

Contact strength of C-S-H cement phase

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Abstract. The object of the study was the cement phase C-S-H – X-ray amorphous calcium hydrosilicates, obtained by steaming at 80 °C together limestone and silica at different molar ratios $\text{CaO/SiO}_2 = 0.5; 1.0; 1.5$. The contact strength of the C-S-H phase with additions of portlandite, silica and alumina zols, high-aluminate slag was estimated by hyper-pressing method with subsequent destruction. It was established that the contact strength of the cement phase increases in proportion to the specific pressing pressure, the age of samples and inversely the phase basicity reaching 12 MPa. It was evidenced that additives increase the contact strength of the C-S-H stone. The features of the phase formation during the hydration of calcium aluminates were considered. It was established that there is no negative effect of additional porosity on the strength of the stone, because the restructuring of calcium hydroaluminates takes place during hyper-pressing. The specific behavior of low-basic calcium aluminates in a mixture with the C-S-H phase was established in the case of using high-aluminate slag, which consists in additional formation Al(OH)_3 gel during the hydration, that is provide an increase in the contact strength of the compositions.

1. Introduction

Studies of Canadian scientists [1], V.D. Glukhovskiy and R.F. Runova [2] demonstrate the possibility of obtaining a water-resistant stone from pre-hydrated cement stone or nepheline sludge after pressing. It was shown that the metastable phase of amorphous calcium hydrosilicates C-S-H, the main phase of the hardened cement stone, possesses contact-condensation properties. Later E.M. Chernyshov and his co-workers established [3] that a pure portlandite stone, compressed at 100 MPa, as well as portlandite-aluminosilicate stone obtained by contact hardening, can possess sufficient water resistance [4]. The principle of "contact hardening" is based on the ability of dispersing silicate and aluminosilicate substances, which are in an amorphous unstable state, to form a water-resistant stone with high strength at the moment of an approach of the particles during compaction. The hardening of such binders is considered from the standpoint of the theory of condensation, which is based on the idea that dispersed substances, due to their energy instability, have a condensation capacity that decreases as the free energy of these substances decreases. The ability to contact and condensation hardening has a large group of silicate and

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aluminosilicate substances, both natural and artificial, the products of their hydration and dehydration, the interaction of hydroxides of alkali and alkaline earth metals with granite, basalt, perlite, etc. The pressing pressure during contact-condensation hardening can vary over a wide range - from 20 to 1000 MPa and more.

This approach can be used in the processing of various wastes and by-products of the industry, for example, concrete scrap pressing [5, 6], because hydrated scrap cement is presented of the C-S-H phase and portlandite. Also, the problem of the arrangement of road bases from pre-hydrated materials such as nepheline, bauxite sludge, and cement materials remains urgent.

In paper [7] it is shown that the quality of raw materials significantly affects the operational properties of road concrete. The main reasons for the early destruction of road concrete are high stratification, porosity, and the wrong choice of cement. Contact-hardening concrete can solve the problem of the durability of road surfaces.

That's why it is useful to study the contact hardening of the C-S-H cement phase with additives. The principle of the choice of additives for contact hardening of the C-S-H phase is considered by us on the basis of the crystal-chemical structure of this phase, as well as from other considerations presented below.

The aim of this work is to study the contact hardening of C-S-H cement phase with additives.

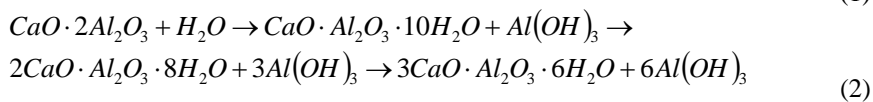
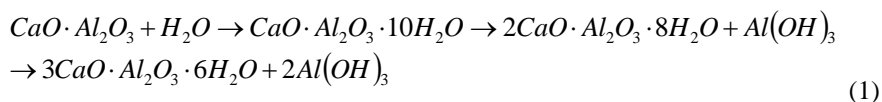
The development of the structure model of the cement phase C-S-H is currently one of the central scientific problems of building materials science. [8–12] The greatest success in the structure of the C-S-H phase modeling at the present time is probably achieved by I.G. Richardson [13]. Many of the proposed models note the extreme defectiveness of the real structure of this phase. Modeling of the structure of hydrogen bonds and defects in the arrangement of silicon-oxygen tetrahedra, established by S.V. Churakov in the Tobermorite and Xonotlite [14], allowed to transform these features into the C-S-H phase.

