Theoretical and experimental study of the effect of wollastonite on the physical and mechanical properties of concrete

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Abstract. As part of the work, an experimental and theoretical study of the effect of adding wollastonite on the physical and mechanical characteristics of concrete was carried out. The internal stress was calculated according to Hooke's law. The change in the specific volume was determined from the change in the volume of the hydrated phase. The calculation of the chemical interaction was carried out within the framework of thermodynamic equilibrium. According to the results of the work, it was shown that the addition of wollastonite leads to a linear decrease in the value of internal stresses, which is consistent with experimental results on the increase in compressive and bending strength.

1. Introduction
The strength characteristics of concrete building products determine their operational properties. Moreover, the strength of concrete products increases over time.

The classical direction of improving the physical and mechanical properties of composite materials is the use of various reinforcing components, both spherical [1] and fibrous [2]. Reinforcing components can act as inert additives [3] and components that enter into a chemical reaction with the matrix material [4]. In the production of concrete products, one of the problems is the change in the specific volume during the hydration process. Also, as a negative factor affecting shrinkage processes, one can note the formation of calcium hydroxide during hydration [5]. In this case, additional internal stresses arise, which lead to the formation of cracks and, as a result, weakening of the material. Additives based on finely dispersed silicon oxide [6] and wollastonite [7] make it possible to bind the formed calcium hydroxide, while additional binding phases are formed, which increase the strength of products, and the relaxation of excess stresses reduces the likelihood of cracking.

At the same time, the degree of influence of excessive stresses is determined both by the rate of the chemical reaction and by the physiochemical characteristics of the hydration products. At a slow speed, relaxation of excess stresses occurs, and an increase in speed leads to a decrease in strength [8].

The main astringent phases in Portland cement are calcium aluminate (C\textsubscript{3}A), alite (C\textsubscript{3}S), belite (C\textsubscript{2}S) and alumоferite (C\textsubscript{4}AF), with different reaction rate of each compound. At the first stage, calcium aluminate sets (4-7 days), which leads to the initial strength of the product. In the future (28 days or
more), other phases react, which determine the strength of the final product. At each stage in the process of hydration, new phases are formed, each of which corresponds to its own change in the specific volume, and, as a consequence, the formation and relaxation of internal stresses.

The use of nano and microcomponents makes it possible to evenly distribute a small amount of the additive throughout the entire volume of the material, and by controlling the chemical interaction, it is possible to control the structure of the material. At the same time, the uniform distribution of the additive will make it possible to quickly relax the excess stresses formed in the structure.

The main purpose of this work is to study the internal stresses in the cement matrix arising from the hydration of calcium aluminate, alite, belite and alumoferrite, as well as to evaluate the effect of wollastonite on the binding of calcium hydroxide by numerical simulation.

2. Hydration of calcium aluminate, alite, belite and alumoferrite

The physical properties of the components involved in hydration are presented in table 1.

**Table 1.** Properties of calcium aluminate, alite, belite and alumoferrite.

| №  | Phase              | Chemical formula | Chemical formula in a hydrated state | Density, g / cm³ | Density in hydrated state, g / cm³ | Change in the specific volume of the solid phase, % |
|----|--------------------|------------------|--------------------------------------|-----------------|----------------------------------|-----------------------------------------------|
| 1  | Calcium aluminate  | 3CaO·Al₂O₃       | 3CaO·Al₂O₃×6H₂O                      | 3.04            | 2.52                             | 17                                            |
| 2  | Alite              | 3CaO·SiO₂        | 2CaO·SiO₂×H₂O/Ca(OH)₂              | 3.2             | 2.67/2.21                        | 16/31                                         |
| 3  | Belite             | 2CaO·SiO₂        | 2CaO·SiO₂×H₂O/Ca(OH)₂              | 3.07            | 2.67/2.21                        | 13/28                                         |
| 4  | Tetracalcium alumoferrite | 4CaO·Al₂O₃×Fe₂O₃ | 3CaO·Al₂O₃×6H₂O/CaO·Fe₂O₃×13H₂O | 3.77            | 2.52/2.31                        | 33/39                                         |

*a* In reality, the alite phase is a solid solution of Al₂O₃ and MgO in 3CaO × SiO₂, for the possibility of numerical simulation, we represent it in a simplified form [9].

According to the literature [10], cement hydration can be decomposed into 4 stages. The first three are associated with the formation and development of the helium shell. The coarsening of grain begins at the fourth stage, which begins approximately 1-2 hours after the start of hydration. Consequently, internal stresses arise mainly at 4 stages of hydration, and the processes taking place at the first three stages were not considered in the work.

Let us approximate the available experimental literature data on the rate of hydration [11] with a quadratic function (figure 2). In this regard, the quadratic function describes well the experimental data, and the surface area of a spherical particle is determined by the square of its radius, therefore, the growth of the hydrated phase occurs from the surface of the particle.
Based on the presented results, it can be assumed that since the specific surface area of a particle depends on the radius squared, the reaction occurs on the surface of the particle and is limited only by its size.

