Research of the features of the formation of the structure and properties of building composites based on clinker-free binders of alkaline activation with the use of unconditional natural and secondary raw materials

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Abstract. The anthropogenic load on the natural resource potential of the planet is growing rapidly. Therefore, special attention is paid to the development of less costly and low energy-consuming technologies for obtaining new building materials. Those materials do not require high-temperature and expensive technological processing, and this will allow the use of local secondary and substandard raw materials. The development of formulations for clinker-free binders of alkaline activation based on fine powders of aluminosilicate nature will make it possible to obtain new effective building composites. The work reveals issues related to the theoretical foundations of the structure formation and strength of cement stone based on an alkaline activator. The research results, in our opinion, have a practical importance for the construction industry, since the proposed formulations of clinker-free cements can replace expensive and energy-intensive Portland cement, allowing creating strong and durable concrete and reinforced concrete structures. The results presented in this article were obtained in the framework of research on the implementation of scientific project No. 05. 607.21.0320. "Development of technology for new building composites based on clinker-free binders of alkaline activation using substandard natural and secondary raw materials" supported by the Federal Target Program "Research and Development in Priority Areas of Development of the Scientific and Technological Complex of Russia for 2014-2020". The unique identifier for the agreement is RFMTF60719X0320.

1. Introduction
The use of substandard natural and secondary resources makes it possible to expand the range of technological solutions and raw material potential of clinker-free technology for the production of alkaline activation building composites. These activities are highly relevant in the present time in connection with the concept of sustainable development of the construction industry all over the world as a whole.

The synthesis of high-quality binding systems activated with an alkaline solution becomes a promising direction in case of the possibility of utilizing industrial waste. This will affect a decrease in the volume of large-tonnage natural raw materials used for the production of cements and a decrease in environmental pressure on the ecosphere due to the introduction of technologies that do not require...
high-temperature treatment and decarbonization, accompanied by huge emissions of carbon dioxide into the atmosphere. Therefore, energy and resource-saving measures in the production of an irreplaceable component of almost any composite are of great economic importance and provide the construction industry with less material-intensive raw materials, being an indicator of its development [1, 2].

There were developed special compositions using a fairly widespread technogenic modifier "microsilica (MS)" to obtain concretes with increased strength indicators of at least 60 MPa. This microsilica consists of ultrafine particles of amorphous glass with a SiO₂ content of 98% and a size of 0.1 - 0.2 microns, which is 50 - 100 times the size of Portland cement particles. A high specific surface area increases the solubility and reactivity of this powder, 150 - 300 mg for the absorption of CaO from the solution [3-11].

The advantages of microsilica are endless. MS reacts with calcium hydroxide to form an additional portion of low-basic calcium hydrosilicates [8, 9], due to their purity and dispersion of highly active microspheres. Covering the particles of the components of the composite mixture, they create plasticizing and densifying effects, filling the intergranular space with strong new formations, thereby increasing adhesion with the filler [7, 10].

It is established that microsilicon has the ability to influence the alkalinity of the liquid phase in the pore space of the cement gel by binding alkali metal cations, the pH level in the pores of concrete stone decreases from 14 to 12.5 with the addition of 15% MS, and at a dosage of 25%, the bonds of free lime are practically neutralized.

The addition of silica fume contributes to an increase in strength and an increase in the cycles of alternating freezing and thawing. This ensures the stability of the properties of concrete, and increases these indicators by 20–25% the values of heavy ones without additional concrete. An important property of microsilica should be considered the ability to bind alkaline oxides that freely migrate on the surface of composites and, as a result of carbonization, form efflorescence. So the MS additive is capable of preventing carbonization, alkaline corrosion and efflorescence.

If MS is compared with additives of volcanic tuff, dune sand, containing a high proportion of silica matter, then it should be noted that the nature of the properties is completely opposite. So, the previously studied additives consist of 100% crystalline structure, and silica fume is 98% amorphous phase, while if mineral powders are prepared by prolonged grinding in a grinding unit, then MS is initially a highly dispersed material with a specific surface area of more than 1600 m²/kg.

