Anisotropy of strength properties of aluminate cement after exposure to single-axis loading at early stage of hardening

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Abstract. The article considers the impact of short-term compression at an early age on the flexural strength of aluminate cement. Taking into account the results of the previous research, the authors took the samples with the identical planes instead of prisms. The change in splitting tensile strength of pre-stressed samples at different planes has been analyzed. The studies have shown cement hardening in a plane perpendicular to the direction of short-time compression. It can be explained by the compaction of cement stone, decrease in porosity and formation of additional bonds through the chemical-plastic hardening, as noted by F. J. Ulm and O. Coussy. The research revealed that, after the removal of load, the difference between the strength of pre-stressed and control samples tends to reduce. The X-ray phase analysis demonstrates the difference in the hydration process in the first 24 hours after loading and change in the recrystallization of hexagonal hydroalumates into cubic crystals.

1. Introduction
It is widely known that flexural strength of cement tends to be 7-10 times lower than compression strength [1-2]. Therefore, the increase in flexural strength, leading to higher crack resistance, by loading the cement at an early age is relevant not only for Portland composite cement but also for aluminate cement (for example, for refractory concrete linings [2-5]), among the advantages of which it is necessary to emphasize the resistance to high temperatures [6-10].

The other researches [11-13] also indicated the increase of the crack resistance of composites based on Portland cement after loading in the early stages of hardening. The issue of maximizing of the bending resistance at an early age still remains relevant nowadays [14-17]. However, just a few number of papers have been focused on the analysis of this characteristic for aluminate cements [18-20].

Our previous research [21] has revealed that the early loading of aluminate cement led to an increase in tensile strength in bending. The maximum increase was 29% if to compare with tensile strength of prisms that were not exposed to load. For compressive strength, the changes were less significant (ΔR ≤ 5%), and even a decrease was observed. Prisms taken as samples in this research were exposed to vertical loading, and then tested to a single point bending in horizontal position. According to [21], the pre-stressed samples required higher amount of effort to force a flexural failure mechanism.

It can be argued that the hardening took place in the plane of the prism (cross section plane), because the early loading probably led to a later crack opening and, as the consequence, to the
destruction (split) of the sample. The explanation might be found in the plastic deformation of aluminate cement, in line with the Portland cement, accompanied by compaction [11, 22-24] and hardening under constrained conditions. It allows the composite to form additional bonds, which are indicated in [25-26].

Regarding the position of the prism under load, the prism bending plane is perpendicular to the direction of the compressive force during short-term and long-term exposure. We are able to assume the appearance of anisotropy of the structure caused by the compaction force by of the load. It leads to increase in the maximum bending stress in a certain direction. The orientation of the sample under load in this case can play a decisive role. In this case sample orientation under load can play a decisive role.

The purpose of the research is to estimate the possible effect of increase of the flexural strength for different orientations of the samples exposed to the early loading.

With a view to the purpose, the following objectives have been identified:

- apply samples with identical linear dimensions (unlike prisms) to estimate the splitting tensile strength by testing of various planes relative to the compression load;
- analyze the differences in compression strength between samples exposed to loading at early stage, changing their position while testing;
- compare the obtained values with those of samples that were not exposed to loading;
- study the change in strength after short-term loading at an early age and conclude on persistence of the effect over time;
- determine whether there are changes in the phase composition by X-ray phase analysis.

2. Materials and methods

In order to confirm the hardening effect in a definite direction, cubes 70 × 70 × 70 mm have been taken as samples and tested for splitting tensile strength in different positions relative to the load plane as per GOST 10180. After removal of the load some samples have been tested for splitting in the same position, in which it was exposed to the early loading. The other ones have been turned 90 degrees to the right, i.e. splitting plane was perpendicular to the compressed plane of the sample.

As a binder, alumina cement GC-50 (GOST 969-91) of Pashiysk metallurgical cement plant was used (Table 1). To identify the main phases, X-ray phase analysis of the initial was carried out prior to tempering. The main detected mineralogical phase is calcium monoaluminate CA. There are also C₁₂A₇, C₂AS, C₄AF and CA₂. X-ray phase analysis was performed on a XRD-7000 X-ray diffraction meter Shimadzu (Japan). The identification of the peaks in the XRD-patterns was carried out using the PDWin 4.0 software and Crystallographica Search-Match, as well as reference books [27-28]. Conditions of taking XRD photographs are the following: anode copper, the wavelength of copper radiation Kα of the line is 1.54051Å, 40kV, 30mA, range of angles 5-70 degrees, the shooting speed 1 deg/min.

