Obtaining sodium silicate solutions for the activation of mineral powders

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Abstract. Currently, the creation of clinker-free binders that do not require high-temperature processing and a substantial natural resource, and have high technical indicators, is an urgent task. The active component of alkali metals characterizes alkaline cement. A distinctive feature of alkali cement is its ability to interact with aluminosilicate minerals during hydration, which leads to the formation of active and hardly soluble compounds. The basis for the production of concrete composites based on chemical activation binders is the domestic and foreign experience in the use of slag-alkali composites in construction. In this work, an energy-dispersive microanalysis of clinker-free compositions based on alkaline silicate of sodium solutions from silica-containing rocks is carried out. The developed formulations of clinker-free binders based on highly dispersed powders of different nature, sealed with an alkaline solution prepared by the wet method at temperatures up to 95 °C and atmospheric pressure. This technology expands the scope of alkaline cement and produces concrete with desired properties. This work was carried out as part of research on the implementation of scientific project No 05.607.21.0320. "Development of technology for new building composites on clinkers alkaline binders using substandard natural and secondary raw materials," which received support from the federal target program "Research and Development in Priority Directions for the Development of the Russian Science and Technology Complex for 2014–2020."

1. Introduction

Modern rates of development of construction require an increase in the production of concrete composites. At the same time, scientists seek to reduce their cost without compromising the reliability and durability of the designed products and structures [1–3]. However, this task is difficult. The conditions faced by developers: a deficit of the developed natural resource, a constant rise in the cost of energy, an increase in anthropogenic impact on the ecological environment. Therefore, the special attention of scientists is focused on the development of less resource- and energy-intensive technologies for producing building composites [4, 5]. Currently, the urgent task is to create clinker-free binders that do not require high-temperature processing and have high technical indicators. This category of binders can be attributed to alkaline cement. A feature of these materials is that the active component is alkali metals, capable of interacting with aluminosilicate minerals during hydration. As a
result, fairly strong sparingly soluble compounds are formed that are identical to the products of hydration of a traditional binder [6–9].

2. **Methods and materials**

Experience in the use of such binders in construction is known [1–8]. Slag-alkali binders based on ferrous metallurgy wastes are studied in the most detail. Slag-alkali binders include blast furnace granulated slag, the chemical composition of which is represented by aluminum and silicon oxides and is similar to the composition of Portland cement clinker [9, 10]. But in many regions of our country, slag from ferrous metallurgy is an expensive and rare material. Transporting data with the material is a considerable cost. On this basis, well-known developments are widely adopted. For several years, we have been researching the production of clinker-free alkaline cement mixing [12–15]. As a result, we have obtained durable and corrosion-resistant composites. In the formulations of binders, finely dispersed mineral powders of different nature were used as a replacement for blast furnace slag of ferrous metallurgy. The following rocks represent highly dispersed mineral powders: silicified marl, limestone, volcanic tuff, sandstone, quartz sand, waste from the cement industry in the form of aspiration, and clinker dust of electrostatic precipitators. All of these powders were individually mixed in predetermined proportions with the fine aggregate of the Alagirskoye deposit (particle size modulus 2.8) and sealed with salable liquid sodium glass, with silicate modulus 2.8 and density 1.24 g/cm$^3$. The prepared samples solidified the first day under normal conditions at a temperature of 20 ± 2 °C. After 2 days, part of the twin samples was placed periodically in an oven at 40 °C for a couple of hours, and part of the heat-treated samples was stored in water. The formulations and test results depending on the hardening conditions are shown in Table 1.

3. **Results**

The test results confirm that the strength characteristics of the obtained binders depend, firstly, on the mineralogical and chemical compositions of the powders understudy, secondly, on the presence of active crystallization centers, thirdly, on the hardening conditions and specific surface area of mineral additives (Table 1). Clinker dust generated at the hot end of a clinker rotary kiln has the desired mineral composition. When mixed with an alkaline solution, clinker dust is hydrated with the formation of calcium and sodium hydro silicates. Therefore, the samples obtained are characterized by high strength values during hardening in an aqueous medium. Siliconized thermally activated marl and volcanic tuff also, when activated by a liquid-glass solution, gained good activity when storing samples in water. The aluminosilicate nature of these powders justifies the data obtained. Mineral powders from limestone, sandstone, and suction dust after activation gained strength with increasing temperature. The results are justified by the high content of alkaline earth compounds.

