Effective Silicate Concretes Properties Using Components of Ultrafine Range

G Zimakova, V Solonina, M Zelig and V Orlov
Tyumen Industrial University, 38, Volodarskogo str., Tyumen, 625000, Russia

E-mail: zimakovaga@tyuiu.ru

Abstract. The article presents an assumption that the introduction of the traditional lime-silica astringent of aleuropelite rock of the Ishim suite of the south of the Tyumen region allows to change the structure and phase composition of the silicate matrix. The applied rock is represented by quartz, sodium-potassium minerals of feldspars with an insignificant amount of chlorites and halloysite with grain sizes from 1 to 35 microns (μm). The peculiarities of the dispersion and grain composition of the raw material impact on the compactability of the silicate mass and the plastic strength of the as-formed raw material are studied. It is revealed that during the processes of hydration interaction of the components of the mixture with the use of aleuropelite, the main products are xonotlite, low-basic hydrated silicates and a small amount of Portlandite. Due to high alkalinity of the medium, finely dispersed feldspar minerals acquire reactivity with the formation of hydro- and aluminosilicate phases. The influence of aleuropelites on the degree of compaction of the raw material mass and the processes of physicochemical interaction under hydrothermal conditions make it possible to increase the strength and water resistance of silicate concrete.

1. Introduction
Nowadays the price competitive ability of silicate products among other wall construction materials is undeniable. The analysis of scientific information and patent data shows that little attention is paid to the issues of theoretical studies of silicate materials, which, along with negative and scientifically unjustified information, affects the scale of their application [1, 2].

Limitations on the use of silica brick are mainly due to its inadequate durability, which is identified by measuring the strength in damp conditions. The service life of structures made of silicate concrete can be extended in different ways: by creating an impeccable constructional system for draining water; water-repelling treatment of the surface of the face surface; by introducing mineral additives into the silicate mixture, including nanoscale components [3,4,5]. All these measures contribute to increasing the water resistance of silicate concrete.

The mechanism of silicate stone deterioration and methods for ensuring durability are not limited to water resistance issues. The processes of destruction of silicate materials are determined by stresses caused by uneven alternating deformations of shrinkage and swelling, freezing and thawing, recrystallization of structure-forming hydrosilicate phases, also accompanied by volumetric changes. The set of destructing factors leads to the development of internal stresses, local micro- and macro flaws.
Changes in the structure and properties of silicate concretes are primarily associated with two-stage carbonate corrosion. In sources [6-9] the possible processes of recrystallization of highly basic calcium hydrosilicates into low-basic ones are described. Carbonization of the structure-forming phases is accompanied by a decrease in the molecular weight and a change in the initial volume of crystalline hydrates [6].

It is known that the properties of lime-silica materials are determined by their compound and chemical composition, the dispersion of the components, the contractibility parameters, the duration and the temperature regime of the hydrothermal treatment [10-14]. Their optimal ratio makes it possible to create silicate concrete with a wide range of properties. In the sphere of silicate concrete, densification by pressing a powdered raw meal is one of the main technological operations. Its effectiveness is affected by the dispersive capacity and the grain composition of the constituents. Humidity and the ratio of grains of various sizes determine the flowability, the conditions for the removal of trapped air, the density and strength of the as-formed product and the resulting conglomerate.

According to the current concept, the dispersive capacity of the siliceous component, along with its chemical-mineralogical composition, is directly related to its reactivity. This determines the completeness of hydrothermal synthesis reactions [15]. However, ultrafine grinding does not meet the requirements of energy-saving technologies, as it is one of the most energy-intensive processes in the technological chain.

Thus, it becomes obvious that it is necessary to optimize the grain composition of the mixture by introducing finely dispersed natural materials that do not require processing in the grinding units. The effect from the application of these materials should appear at all stages of the technological cycle and contribute to improving the operational and technical characteristics of the stone.

The main goal of the research is to obtain high-efficiency silicate concretes by adjusting the formulation, which will allow obtaining an optimum structure composite with stable structure-forming hydro silicates.

2. Materials and methods
The studies were carried out with a set of physicochemical methods: scanning microscopy and X-ray phase analysis. The chemical composition of individual phase formations is established by means of a local microanalyzer of an electron microscope. For the characteristics of density and strength of silicate stone, standard techniques were used; porosity was diagnosed by the kinetics of water absorption. Water resistance of silicate stone was established by the ratio of strength in a water-saturated and dry state, as well as by chemical analysis of water extracts.

The composition of the series was made on the basis of the lime-silica cement (LSC) used industrially by OOO Invest-Silikat-StroyServis (Tyumen), obtained by grinding calcium lime and quartz sand (composition No. 1). The following components were used as fine silica components of the silicate mixture: aleuropelitic rock of the Ishim suite of the Tyumen Region of the Bigila deposit (composition No. 3) [16,17] and ultradispersed silica sand (composition No. 2) obtained by grinding in a laboratory ball mill in the presence of a milling intensifier, triethanolamine (TEA).

Samples of silicate stone were formed on a press unit at a pressure of 1.5 MPa, hydrothermal treatment was carried out in an industrial autoclave.

