Physical and chemical processes of volcanic rock hardening with alkaline silicates

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Abstract. The thermodynamic probability of reactions in volcanic rock compositions — an alkaline silicate binder, which is used to produce artificial stone (concrete) products with high physical and mechanical properties and with wide range of colors for interior and exterior wall tiling and external masonry, manufacturing of decorative architectural details, etc. are considered. Silicate and aluminosilicate rocks of volcanic origin (perlite, pumice, tuff, etc.) of various deposits of Armenia are dispersed volcanic glasses with feldspar inclusions and are characterized by a large variety of colors: white, beige, yellow, orange, violet-pink, pinkish, red, brown, black, greenish, bluish-white, etc. Dolomite hardener is introduced into the composition for manufacturing of waterproof concrete on a base of a chemical binder at low temperatures. The possibility of reactions in a mixture of volcanic rock — alkaline silicate — dolomite — water was assessed by thermodynamic method. The calculation of Gibbs energy of the interaction reactions in the indicated system witnessed the possibility of realization of hydration, hydrolysis, silicate formation reactions even at a temperature of 298K. The formation of hydrated silicates and calcium and sodium aluminosilicates, guarantees the binding properties of the composition under normal conditions. With an increase of the temperature to 375, 475, 574K, the probability of reactions increases.

Introduction
The purpose of the material determines the choice of additives and hardeners used.

This study is devoted to the development of decorative materials based on compositions of volcanic rocks of RA (perlite, pumice, tuff) with a wide variety of colors and a binder-soluble glass (silicate rock), which does not reduce the decorative qualities of concrete.

The binding properties of alkaline silicates — water glass, silicate-rocks for the production of a number of materials using energy—efficient technology have been studied by many researchers [1-18]. It has been established that the formation of the structure of special concretes based on hydrated soluble glass is a complex of physical and chemical processes in which physical and chemical interactions between sodium silicates, hardeners and additives in a complex, provided the hardening of the concrete.

It was established [6,10] by the researches that the binder produced on the base of water glass has high solubility, and at normal temperatures the hardening process is extremely slow.

The use of toxic fluorosilicate hardener does not provide water resistance of concrete [3-6].

The introduction of the hardener containing calcium and magnesium silicates into concrete increases its water and frost resistance. These concretes are characterized by rapid hardening properties, stability of strength characteristics and good performance [6].
Magnesium silicates $MgSiO_3$ and $Mg_2SiO_4$ produced by firing of dunite are also proved to be effective hardeners [13]. In a mixture with liquid glass, as a result of the formation of practically insoluble $Mg(OH)_2$, the basicity of the solution decreases, adhesion properties to the additive and cementitious particles appears, polycondensation and the formation of intergrowth contacts are accelerated.

In silicate – sodium compositions for heat-resistant concrete, dolomite is also used as a hardener [7].

According to [7-14], during the monolithing of the building materials on the base of silicate-sodium compositions (soluble glass), the use of dry grained slowly moving material as a bonding material, allows to achieve a high degree of homogeneity in the mixture, even at a low dosage in the composition. In heat-resistant concretes on the base of anhydrous sodium silicates, a dense packing of grains is provided. Compositions with a limited content of silicate-block of 20-25% and various additives are characterized by high strength (20 ... 40MPa) after 24 hours according to the regime: temperature rise from 20 to 90°C - 1.5 hours, keeping at 90 ± 5°C - 2, 5 hours, raising the temperature to 200°C -1 hour, holding 2 hours and cooling. Taking into account the wetting of the refractory powders, the ratio $H_2O:Na_2SiO_3 = 1: (0.9 – 0.8)$ was established.

The technology for the preparation of compositions stipulated the joint grinding of a silicate block and a mineral additive to a specific surface of 250-400 m²/kg.

As a hardener-finely ground mineral components of silicate – sodium composite binders carbonate rocks (including dolomite) and some industrial wastes are used.