Thus, clinker-free hydraulic binders of alkaline activation were obtained, with a ruler of strength from 10 to 50 MPa, suitable for the production of concrete composites. But in the proposed developments, the most expensive is considered liquid commodity glass, and for the widespread use of alkaline composites. Therefore, it is necessary to find an alternative to this concoction [14, 16–18]. In connection with these circumstances, the goal of the next stage of research is to prepare an effective and less costly alkaline solution. The joint was prepared in a wet way. This method consisted of dissolving finely dispersed silica additives in a 20 % sodium hydroxide solution, followed by heating to 92–95 °C at atmospheric pressure.

The essence of the method is that the amorphous component of the studied additives during dispersion reacts with alkali to form sodium metasilicate by the reaction: $2\text{NaOH} + \text{SiO}_2 = \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O}$. The alkaline solution of sodium metasilicate obtained in this way was filtered as a suspension. As a result of filtration, the solution was separated from the insoluble precipitate. The chemical composition of the proposed alkaline solutions was investigated using a QUANTA 3D 200i scanning electron microscope using an energy dispersive microanalysis system (EDAX). The studies were conducted at the Research Center for Nanotechnology and Nanomaterials, GSTU.
Table 1. Formulations and properties of linker-free cements of alkaline activation

| Composition number | Highly dispersed powders | Alkaline activator, \% | MPa activity, 28 days hardening conditions |
|--------------------|--------------------------|-------------------------|---------------------------------------------|
|                    |                          | \( \text{Na}_2\text{SiO}_3 \) | natural | 40 °C | in water |
| 1                  | Quartz powder, S\text{specific surface} = 810 m\text{kg} | 26.0 | 20.3 | 22.3 | 23.5 |
| 2                  | Mergel (700 °C), S\text{specific surface} = 1150 m\text{kg} | 29.5 | 39.2 | 42.6 | 46.5 |
| 3                  | Volcanic tuff, S\text{specific surface} = 920 m\text{kg} | 26.5 | 33.1 | 37.6 | 39.4 |
| 4                  | Limestone flour, S\text{specific surface} = 1060 m\text{kg} | 29.0 | 13.7 | 16.5 | 9.0 |
| 5                  | Sandstone, S\text{specific surface} = 1020 m\text{kg} | 26.5 | 14.6 | 17.3 | 9.2 |
| 6                  | Clinker dust, S\text{specific surface} = 240 m\text{kg} | 23.0 | 42.1 | 44.7 | 50.5 |
| 7                  | Aspiration dust, S\text{specific surface} = 280 m\text{kg} | 24.0 | 15.4 | 15.6 | 10.1 |

As a siliceous component in the alkaline solution, the beautiful glass sands of the Shatoyskoye field (CR) and the volcanic tuff of the Kenzhenskoye field (KBR) were used. The chemical composition of mineral additives is given in Table 2.

Table 2. Chemical composition of silica additives, %

| Oxide composition | Volcanic tuff | Quartz sand |
|-------------------|--------------|-------------|
| MgO               | 2.20         | 6.32        |
| Al\text{2}O\text{3} | 13.57        | 14.99       |
| SiO\text{2}       | 63.67        | 73.83       |
| K\text{2}O        | 6.00         | 1.83        |
| CaO               | 7.79         | 0.6         |
| Fe\text{2}O\text{3} | 2.52        | 0.97        |
| TiO\text{2}       | 2.85         | 1.32        |
| SO\text{3}        | –            | 0.14        |
| Others            | 1.40         | –           |