3. Results
According to the chemical analysis of aleuropelitic rock, it was found out that its main components are SiO2 (71.4-76.6%) and Al2O3 (11.3-14.3%). The content of Na2O, K2O, Fe2O3, MgO is from 1 to 3%. Cl - is below the determination limit. The results of X-ray phase analysis state that the prevailing minerals of the rock are quartz, sodium-potassium feldspars, and a slight content of halloysite and chlorites. The bulk of the rock is made up of particles up to 50 microns, the content of grains up to 15 microns is 40.0 percent, and up to 30 microns, 88.0 percent. The grains are mostly rounded (figure 1).
Figure 1. The granulometric composition (a) and the shape of grains (b) of aleuropelitic rock

Figure 2 shows the grain size curve of the actual production mixture (LSC) after joint grinding of lime and sand in a commercial grinding plant (the proportions were corrected according to the results of previous studies) (figure 2a) and ground quartz (figure 2b).

Figure 2. Granulometric composition: a) LSC; b) ground quartz in the presence of TEA

Figure 3. Granulometric composition of the mixture LSC + aleuropelitic rock:
   a) integral sieving curve; b) actual sieving curve

The optimal granulometric curve of the composition of the selected mixture of LSC + aleuropelitic rock (figure 3) indicates that there was obtained a polydisperse system with a continuous granulometric composition, most correctly described by the Funk / Dinger equation [18].

Optimization of the grain composition of the mixture made it possible to achieve the criterion of the maximum density and strength of the freshly molded product. The strength of the mixture with aleuropelitic rock prevails over control no-additive composition No. 1 by 20% (the plastic strength of
the control composition is 1.7 MPa). The rheological capacity of mixtures of compositions No. 2 and 3 ensured a decrease in the value of the water-hard ratio from 0.65 (for control composition No. 1) to 0.55 for composition No. 2 and to 0.547 for composition No. 3 at constant compression pressure. For composition No. 2, the decrease in W, at a given dynamic effect, is ensured by introducing TEA, which helps to reduce the energy barrier between grains during pressing.

Testing of samples after autoclave hardening proved that the introduction of aleuropelites in the silicate mass made it possible to increase the strength of the stone by 70-80%. The kinetics of the water absorption process indicates that the silicate stone containing aleuropelites has a sorption moisture of 30% lower. Intensive sorption humidification, reaching 47% of the maximum value, is provided within 30 minutes, which is due to the microporous structure of the silicate stone.

The structure of the obtained silicate conglomerates of various compositions is given in Fig. 4. The following conclusions can be made: the introduction of ultrafine-dispersed components allows to increase the density and massiveness of the stone, reduce the pore size, and change the pore structure.

![Figure 4. The microstructure of the silicate stone: a) composition No. 1 - LSC; b) composition number 2 - LSC + ground quartz; c) composition number 3 - LSC + aleuropelite rock](image)

![Figure 5. X-ray diffraction pattern of silicate matrix: a) composition number 1 - LSC; b) composition number 3 - LSC + aleuropelite rock](image)
Hydrosilicates of a variable composition with a sufficient degree of crystallinity of the tobermorite group of the approximate composition $\text{C}_5\text{Si}_6\text{O}_{16}(\text{OH})_2$, xonotlite $\text{C}_6\text{Si}_6\text{O}_{17}(\text{OH})_2$ with the presence of bound water in the form of $\text{OH}^-$ groups (figure 5) were diagnosed in hydrothermal synthesis products of all compositions.

A small amount of free quartz was detected in the silicate stone of the control composition (figure 5a), the presence of portlandite was noted, and the highly basic hydrosilicates were represented by the hillesbrandite $\text{C}_2\text{SiO}_3(\text{OH})_2$.

The aleuropelites intensify the phase formation in the C-S-H system, contribute to the directed formation of a greater number of low-basic calcium hydrosilicates, participating in formation of the dicalcium $\alpha$-hydrate. Free quartz and portlandite are not diagnosed (figure 5b).

The peculiarities of the influence of the feldspar component of aleuropelites on the processes of the new phases synthesis are presented in figure 6.

![Figure 6](image)

**Figure 6.** Morphological features of structure-forming neoplasms of silicate stone:

- a) hydrosilicate;
- b) anorthized feldspar surface and thomsonite;
- c) plate and prismatic hydrosilicates

Mineral formations of the approximate composition $(\text{Na},\text{Ca})_3\text{Al}_5\text{Si}_5\text{O}_{20}\cdot5\cdot6\text{H}_2\text{O}$, whose morphological features (radial-radiant and sheath-like aggregates) and X-ray characteristics are identical to minerals of the thomsonite-aqueous sodium-calcium aluminosilicate type are diagnosed in hydration products [19, 20]. Anorthite was found in products of hydrothermal synthesis, which is connected with the peculiarities of the feldspars structure. Under the influence of high temperatures and steam electrostatic neutrality is achieved by $\text{Ca}^+$ ions entry into the structure and framework voids.

4. Conclusion

The carried out studies of the main regularities of the influence of silica-containing fine-grained aleuropelites, including experimental determination of the structural and mechanical parameters of the silicate matrix, convincingly confirmed the effectiveness of their application in the composition of the raw mix at the optimal dosage of 18% by weight of the LSC. Comparative evaluation of the quality parameters of the silicate stone obtained on the basis of the traditional mixture and proposed in the paper shows that the strength increases by 70-100%, the content of water-soluble components decreases threefold, the carbonation resistance is ensured by the absence of "free" portlandite, the probability of the recrystallization of the structure-forming phases reduced significantly. The results of the research have proved the possibility of obtaining weather-resistant silicate concrete with strength of 35-50 MPa.

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