At the present time, it is considered recognized to distinguish the central portlandite layer in the structure of the C-S-H phase, to which the incomplete chains of silicon-oxygen tetrahedra adhere on both sides. [15] At the same time, due to the non-correspondence of the sizes of the basic elements of the structure (silicon-oxygen tetrahedra and calcium octahedron), tetrahedra are forced to group into five members (two dimers $[\text{Si}_2\text{O}_7]$ and one bridging tetrahedron connecting them). To ensure proportionality, in a third of bridged tetrahedra, it is more advantageous to have the cation Al^{3+} instead of Si^{4+} .

Proceeding from these crystal-chemical features of the structure of the C-S-H phase as additives for its condensation into a high-strength artificial stone, it is advisable to consider the additions of nano- and microsilica (to complete the formation of the silicon-oxygen chains), nano-alumina for the formation of a silica-alumino-oxygen layer commensurate with the calcium.

Nano-alumina can be used both in the form of a suitable zol and in the form of hydration products of calcium aluminates.

The latter method has a number of features, the main of which consists in the step-by-step formation of increasingly basic calcium hydroaluminates with increasing isolation of the gel $\text{Al}(\text{OH})_3$. This is evident from the hydration reactions of minerals of alumina cement, high-alumina slag [16–18]:



The separated alumina gel $\text{Al}(\text{OH})_3$, in addition to the possible participation in the construction of the silica (alumina) oxygen layer of the C-S-H phase, is "contact-active", i.e. when pressed, it provides a high-strength stone. In this case, unlike the hydration of CA, the gel $\text{Al}(\text{OH})_3$ during hydration of low-basis calcium aluminates CA_2 and CA_6 should be released already when the primary hydrate CAH_{10} is formed, otherwise the stoichiometry of the initial aluminates and hydration products is disturbed. In addition, when hydration of low-basis aluminates of the gel $\text{Al}(\text{OH})_3$ should be allocated more.

The authors [18] note that during the restructuring of CAH_{10} to C_2AH_8 , there is a rapid decrease in the moisture content of the cement stone and an increase in shrinkage. In the case of contact-condensation hardening, this effect will be absent, which will improve the properties of the resulting materials.

The use of calcium aluminates to obtain a high-strength stone conceals the danger of dumping strength when transitory hexagonal calcium hydroaluminates (CAH_{10} , C_2AH_8) to C_3AH_6 , because while the volume of the solid phase is reduced by 52%. Such hydrate transitions may be slow to flow for decades at low temperatures or for days, hours and minutes at elevated temperatures and increased alkalinity of the system. Therefore, it is forbidden to mix Portland and alumina types of cement, aluminous cement and lime.

However, compression of such compositions makes it possible to obtain a stone of high strength [19]. This is probably due to the elimination of the emerging porosity in the transition of hexagonal hydrates to cubic.

Thus, to enhance the contact strength of the cement phase C-S-H, it is advisable to consider additives such as portlandite, nano-silica, and nano-alumina.

2. Methods

Cement phase C-S-H was synthesized from calcium oxide and silica (anhydrous silicic acid according to GOST 9428) with a content of basic substances of not less than 97%. Mixtures of these components in various molar ratios ($\text{CaO}:\text{SiO}_2 = 0.5, 1.0, 1.5$) were averaged by grinding in a porcelain ball mill. It was mixed with distilled water and was hydrated in closed polyethylene containers at 40 °C until the complete transition of CaO to $\text{Ca}(\text{OH})_2$. From the "quenched" mixtures at 20 MPa, cylinders with a height and diameter of about 50 mm were pressed, which, in accordance with the CaO-SiO₂-H₂O phase diagram, were steamed at a temperature of 80 °C until the complete assimilation of CaO to obtain the C-S-H phase of this or that basicity. Solid additives – portlandite and calcium aluminates in the form of high-alumina slag (HAS) according to TU 14-00186482-048-03 – were averaged in a porcelain mill.