After preparing the alkaline solution, visual inspection of the resulting suspensions was carried out for a week (Fig. 1a, 1b). Visual inspection showed that after a day, the level of sediment in the solution based on finely dispersed quartz powder is higher than in the solution with volcanic tuff. This fact can be explained by the fact that quartz is contained in an increased amount. Quartz is a reasonably solid mineral, which in the initial period, interacts more difficult with alkali. After a week, the level of sediment changed, it decreased in the same solution, it is likely that the process of dispersion of quartz in a solution of caustic soda was activated, due to the amorphous component of this additive. Energy dispersive analysis and microphotographs of the corresponding solutions were carried out both of the pure filtrate and the precipitate. The results are presented in Figures 2–5.

The results of microanalysis show that precipitates of alkaline solutions contain a more significant amount of unreacted silica. In the filtrates of an alkaline solution based on volcanic tuff, studies showed a higher SiO\text{2} content of up to 2.85 %, while in a solution based on quartz SiO\text{2} powders up to 1.99 %, and microphotographs confirm the presence of a glassy phase.
Figure 1. Pictures of alkaline solutions based on quartz sand and volcanic tuff, in a day (a) and in a week (b)

Figure 2. Energy dispersive analysis of an alkaline solution based on quartz sand, without sediment (a), with sediment (b)

Figure 3. Micrographs of an alkaline solution based on quartz sand, without sediment (a), with sediment (b)
Figure 4. Energy dispersive analysis of an alkaline solution based on volcanic tuff, without sediment (a), with sediment (b)

At a further stage, studies were conducted confirming the effectiveness of the developed solutions of sodium metasilicate. For this, beam samples were prepared from finely dispersed powders (Table 1), sealed with the alkaline solutions under study. After stripping, the samples were subjected to thermal action for two days in an oven (3 hours at \( t = 40^\circ\text{C} \)). Next, one part of the samples were placed in water to establish the hydraulicity of the binders. The other part was placed in air to interact with carbon dioxide and to form a gel of silicic acid, at least on the surface layers of the samples. The research results are shown in Table 3.

Figure 5. Micrographs of an alkaline solution based on volcanic tuff, without sediment (a), with sediment (b)

4. Conclusion
The test results confirm the effectiveness of the alkaline solution based on volcanic tuff; this is especially evident in compositions No. 2 and 3. Thermally activated silicified marl and volcanic rocks of aluminosilicate nature form a durable geopolymer stone by activation with an alkaline solution. Geopolymer stone is represented by a framework aluminosilicate trapped in an alkaline medium with the formation of a three-dimensional aluminosilicate hydrogel [19, 20]. Powders of carbonate nature do not have hydraulic properties and showed low strength results.
Table 3. Formulations and properties of linker-free cements of alkaline activation

| Composition number | Highly dispersed powders | Alkaline activator, % | MPa activity, 28 days hardening conditions |
|--------------------|--------------------------|-----------------------|---------------------------------------------|
|                    |                          | Na$_2$SiO$_3$         | quartz sand | volcanic tuff | natural | in water |
| 1                  | Quartz powder, S specific surface = 810 m$^2$/kg | 26.2 | – | 14.7 | 13.5 |
| 2                  | Mergel (700 °C), S specific surface = 1150 m$^2$/kg | 29.5 | 26.2 | 15.3 | 14.1 |
| 3                  | Volcanic tuff, S specific surface = 920 m$^2$/kg | 26.6 | – | 22.9 | 25.4 |
| 4                  | Limestone flour, S specific surface = 1060 m$^2$/kg | 29.3 | 26.6 | 23.4 | 25.8 |
| 5                  | Sandstone, S specific surface = 1020 m$^2$/kg | 26.7 | – | 17.6 | 19.3 |
| 6                  | Aspiration dust, S specific surface = 280 m$^2$/kg | 24.2 | 24.2 | 18.2 | 19.7 |

Of course, the strength results differ from those obtained when mixed with salable liquid sodium glass. However, given the energy efficiency of this technology, it can be considered that the proposed solutions will expand the scope of the use of clinker-free alkaline binders and produce concrete with desired properties.

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