2. Materials and methods
Investigation of the properties of concrete composites using a highly active micro-silica additive as a component that serves as a modifier and plasticizer, regulating the properties of the binding bond "aspiration dust 60% - clinker dust 40%" of alkaline mixing will allow evaluating its effect and effectiveness. The following components were used to develop special compositions of concrete: aspiration and clinker dust from electrostatic precipitators of rotary kilns, microsilica from the Chelyabinsk metallurgical industrial complex. The chemical composition of silica fume, % of weight: SiO₂ = 94.4 - 96.2; (Na₂O + K₂O) = 1.7-2.1; CaO = 0.62 - 1.2; loss on ignition = 0.48 - 3.28. The specific surface of microsilica studied on a PSKh-12 device reached an average value of 1620 m²/kg. It was decided to use as fillers high-quality material, coarse sands and granite-diabase crushed stone of the 5-20 mm fraction of the Alagir deposit to obtain a sufficiently high strength. The characteristics of the fillers are given in tables 1 and 2.
Table 1. Characteristics of Alagir sand.

| Indicator name                          | Indicator value |
|-----------------------------------------|-----------------|
| Size module                             | 2.9             |
| Content of dusty and clay particles, %  | 0.83            |
| True grain density, kg/m³               | 2691            |
| Bulk density, kg/m³                     | 1472            |
| Sand class by grain size                | 1               |
| Sand voidness, %                        | 43.6            |

Table 2. Properties of crushed stone from granite-diabase rocks.

| Indicator name                                      | Indicator value   |
|-----------------------------------------------------|-------------------|
| Crushed stone strength (grade by crushing) Fr. 5-10 mm | 1200-1400         |
| Fr. 10-20 mm                                        | 1200-1400         |
| Bulk density, kg/m³                                 | 1485              |
| True density, kg/m³                                 | 2720              |
| Average density, kg/m³                              | 2620              |
| Content of crushed grains, %                        | 92.5              |
| The content of lamellar (flaky) and needle-shaped grains, % | 9.2               |
| Grain content of weak rocks, %                      | 2.2               |
| Content of dusty and clay particles, %              | 0.6               |
| Clay content in lumps, %                            | non               |
| Crushed stone voidness, %                           | 43.3              |
| Crushed stone frost resistance                      | F300              |

3. Results

Previous studies have established a short setting time of binders based on aspiration dust with Ssp = 210 m²/kg when mixed with an aqueous solution of sodium water glass with a density of 1420 kg/m³ and a silicate modulus of 2.4. Various recipe and technological measures were taken to slow down this indicator, therefore, first of all, it is necessary to study the effect of MS on the properties of cement paste (Table 3).
Table 3. Properties of binders on industrial waste.

| Content MS, % | Normal density, % | Aspiration + clinker dust + Na$_2$SiO$_3$ | Setting time, hour - minute |
|---------------|-------------------|------------------------------------------|----------------------------|
|               |                   | Start                                    | End                        |
| 0             | 60.3              | 00 – 32                                  | 00 – 51                    |
| 5             | 56.7              | 00 – 28                                  | 00 – 47                    |
| 8             | 55.4              | 00 – 28                                  | 00 – 45                    |
| 10            | 54.1              | 00 – 25                                  | 00 – 42                    |
| 15            | 53.2              | 00 – 22                                  | 00 – 38                    |

Silica fume was effective in relation to the normal density of the alkaline dough as it shown by the results of the study. The need for liquid sodium glass decreased by 10.2 - 11.7% with the introduction of the additive in the range of 5 - 15%. The flow rate of the alkaline grout varied in the range 80 - 100 l/m$^3$. Silica fume material is highly dispersed and its particles have a rounded shape of microspheres (Figure 1), the surface relief is smooth.

![Micrograph of microsilica particles](image)

Figure 1. Micrograph of microsilica particles.