| Table 1. Chemical composition of the cement GC-50 (%) |
|-----------------------------------|---|---|---|---|---|
| Al₂O₃ | CaO | SiO₂ | Fe₂O₃ | MgO | TiO₂ |
| 38-42 | 27-29 | 10-12 | 5-8 | <5 | <10 |

Composition of the cement C: P: W = 1: 1: 0.4. The cement age at the time of application of load is 24 hours. Loading impact equals to 10% of the destructive force in the compression test. It has been applied for 24 hours. 12 samples were kept pre-stressed. After that, six of them were tested after 90-degrees turn. The remaining six samples were split along the direction of the load applied. The evaluation of the reliability of the experiments was established by means of statistical processing of data, including gross error assessment.
3. Results

The obtained data on the strength characteristics and their processing by statistical methods are given in Tables 2 and 3. As it can be seen from the Table 2, which reflects the results of the determination of the splitting tensile strength, the splitting strength applied to the samples "after one 90 ° turn" was 18% higher than the one applied to the samples tested without rotation. As for the control samples that were not exposed to loading, increase of the strength was 23%.

| Type of loading | Position of the sample subjected to the bending test | Splitting strength, kN | $R_t = \frac{2F}{\pi A}$ | $\gamma = 0.87$ | Rtt, MPa average | $x_{T1}$ | $x_{T2}$ | $(x_{T1} - x_{T2})^2$ | $\sum S$ | $V_c$, % | $m$, ± | Accuracy ε, % | τ | Gross error |
|----------------|------------------------------------------------------|----------------------|-----------------|----------------|-----------------|--------|--------|-----------------|--------|--------|--------|-------------|---|-------------|
|                |                                                      |                      |                 |                |                 |        |        |                 |        |        |        |             |   |             |
| Control samples (unstressed) |                                                      |                      |                 |                |                 |        |        |                 |        |        |        |             |   |             |
| 15.8           | 1.787                                                | 1.843                | 0.041           | 0.002          | 0.015           | 0.000     |        |                 |        |        |        | 0.74 N/A   |   |             |
| 14.8           | 1.674                                                | 1.843                | 0.057           | 0.003          | 0.001           | 0.000     |        |                 |        |        |        | 0.50 N/A   |   |             |
| 16.3           | 1.843                                                | 0.013                | 0.013           | 0.003          | 0.001           | 0.000     |        |                 |        |        |        | 1.00 N/A   |   |             |
|                |                                                      |                      |                 |                |                 |        |        |                 |        |        |        |             |   |             |
| Control samples (unstressed) |                                                      |                      |                 |                |                 |        |        |                 |        |        |        |             |   |             |
| 15.8           | 1.787                                                | 1.843                | 0.041           | 0.002          | 0.015           | 0.000     |        |                 |        |        |        | 0.74 N/A   |   |             |
| 14.9           | 1.685                                                | 1.730                | 0.057           | 0.003          | 0.001           | 0.000     |        |                 |        |        |        | 0.40 N/A   |   |             |
| 15.3           | 1.730                                                | 0.000                | 0.000           | 0.003          | 0.001           | 0.000     |        |                 |        |        |        | 0.00 N/A   |   |             |
|                |                                                      |                      |                 |                |                 |        |        |                 |        |        |        |             |   |             |

The difference in tensile strength of the control samples and the ones tested along the direction of load application was 4.2%. The increase of strength in the case of the rotation of the sample may indicate a hardening in the direction perpendicular to the impact of the compression load. This may be due to the manifestation of the contact-condensation properties of the cement stone (see papers of V.D. Glukhovsky [25]), which occurs when the layers are brought together as a result of plastic deformation, as mentioned in [29-30].

Through the same procedure that was used for determination of the splitting strength (see Table 2), the cubes exposed to early loading both "after one 90° turn" and without rotation were tested for determination of compression strength as per GOST 10180. The results are given in Table 3.
The compression strengths of all series of samples were approximately the same (average difference was not more than 8%). Therefore, loading at the early stage did not cause an increase in compression strength. As for the difference within a series of stressed samples tested in different positions, it was not more than 1.2% (for the splitting tensile test, this value was 18%). This fact might indicate the compaction of the structure of the cement stone, which increases bending characteristics of the cement. It can be explained by the indicated above rapprochement of the particles [25-26, 29-30] and the probable interaction between them leading to the formation of additional bonds and a decrease in the porosity.

The change in splitting tensile strength after removal of short-term loading, i.e. in the absence of stress, is shown in Figure 1. For the test, the same composition as the one above was used. The duration of the load applied on the first day of hardening was 24 hours. Then the load was removed, and the samples were tested for tensile strength in different positions. Then the test was repeated in 2, 3 and 5 days after the removal of the load. Each point of the flexural strength curve corresponds to the arithmetic mean of three values. Each point of compression strength curve corresponds to the arithmetic mean of six values. For the obtained series of points, trend lines are drawn, as well as the approximate regression equations are given in the form of polynomials of the second and third degree.