The binding properties of a composite binder on the base of a silicate block is revealed due to gaining adhesive properties of anhydrous sodium silicate-determining the adhesive ability of this component (up to 90 ± 5°C) and the cohesive strength of adhesive contacts (up to 190 ± 5°C) [7,14,15].

In accordance with the basic principles of the selection of new cementitious compositions [19], this is the reactivity of the starting components with respect to each other, the conditions for the implementation of this interaction and the intensity of structure formation processes, for the development of a new composite material based on volcanic aluminosilicate rocks (pumice, perlite, tuff) and sodium-silicate binder with a dolomite hardener was determined by the reactivity of the components of the compositions.

To assess the possibility of reactions between the components of the mixture, the thermodynamic method of analysis was used [20]. The Gibbs energy ($\Delta G^o$) was calculated in the temperature range of 298 ... 573 K and the negative values of which are more than 0.5 kcal / mol (2.09 KDm / mol), which indicates the possibility of the reactions.

For the calculation, standard thermodynamic parameters were used [20,21]. Reactions involving substances for which the initial thermodynamic data were absent were not considered.

The thermodynamic data of the starting materials: sodium silicates with a module of 0.5 ... 3, hardener—dolomite and aluminosilicate rocks containing mainly volcanic glass and feldspar minerals and $SiO_2$, as well as data for possible reaction products are given in Table 1.

**Table 1. Initial thermodynamic data [20,21].**

| Compound     | $-\Delta H^o_{298}$, Kcal / mol | $-\Delta G^o_{298}$, Kcal / mol | $CT = f(T)$, Kcal / (deg · mol) | T, K  |
|--------------|-------------------------------|-------------------------------|---------------------------------|-------|
| $Na_2SiO_4$  | 500.25                        | 470.21                        | 43.35                           | 298-1200 |
| $Na_2SiO_3$  | 363.06                        | 341.35                        | 25.45                           | 298-1361 |
| $Na_2Si_2O_5$| 584.35                        | 550.57                        | 32.91                           | 298-1147 |
| $Na_2Si_3O_5$| 801.75                        | 775.76                        | 40.55                           | 297-1023 |
| $H_2SiO_4$   | 354                           | 318.6                         | -                               | -     |
| $H_2SiO_3$   | 284.1                         | 261.1                         | -                               | -     |
| $H_2Si_2O_5$ | 499.2                         | 464.5                         | -                               | -     |
| $NaOH$       | 101.99                        | 90.1                          | 19.2                            | 298-593 |
The calculation results of determining the thermodynamic possibilities of reactions in a mixture of soluble glass - dolomite - water - powder - volcanic rock for compounds with known thermodynamic characteristics are given in Table 2.

**Table 2.** Gibbs energy of the reactions considered

| N  | Reactions                             | \(\Delta G^\circ_T\) at temperatures (K), kJ / mol |
|----|--------------------------------------|--------------------------------------------------|
|    |                                      | 298     | 375    | 475    | 574    |
| 1  | \(\text{Na}_2\text{Si}_4\text{O}_7 + 4\text{H}_2\text{O} = 4\text{NaOH} + 3\text{H}_2\text{SiO}_3\) | 75.3    |        | -2131  |        |
| 2  | \(\text{Na}_2\text{Si}_4\text{O}_7 + 2\text{H}_2\text{O} = 2\text{NaOH} + 3\text{H}_2\text{SiO}_3\) | 57.0    |        | 473     |        |
| 3  | \(\text{Na}_2\text{Si}_2\text{O}_5 + 2\text{H}_2\text{O} = 2\text{NaOH} + 3\text{H}_2\text{SiO}_3\) | 80.55   |        | 2252    |        |
| 4  | \(\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{NaOH} + 3\text{SiO}_2\) | -757.8  |        | -       |        |
| 5  | \(\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{NaOH} + 3\text{SiO}_2\) | 89.6    |        | 1017    |        |
| 6  | \(\text{Na}_2\text{Si}_2\text{O}_5 + 4\text{H}_2\text{O} = 2\text{NaOH} + 3\text{H}_2\text{SiO}_3\) | -779.4  |        | -       |        |
| 7  | \(\text{Na}_2\text{Si}_2\text{O}_5 + 7\text{H}_2\text{O} = 2\text{NaOH} + 3\text{H}_2\text{SiO}_4\) | -789.7  |        | -       |        |
The analysis of the data obtained to establish the probability of interaction between the components of soluble glass, dolomite hardener and the additive from volcanic rock allowed us to establish the following.