Smooth particles of microspheres reduce friction forces in the solid phase and do not create engagement on the surface. Due to their ultra-dispersion, microspheres are deposited on the grains of the reaction component and play a role of a kind of "lubricant" in the process of physical and mechanical interaction of solid particles with each other, as a result, the cement alkaline paste is plasticized, which reduces the normal density. But the introduction of a highly dispersed additive provides the cement paste greater cohesion, due to which the setting time is reduced by 7-14 minutes at the beginning and 9-14 minutes at the end of setting. All the additives are obtained under the study: aspiration dust, clinker dust, microsilica are products of high-temperature processing, collected in dust-cleaning systems and have chemical activity, therefore, the accelerated formation of the primary structure of the cement stone occurs.

Further, the effect of the MS additive content on the strength of 28-day-old cement stone was investigated, depending on the aging conditions. Part of the samples after preliminary holding for 10 hours were subjected to heat and humidity treatment (HNT) according to the regime $3+4+2$ at an isothermal holding temperature of 80 °C, the part solidified under normal humidity conditions (NHC), figure 2 shows the test results.
Figure 2. Dependence of the influence of the content of microsilica on the strength of the cement stone after HMT and NHC.

The introduction of silica fume additives had different effects on the properties of a cement stone based on a binding binder of two components "aspiration - clinker dust"; heat and moisture treatment is favorable for strength gain. With an MS additive content of 5%, the strength increased by 25.4% and amounted to 65.7 MPa. Hardening in normal humidity conditions has a slightly different effect on the strength of the cement stone, the introduction of MS in a dosage of 7% contributed to the achievement of a maximum strength of 62.2 MPa. This made it possible to increase the strength by 33.1% in comparison with the control sample. The addition of microsilica has a strengthening effect, at a dosage of 5% in the conditions of HMT, and 7% when hardened in the NHC; after preliminary exposure, the temperature is considered a catalyst for curing.

The obtained results showed that the MS additive is an active mineral additive with a plasticizing effect; high specific surface area of ferrosilicon particles fills the intergranular space of the cement stone, compacting it; binds calcium and sodium oxides to form difficultly soluble compounds such as calcium and sodium hydrosilicates; increases the solubility of aspiration and clinker dusts.

The effectiveness of microsilica appears only within certain limits of its presence in the composition of the system and depends on the conditions of hardening of the binder samples. When hardened after HMT, this range is 4–6%. With the NHC holding of 6–8%. In both cases, a uniform decrease in strength is observed with an increase in the dosage of silica fume above the indicated ones. This is justified by the chemical transformations of active silica under conditions of high content of this substance, leading to changes in the pH of the medium. The high alkalinity of the system medium causes rapid dispersion of powder components, and microsilica in particular, and the processes occurring in the composition can be described by the equation: \( (\text{SiO}_2)_{\text{n}} + 2n\text{H}_2\text{O} \leftrightarrow n\text{Si(OH)}_4 \).

Depending on the pH of the medium, the dispersion of silica changes. At pH < 8, the solubility of microsilica is \( \approx 2 \cdot 10^{-3} \) mol/l, and at pH = 11 it significantly increases to 50 \( \cdot 10^{-3} \) mol/l. This occurs due to the precipitation of unstable orthosilicic acid \( \text{Si(OH)}_4 \) and ions \( \text{Si(OH)}_4 \text{H}_2^2- \). As a result of transformations with changes in the alkalinity of the medium, chain reactions of polycondensation occur, leading to crosslinking of chains and the formation of polysilicic acid [7, 9, 11].
Silicic acid gel has several ionized forms that change depending on the pH of the medium, so if pH < 8, $\text{H}_4\text{SiO}_4$ is formed, at $\text{pH} = 11.5 - \text{SiO}_4^-$ [12]. The polymerization reaction of the monomeric anion $\text{H}_3\text{SiO}_4^-$ proceeds in a very short time:

$$\begin{align*}
\text{Si(OH)}_6^- & \quad \text{OH}^- \\
\text{Si(OH)}_6^- & \quad \text{OH}^- \\
\text{Si(OH)}_6^- & \quad \text{OH}^- \\
\text{Si(OH)}_6^- & \quad \text{OH}^- \quad \text{OH}^- + \text{H}_2\text{O}
\end{align*}$$

Microsilica is an active additive consisting of 94 - 96% of the amorphous component. With increasing dosage, the pore space of the hardening system is saturated with a significant amount of silicic acid, which leads to a decrease in the pH of the medium due to acidic oxide SiO2, as a result, polycondensation of Si(OH)6 ions begins and the pores and capillaries of the cement stone are occupied by weakly bound colloidal gel from watered SiO2 and this is what impairs the properties of the binder at high doses of MS. Visually, even the color of samples with a high microsilica content changes, becoming grayish.