Chemical composition of high-alumina slag (HAS) consists from Al_2O_3 (73–75 %), CaO (17–19 %) and others.

The silica and alumina zol were introduced by quenching. A silica zol with a SiO_2 concentration of 30% with a particle size of 30-50 nanometers and an alumina zol of 15% concentration and a particle size of about 80 nm was used. The prepared mixtures of C-S-H with additives were mixed (if necessary) with distilled water to a molding humidity of 10-12% and pressed at a specific pressure of 20-100 MPa to obtain cylinder samples with a diameter and height of 50×50 or 35×35 mm. Samples were tested for compressive strength immediately after pressing or after normal aging at 1-28 days. Based on the results obtained, the corresponding statistical mathematical models were constructed.

3. Results

The strength and water resistance of materials is formed as a result of surface physical phenomena that occur when particles approach each other at the moment of contact between them. Stone strength increases with increasing number of contacts between particles, and accordingly depends on the pressing pressure during molding.

In our researches [20] we showed that the strength of the pressed stone from the C-S-H phase synthesized by the above-described method increases with the growth of the specific pressing pressure, the time of normal exposure to compacts and little depends on the basicity of the C-S-H. The maximum values of strength are reached at a daily age of 10 MPa, in the 28-day period - 12 MPa.

The addition of portlandite to the C-S-H phase raises the strength of the pressed stone 1.5 times. The samples with basic $\text{CaO}/\text{SiO}_2 = 0.5$ have the highest values in all terms (Fig. 1).

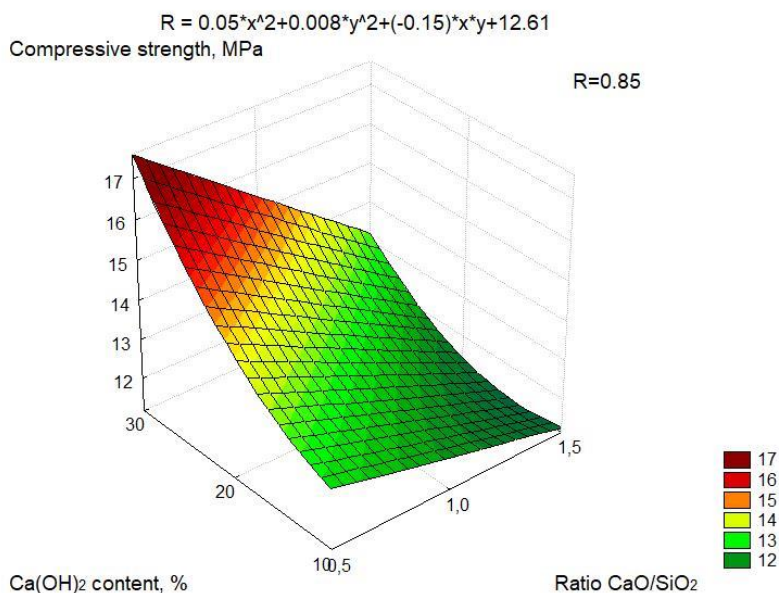


Fig. 1. Dependence of the compressive strength of a stone from C-S-H from the ratio of CaO/SiO_2 and the $\text{Ca}(\text{OH})_2$ content at the compressive pressure of 80 MPa after 28 days of normal hardening.

The addition of the alumina zol to the mixture of C-S-H phases and portlandite changes the values. Consequently, the behavior of the alumina zol in the C-S-H composition depends on the presence of portlandite. The contact strength of the phase without portlandite with the addition of 2% alumina zol (by Al_2O_3) increased the strength of the stone 1.7 times immediately after pressing. At the same time, the addition of alumina zol to the mixture of C-S-H and portlandite reduces the contact strength 2 times. This is probably explained by the above described mechanism of formation and restructuring of calcium hydroaluminates.

The addition of 4% (by solid) to the mixture of C-S-H phases and 15% of portlandite of silica zol raises the daily strength of the pressed stone 1.5 times to 15 MPa, and 28-day to 2.5 times to 28 MPa (Fig. 2).

