength and bulk density of the products). On the basis of results, implemented for the established values of the percentage content of the  $X1$  admixture ( $Li - 1\%, 4\%, 7\%, 10\%$ ),

a curve was plotted showing the relation between the use of lithium silicate in the product, and the compressive strength values, and then – bulk density values – as is shown in the figures (Fig. 4, 5).

Modifying silicate paste with lithium silicate, which served as a filler, provided a 4% water absorption reduction rate in relation to the standard silicates.

The use of lithium silicate resulted in the unification of the internal structure of silicate. SiO<sub>2</sub> grains were more compact and surrounded almost entirely by the C-S-H phase, which then transformed into better developed forms of hydrated calcium silicates. Lithium silicate gave rise to the formation of new bonds and phases, namely xonotlite that (albeit rarely) appeared alongside the mentioned before tobermorite and the C-S-H phase (Fig. 6, 7).

One can also see other peak characteristics of silicate products (quartz, aragonite, calcite, rutile) and tobermorite. Lithium, as a chemical element and the lightest metal among the existing ones, which will not be visible as this can only be observed in the form of compounds with other elements, although not at always, as this also depends on external factors (including the method of preparing the specimens for the analysis, the structure crystallization stage, chemical processes occurring during the hydrothermal treatment of the product). The research has shown that the introduction of lithium silicate into the silicate paste does not altered the internal structure of the silicate.

Table 2

**The matrix of the experiment design, the factor level and the tests results**

№ of test	Factor		Compressive strength [MPa]
	Contractual scale	Natural scale	$\sigma$
	$x_1$	$X_1(Li)$ (Lithium silicate) [%]	
1	1	1	43.9
2	2	4	4.8
3	3	7	44.1
4	4	10	39.1

Table 3

**Regression coefficients for the adopted model with the examined compressive strength of the modified silicate products with the addition of lithium silicate**

Examined assumed factor	Regression coefficients for the adopted model with the examined compressive strength			Correlation coefficient
	$A_0$	$A_1$	$A_2$	
Compressive strength [ $\sigma$ ]	42.441	1.8439	-0.2194	0.9823

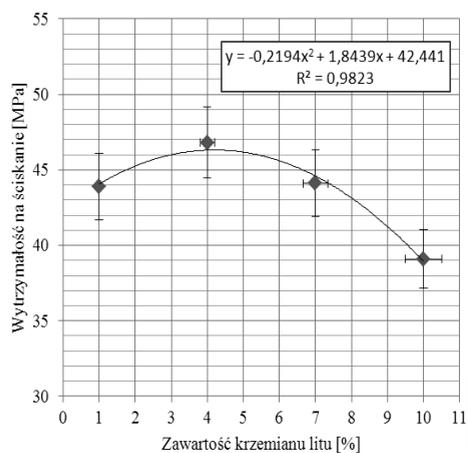


Fig. 4. Compressive strength

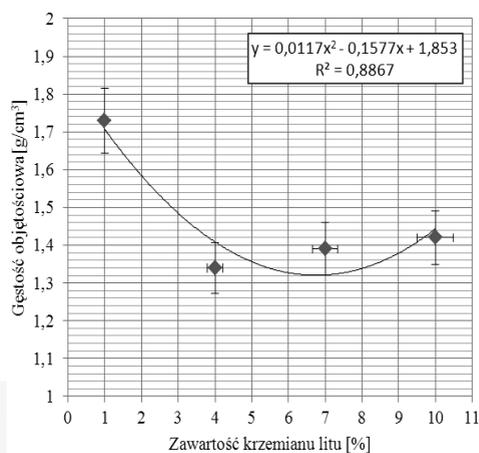


Fig. 5. Bulk density

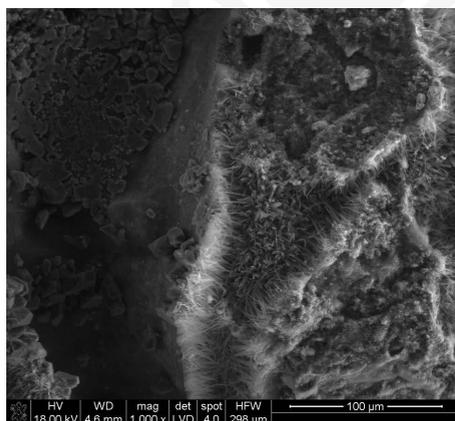


Fig. 6. C-S-H and tobermorite

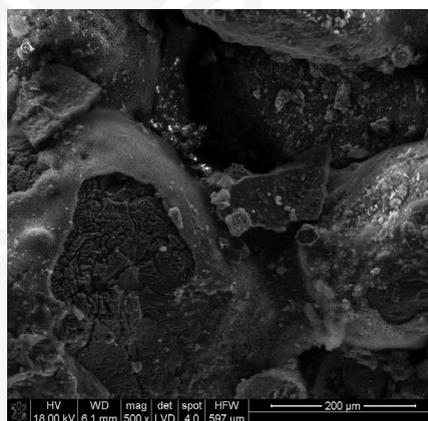


Fig. 7. Inner structure of silicate modified with lithium silicate

#### 4. Conclusions

Modifying the composition of silicate products with the use of an admixture of lithium silicate had a positive impact on:

- 1) improving the compressive strength of the modified silicate product.  
The compressive strength of the product thus manufactured was 46.8 MPa at 4% content of lithium silicate in the silicate paste.
- 2) reducing the absorbability and water absorption down to 12% (from 16% in the traditional silicate product) with 1–7% content of lithium silicate in the silicate paste.

- 3) the microstructure of the modified silicate product has an increased strength due to pore densification and a phase in which xonotlite emerged, referred to as a high-strength phase.
- 4) the emergence of the xonotlite phase is associated with the value of a compressive strength of the modified product, which increased by over 20 MPa (from the standard value of 20 MPa to the value of 46.8 MPa).

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