In case, when the dosage of MS additive is lower than the recommended one, the intergranular space contains a small amount of silicic acid, and this does not particularly affect the pH of the medium. As a result of polymerization reactions are not observed, the binder system hardens, forming a strong structure.

The reactivity of aspiration dust is determined as it was established not only by the presence of a glass phase and the pH of an alkaline medium, but by the presence of active mineral additives that interact with the products of dissolution of aspiration minerals with the formation of a crystalline aggregate of cement stone. The microsilica addition belongs to this type of substance, it has a strong effect on the destruction of alumino-silicon-oxygen chains and binds them as a result of $2\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$ cation exchange, providing a stimulating effect. Also, the amorphous modification of silica can be dispersed in a NaOH solution to form $\text{Na}_2\text{O} \cdot n\text{SiO}_2$ sodium silicates and complex sparingly soluble compounds such as low-basic calcium silicates:

$$\text{Na}_2\text{O} \cdot n\text{SiO}_2 + p\text{Ca(OH)}_2 + m\text{H}_2\text{O} \rightarrow 2\text{NaOH} + p\text{CaO} \cdot n\text{SiO}_2 \cdot (m-1) \cdot \text{H}_2\text{O}$$

$$\text{SiO}_3\text{H}_n + 2n\text{H}_2\text{O} \rightarrow n\text{Si(OH)}_4$$

$$2\text{CaO} + 4\text{H}_2\text{O} + \text{Si(OH)}_4 \rightarrow 2\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} + \text{H}_2\text{O}$$

Consequently, the increase in strength in the first periods of hardening is due precisely to the physical interaction of highly dispersed particles and their surface energy. Figure 3 shows the results of a study of the effect of the addition of microsilica on the properties of the modified cement stone: water saturation and density. The introduction of the MS additive at a dosage of 5% reduces the need for an alkaline solution, thereby increasing the density of the cement stone after HMT from 1.8 to 2.0 g/cm³, and the water saturation decreases from 6.0 to 3.5%.
To study the properties of concrete composites on the proposed binders, consisting of two components "aspiration-clinker powders" and the introduction of silica fume additives into the molding mixture, samples of a cube with a size of 100 mm and a prism with a size of 100x100x400 mm were made. Some of these samples, after preliminary exposure for 10 hours, were subjected to HMT, after which they hardened for 27 days in an NHC. The other part hardened for 28 days in NHC. A mixed alkaline solution of sodium water glass with a silicate modulus of 2.8 and a density of 1420 kg/m$^3$ and a 20% sodium hydroxide solution with a density of 1250 kg/m$^3$ were used as a grout.

For a comparative analysis and comparison of the results, the dosage of the additive was decided to use the same 5%, based on the mass of the binder. The compositions and physical and mechanical properties of concretes are presented in table 4.

| Composition number | Consumption of concrete components, kg/m$^3$ | AS consumption, l/m$^3$ | Strength, MPa | Elastic modulus, MPa | Concrete class |
|--------------------|---------------------------------------------|-------------------------|----------------|----------------------|----------------|
|                    | AD  | CD  | S   | CS | MS | Na$_2$SiO$_3$ | NaOH | cubic | prismatic | -10$^3$ |                     |
| 1                  | 200 | 120 | 660 | 1100  | 160 | 180 | 40 | 30   | 40.1 | 35.0 | 30 |
| 2                  | 250 | 150 | 600 | 1100  | 180 | 50  | 40  | 37.5 | 42.5 | 40.0 | 40   |
| 3                  | 200 | 150 | 600 | 1100  | 1100 | 20 | 40 | 40      | 40.1 | 31.5 | 30 |
| 4                  | 250 | 150 | 600 | 1100  | 1100 | 15 | 50 | 40.1 | 40.1 | 32.4 | 40   |