With an increase in the pressing pressure, the strength increases, and a change in the basicity of the phase does not lead to a significant change in the strength parameters in the early periods of hardening. With a basicity of 0.22 on the first day, the strength is 38% of R_{28} , and with a basicity of 1.0 - 70% of R_{28} .

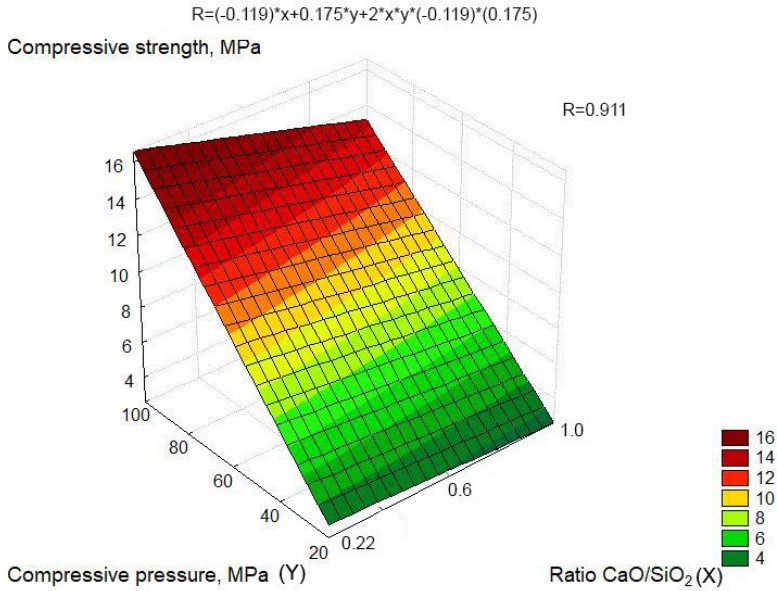


Fig. 2. Dependence of the compressive strength of a stone from C-S-H with the addition of 4% (on solid) silica zol from the ratio of CaO / SiO₂ in the gel and the compressive pressure after 1 day of normal hardening.

At the same time, the addition of high-alumina slag (HAS) significantly increases the strength of the pressed stone to 34 MPa (Fig. 3). In this case, a quadratic (exponential) dependence of strength growth with the dosage of HAS is observed. It is also noted that the compacts are self-heating to high temperatures (Fig. 4), which should lead to an increased rate of hydration and the rapid rearrangement of hydroaluminates towards the cubic.

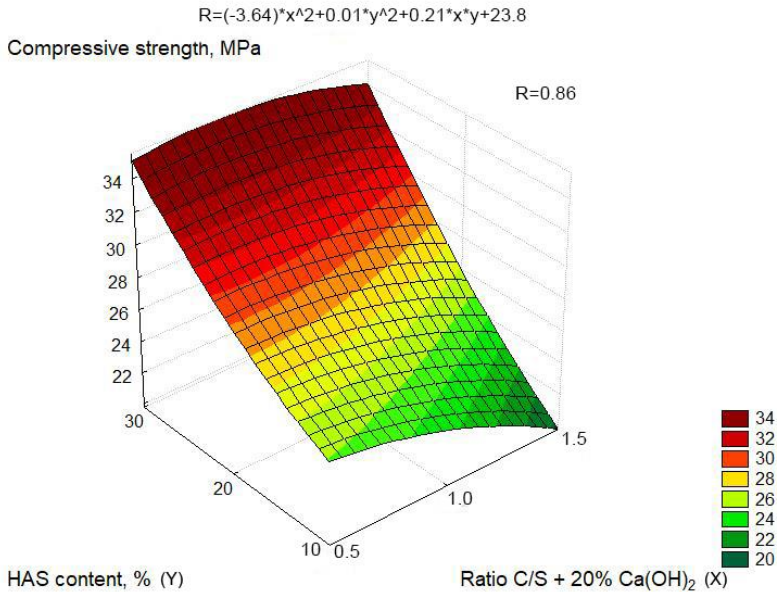


Fig. 3. Dependence of compressive strength of pressed stone from C-S-H + 15% portlandite on HAS content and on the ratio of CaO / SiO₂ in the gel at a compressive pressure of 80 MPa after 28 days of normal hardening.