3. Thermodynamics of hydration processes

In the process of hydration, the specific volume of hydrated phases changes (table 1), a change in the specific volume leads to the formation of excessive stresses. The main chemical reactions of hydrating phases can be represented as follows [12], for belite:

\[ Ca_2SiO_4 + H_2O = 2CaO \cdot SiO_2 \cdot H_2O \]
\[ 2Ca_2SiO_4 + 4H_2O = 3CaO \cdot 2SiO_2 \cdot 3H_2O + Ca(OH)_2 \]

For tricalcium silicate:

\[ Ca_3SiO_5 + 2H_2O = 2CaO \cdot SiO_2 \cdot H_2O + Ca(OH)_2 \]

For calcium aluminate:

\[ 3CaO \times Al2O3 + 6H_2O = 3CaO \times Al2O3 \times 6H_2O \]

For tetracalcium alum ferrite:

\[ 4CaOAl_2O_3Fe_2O_3 + 16H_2O = 3CaOAl_2O_3 \times 6H_2O + CaO \cdot Fe_2O_3 \times 10H_2O \]
Let’s calculate thermodynamic equilibrium for two cases. The first composition in the system is alite (wt. % 58), belite (wt. % 17), calcium aluminate (wt. % 8) and tetracalcium alumina ferrite (wt. % 13), and there is a gradual increase in the amount of water. The second in the system of composition is alite (wt% 58), belite (wt% 17), calcium aluminate (wt% 8) and tetracalcium alumina ferrite (wt% 13), there is a gradual increase in the amount of wollastonite [7]. For the calculation were taken thermodynamic parameters presented in table 2, the calculation was carried out under normal conditions [13].

Table 2. Thermodynamic parameters of phases used in calculating thermodynamic equilibrium.

| №  | Chemical formula | S, J/mol | H, J/mol |
|----|-----------------|----------|----------|
| 1  | 3CaO·Al₂O₃       | 206      | -3587    |
| 2  | 3CaO·Al₂O₃·6H₂O  | 376.5    | -5547.984|
| 3  | 3CaO·SiO₂        | 241.4    | -6646.1 59|
| 4  | 2CaO·SiO₂·H₂O    | 171      | -3139    |
| 5  | Ca(OH)₂          | 83.4     | -986     |
| 6  | 2CaO·SiO₂        | 121      | -2315    |
| 8  | CaSiO₃           | 82       | -1635    |

The results of calculating thermodynamic equilibrium are shown in figure 2.

![Figure 2](image)

Figure 2. The results of calculations of thermodynamic with an increase in the concentration of (a) water; (b) wollastonite.

As follows from the results (figure 2a), the most thermodynamically stable phase is Ca(OH)₂. Of course, under real conditions, the amount of calcium hydroxide formed is determined by the rate of the chemical reaction. The main factor leading to the formation of excess stresses is the calcium hydroxide phase, which corresponds to the literature data [8].

4. Mathematical model
To calculate the internal stresses formed in the material, we use Hooke’s law:

\[
\vec{F} = -k \Delta V,
\]

\[
\Delta V = i \Delta x + j \Delta y + k \Delta z
\]
there \( k \) is the coefficient of elasticity, Pa; \( \Delta \vec{V} \) – change in the specific coordinates in the Cartesian system \( \Delta x, \Delta y, \Delta z, \text{Pa} \); \( \vec{F} \) – strength, N; \( i, j, k \) - unit vectors

Internal stress is determined as follows:

\[
\vec{\sigma} = \frac{\vec{F}}{S}
\]

there \( \vec{\sigma} \) – internal stress, Pa; \( S \) is the area to which the force is applied, m\(^2\).

To compare the results obtained, let us integrate the value of internal stresses over the volume, and obtain the average stress in the volume of the material:

\[
\bar{E} = \frac{1}{V_0} \iiint E \, dV
\]

there \( V_0 \) – volume, m\(^3\).

To assess the effect of the addition of wollastonite on the value of internal stresses, we will take the values of the elastic modulus of 36 GPa in all directions, and the boundaries of the computational domain will be taken as stationary. Of course, the modulus of elasticity depends on the phase, but these calculations are of an estimate nature, therefore the results are presented in a reduced form. The complete change in the specific volume is presented in table 1, and a part of the reacted phase was determined according to figure 1.

To verify the obtained calculations, we synthesized model compositions of concrete samples containing 25% cement 75% sand at various concentrations of wollastonite. The synthesis was carried out according to the classical concrete technology, the samples were obtained by the method of vibration pressing. The test was carried out on 3 samples.

5. Results and discussion

Let us assume that the effect of wollastonite leads to a decrease in the specific volume during hydration (the reaction rate is limited by the specific surface). Let’s calculate the value of internal stresses in the material, the calculation results are shown in figure 3. The results are presented in relative terms.

![Figure 3. Reduction of the value of internal stresses in the structure of concrete with the addition of wollastonite.](image-url)
As follows from the presented results, the addition of wollastonite leads to a linear decrease in the value of internal stresses in the material. This result is due to the fact that the addition of wollastonite leads to a linear decrease in the specific volume due to the binding of the calcium hydroxide phase.

Let us compare the calculated data with the experimental results.

![Figure 4](image_url)

**Figure 4.** Experimental dependence of compressive strength (a) and bending strength (b) depending on the time of hydration, with different amounts of wollastonite.

As follows from the presented results, the addition of wollastonite leads to an increase in strength, with an explicit dependence for compression, and a more complex form for bending. However, for both cases, the optimal composition of the additive is 0.25%, which leads to a compression hardening of 57% and a bending hardening of 12.5%. The decrease in strength at high concentrations of the additive is probably associated with an increase in the viscosity of the concrete mixture, and, as a consequence, a decrease in workability.

6. Conclusion
As part of the work, theoretical and experimental studies of the effect of adding wollastonite on the physical and mechanical characteristics of concrete were carried out.

Within the framework of theoretical studies, it has been shown that the introduction of an additive of wollastonite leads to a linear decrease in internal stresses in the material, which leads to an increase in strength, as shown by experimental studies.

The addition of 0.25% wollastonite increases the compressive strength by 57% and the flexural strength by 12.5%.

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