Note: AD - aspiration dust; CD - clinker dust; S - sand; CS - crushed stone; AS - alkaline solution; MS - microsilica; NHC - normal humidity conditions; HMT - heat and moisture treatment

The MS additive, being a plasticizing component in the binder, in the molding mixture for the preparation of concrete, has not showed the ability to reduce the ratio of alkaline solution / reaction powder.
This was previously noted the ability of microsilica to affect the normal density of the cement paste, its cohesion and deterioration of thixotropy, therefore, to obtain an equally mobile concrete mixture, almost the same consumption of an alkaline solution is required. The presence of amorphous substances of microsilica increases the concentration of products of destructive decomposition of mineral compounds of the reaction powder. It also increases the volume of low-basic hydrosilicates of calcium and sodium, reinforces the dispersion medium, increasing the strength, promotes the rapid transition of hydrosols into the solid phase as a result of crystallization of the coagulation structure.

The results obtained confirmed the effect of the addition of microsilica, the cubic, prismatic strength and elastic modulus increased in comparison with no additive compositions. Cubic strength with the introduction of 5% MS (composition 4) increased by 44.1% under normal humidity conditions of hardening; by 36.5% with samples after HMT. The prismatic strength also increased, MS has a beneficial effect on this indicator, with NHC the increase was 43%, after HMT is 31.2%.

The elastic modulus has increased by 42 - 44%. Concrete grade increased from B30 to B40. The addition of highly active microsilica contributes to the strengthening of the stiffness of the cement stone, due to the formation of an additional amount of felt hydrosilicates and hydroaluminosilicates of calcium and sodium, electron probe analyzes confirm this (Figure 4, Table 5).

![Typical aggregates of calcium silicate crystals.](image)

**Figure 4.** Typical aggregates of calcium silicate crystals.

**Table 5.** The results of the analysis of the aggregate of crystals of calcium silicates (the areas of analysis are shown in Figure 4).

| Range | Na₂O | MgO | Al₂O₃ | SiO₂ | K₂O | CaO | FeO | Result |
|-------|------|-----|-------|------|-----|-----|-----|--------|
| 1     | -    | -   | 2.68  | -    | 64.97 | 8.94 | 85.90 |        |
| 2     | -    | -   | 1.80  | -    | 55.05 | 16.66 | 85.00 |        |
| 3     | 0.58 | 1.15| 3.73  | 25.47| 11.56 | 9.45 | 94.50 | 89.66  |
| 4     | 0.54 | 0.51| 2.30  | 3.09 | 3.194 | 25.47| 11.56 | 85.90  |
| 5     | -    | -   | 1.32  | 2.50 | 31.94 | 22.07| 9.45 | 89.66  |
Samples of the prism with the introduction of 5% MS additive, hardening within 6 months with NHC and after HMT, during visual inspection, the presence of efflorescence was not detected. This is the merit of active silica, which binds free alkalis and interacts with the dispersion products of aspiration and clinker dusts. Figure 5 shows experimental concrete samples.

4. Conclusion

Thereby, the high efficiency of the addition of active silica, which is both a plasticizer and participates in the processes of structure formation, has been proved. Special compositions of concrete with strength above 60 MPa, class B40, regardless of hardening conditions, modulus of elasticity more than $30 \times 10^3$ MPa were obtained. Therefore, it is the addition of active silica at a dosage of 5−7% that creates favorable conditions for obtaining a strong and durable artificial stone.

![Figure 5. Samples of a prism with 5% MS: a) NHC hardening; b) after HMT.](image)

There is a uniform distribution of aggregate grains in the matrix of the mortar part, which is characteristic of the porphyry structure; the grains of crushed granite give architectural attractiveness to the products when carrying out appropriate mechanical processing of this type of concrete. The obtained building composites at CBAA, which have good physical and mechanical properties and resistance to aggressive influences when carrying out appropriate technological measures, will find their recognition in the production of small architectural elements, since the obtained package of characteristics allows this.

5. References

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