**Table 3.** Compression strength of the samples exposed to loading at an early age.

| Type of loading | Position of the sample subjected to compression | Compressive strength, kN | $R = \frac{F}{A}$ | $\alpha = 0.85$ | $R$, MPA | Average $x_i - x_{\text{mp}}$ | $(x_i - x_{\text{mp}})^2$ | $\sum S$ | $V_c$, % | $m$, ± | Accuracy ε, % | Gross error |
|-----------------|---------------------------------|------------------------|------------------|---------------|----------|---------------------|-----------------|----------------|----------------|-------------|---------------|-------------|
| Control samples (unstressed) | 147.8 | 16.330 | 90% | 0.814 | 0.71 | N/A |
| 139.1 | 15.369 | 80% | 0.814 | 0.71 | N/A |
| 169.2 | 18.695 | 80% | 0.814 | 0.71 | N/A |
| 153.6 | 16.971 | 80% | 0.814 | 0.71 | N/A |
| 166.7 | 18.419 | 80% | 0.814 | 0.71 | N/A |
| 159.4 | 17.612 | 80% | 0.814 | 0.71 | N/A |
| 148.3 | 16.386 | 80% | 0.814 | 0.71 | N/A |
| 145.7 | 16.098 | 80% | 0.814 | 0.71 | N/A |
| 173.8 | 19.203 | 80% | 0.814 | 0.71 | N/A |
| 157.8 | 17.435 | 80% | 0.814 | 0.71 | N/A |
| 166.2 | 18.363 | 80% | 0.814 | 0.71 | N/A |
| 155.4 | 17.170 | 80% | 0.814 | 0.71 | N/A |
| 162.1 | 17.910 | 80% | 0.814 | 0.71 | N/A |
| 172.3 | 19.037 | 80% | 0.814 | 0.71 | N/A |
| 166.0 | 18.341 | 80% | 0.814 | 0.71 | N/A |
| 170.9 | 18.883 | 80% | 0.814 | 0.71 | N/A |
| 174.2 | 19.247 | 80% | 0.814 | 0.71 | N/A |
| 169.5 | 18.728 | 80% | 0.814 | 0.71 | N/A |
Figure 1 shows that immediately after removal of the load the splitting tensile strength is maximum for cubes with load application planes turned perpendicular to the direction of splitting for all series of samples. It is consistent with the data of Table 2. After three days, the strength curve of control sample lies above the curves of pre-stressed ones, and after five days of observation the difference between the strength of control samples and pre-stressed ones split along the direction of load application is 12%. For samples split after a turn, this value is 3%. With the passing of time, the growth in strength, noted during the first 24-hours, decreased.

The observations conducted after removal of the load indicate that compression stress contributes significantly to the increase in strength. The main affecting factors are the parameters of the force, its magnitude and duration. As it can be seen, after removal of the load the course of the hydration process led to the similarity of arithmetic means of strength. Perhaps, increase of loading duration and pressure will allow to retain the effect also at later stages of hardening. In this vein, it is especially important to control the integrity of a sample at early age and to avoid any defects.

Figure 2 shows a comparison of the X-ray diffraction patterns of pre-stressed and control aluminous cement stone. Strength characteristics were considered in Table 2.

As a result of the loading at an early stage, the difference of the peaks of the main phases (such as CA and CA₂) is observed at angles 2Θ = 16.1°; 18.94°; 25.54°; 28.9°; 33.18°; 41.02°; 42.62°; 59.36° for the CA, and at 2Θ = 30.08° for CA2. This may be the result of different hydration in the samples being compared. It is confirmed by changes of the hydration phases: the shift of the peaks of hexagonal hydroaluminate C₂AH₈ to 2Θ = 8.42° and 16.32°, the hydroaluminate CAH₁₀ at 2Θ = 34.43° and 35.7°. The difference is also noted in the peaks of cubic crystals of C₃AH₆ (2Θ = 16.1°, 18.94°), which allows to assume that the load application to cement stone changes recrystallization of hexagonal hydroaluminates into cubic form.
4. Conclusions

- compression load at an early stage of hardening contributes to anisotropy of properties in a certain direction, increasing the splitting force of a plane perpendicular to the load applied;
- maximum increase in the splitting tensile force is noted in a plane perpendicular to the direction of applied load;
- growth of tensile strength after the removal of compression stresses decreases with time;
- X-ray phase analysis revealed a change in the phase composition of cement stone after loading at an early stage, as well as a difference in recrystallization processes.

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