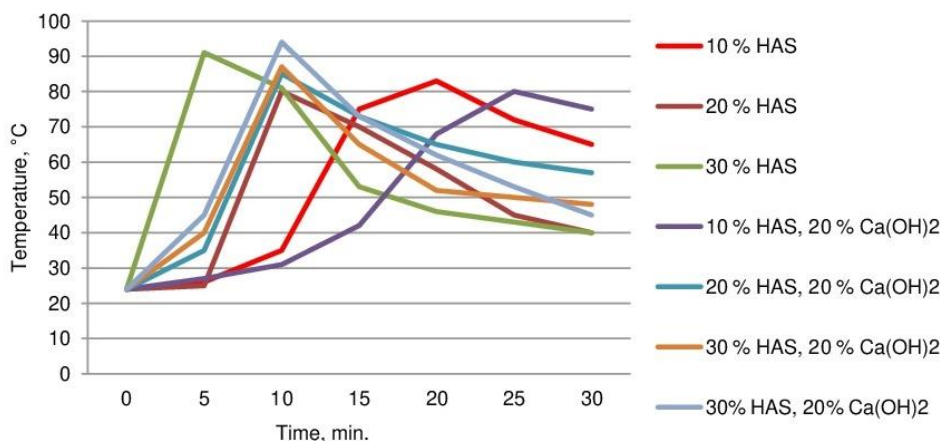


Fig. 4. Temperature development in samples from C-S-H with additives after pressing at 80 MPa.

4. Discussions

Studies of the hydration processes of calcium aluminates most often boil down to the consideration of the kinetics of the interaction of pure high-basic compounds or calcium monoaluminate with water from the transition from hexagonal aluminates such as C_4AH_{13-19} to cubic C_3AH_6 calcium hydroaluminate with characteristic durability. The increase in compressive strength of the pressed stone from CSH + 15% portlandite with the addition of HAS is due to the fact that the high-alumina slag consists entirely of calcium aluminates (60% of calcium bi-aluminate) and during the pressing process there is a rapid conversion of hydroaluminates according to the reactions (1) and (2) to form an increased amount of $Al(OH)_3$ gel.

Since the hydration of calcium aluminates is accompanied by the release of alumina gel $Al(OH)_3$, it can be assumed that the increase in strength is also associated with its formation, since The alumina gel is a highly disperse system with a developed surface and can significantly improve the contact strength of the stone.

Thus, this study shows that a significant increase in the contact strength of the C-S-H cement phase is possible both with the use of silica additives and high-alumina slag containing low-basic calcium aluminates (CA_2 , CA_6), in the process of hydration of which the $Al(OH)_3$ is formed, which provides an increase in the contact strength of the composition.

5. Conclusions

1. The contact condensation properties of the C-S-H phase increase with a decrease in its basicity, especially in the later periods of hardening. High compressive pressure (80–100 MPa) provides high strength samples (up to 12 MPa).
2. The addition of portlandite to calcium hydrosilicates C-S-H increases the strength of artificial stone in comparable conditions 1.3-1.5 times.
3. Alumina additives in the form of alumina zol increase the contact strength of a C-S-H stone 1.7 times, but decrease it 2 times in the case of pressing C-S-H in a mixture with the additive of 15–20% portlandite. It is explained by the special behavior of calcium hydroaluminates.

4. The addition of silica zol has a positive effect on the contact strength of the C-S-H phase. Compared with the pure C-S-H system, the strength of this material is higher 1.5 times (up to 15 MPa) in the early periods of hardening and to 2.5 times (up to 28 MPa) in the late ones.
5. The addition of high-alumina slag increases the strength of the material with a content of 30%: up to 12–15 MPa in the early periods and up to 34 MPa in the later periods of hardening. This is due to the formation of $\text{Al}(\text{OH})_3$ gel in the process of hydration of such a composition, despite the rapid formation of cubic C_3AH_6 in such conditions.

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