Using the equipment for calculating the Gibbs energy of the hydration and hydrolysis of sodium silicates reactions (reactions 1-7), we can conclude that under normal conditions, only hydrolysis reactions of high-module sodium silicates (reactions 4,6,7) with the formation of NaOH, SiO\(_2\)\(\cdot\)H\(_2\)SiO\(_3\), H\(_2\)SiO\(_4\) are possible.

The dolomite hardener introduced into the composition interacts with both the hydroxide formed (reaction 8) and low-module sodium silicates. Moreover, the lower the module of sodium silicate, the greater the probability of the reaction (reactions 9-10). Dolomite does not react with Na\(_2\)Si\(_3\)O\(_7\) (reaction 12).

As a result of reactions 8–11, the resulting hydroxides and calcium metasilicate and magnesium participate in derivative reactions with sodium silicates and products of hydrolysis reactions. As a result of these derivative reactions, it is already possible, under normal conditions, the formation of calcium and
magnesiumsilicates:Ca\( \text{Si}_3 \), Mg\( \text{Si}_2 \text{O}_6 \), Mg\( \text{Si}_2 \text{O}_5 (\text{OH})_4 \), 2Ca\( \text{O}_3 \text{Si}_2 \text{O}_2 \cdot \text{H}_2 \text{O} \) (reactions 11, 13, 14, 16, 17, 19-21).

The mineral components of volcanic rocks can also interact with silicates and calcium hydroxide (reactions 22, 25, 26) with the formation of aluminosilicates as well. In compositions with a tuff additive, anorthite, as the main component of tuff, reacts with the most stable hydrosilicate-calcium-gillebrandite to form a grossular (reaction 25), with a metasilicate and calcium hydroxide, a grossular formation is also possible (reaction 26), with an albite, gillebrand forms CaO \( \cdot \) Al\( \text{Si}_2 \text{O}_5 \) \( \cdot \) 2Si\( \text{O}_2 \) sodium silicate and SiO\(2 \) (reaction 27), which are also reaction active.

Among the reactions considered at a temperature of 298K, only reactions 1, 2, 3, 5, 12, 15, 18, 26 are not feasible.

The formation of hydrated silicates and calcium and magnesium aluminosilicates guarantees the binding properties of the composition even at a temperature of 298K. For these reactions with increasing temperature, the probability the of reactions is increasing.

Summary
The analysis of the negative values of Gibbs energy suggests a roadmap for the implementation of the possible reactions.

The process starts at a temperature of 298 K with hydration and hydrolysis of high-modulus sodium silicates with the formation of sodium hydroxide and hydrosol SiO\(2 \).

Dolomite in a combined binder interacts with low-module sodium and sodium hydroxides to form silicates and calcium and magnesium hydrosilicates.

Feldspar minerals and glass of volcanic rock actively react with alkaline and alkaline-earth silicates with the formation of silicates and aluminosilicates, which possess binding properties.

Although the thermodynamic probability of the reactions with the calculations is confirmed, however, the kinetic process parameters: concentration, temperature, pressure should contribute to their implementation. Since the reactions under consideration are feasible already under normal conditions (1 atm and 25 °C), when selecting the compositions of new compositions and curing modes should be guided by:

- low content of the binder, when it is finely ground together with the hardener and their uniform distribution in the mass,
- the optimal amount of water required for hydration of soluble glass, homogenization of the mass and molding of the products,
- temperature-duration binding regime necessary for obtaining materials with specified physical and mechanical properties.

The presented results of thermodynamic analysis allow us to adjust the composition of the masses and the conditions of their hardening.

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