

Fine-Grained Concretes with Clinker-Free Binders on an Alkali Gauging

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Abstract – To date carbonate technology for producing Portland cement is the only, and the resulting product is a leader in the production of binders and, according to Russian and foreign scientists, this situation does not change even for many decades. But most researchers hope that a more effective binder with considerably less energy and resource consumption for its production will be in the nearby future. As an alternative to Portland cement, alkali binder based on highly dispersed powders of various natures can be considered in the future. This paper presents the results of research and formulation of alkaline activation binders and fine-grained concretes based on them. The mechanism of formation of the structure and strength of the geopolymer stone is given, which is a consequence of the occurrence of complex physicochemical processes.

Keywords – alkali activated binders; aluminosilicate framework; hydrogel; portland cement clinker; silicified marl; highly active materials; metakaolin; mechanoactivation.

I. INTRODUCTION

Portland cement production at the global level has reached 3 billion tons, and it is growing rapidly from year to year at the expense of developing countries such as China and India. Of course, on the one hand, this is a positive trend, but, on the other hand, the volumes released in the production of cement and carbon dioxide increase. It was established that during the burning of 1 ton of Portland cement clinker, 0.37 tons of carbon

dioxide are formed as a result of the dissociation of calcium carbonate; at the same time, an additional portion of about 0.35 tons of CO₂ is produced during fuel combustion and other technological conversion. The global cement industry occupies one of the leading places after the power industry and transport for the formation of greenhouse gases (5-8%). A huge amount of carbon dioxide is consumed, which for billions of years was conserved in rocks and minerals of various geneses, which ultimately affects the ecological situation of the troposphere [1, 2].

Therefore, the main problem of researchers is the reduction of carbon dioxide emitted, which is formed during the production of Portland cement. As an alternative to Portland cement, alkaline binder based on highly dispersed powders of various natures can be considered in the future.

According to Glukhovskiy V.D. [3–5], alkali activated binders can be represented by a system of the following oxides: alkali, alkali-earth and amphoteric (Figure 1).

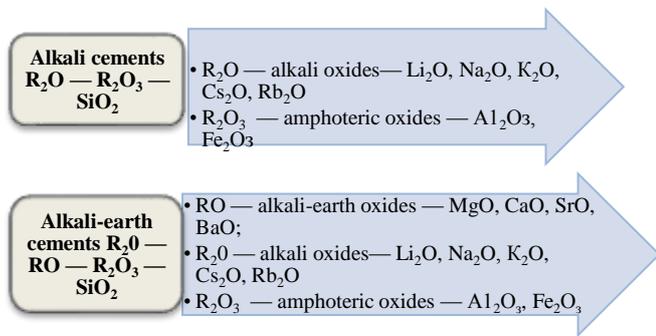


Fig. 1. Alkali binders

The process of hardening and structure formation of binders of alkali activation is in many respects similar to the reactions of the formation of the structure of lime-silica binders. Alkalies react with silicon dioxide according to the following scheme: during crystallization, sodium hydroxide loses moisture and forms crystalline hydrates, enveloping the aggregate grains, then reacts with carbon dioxide by the reaction: $2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$, parallel links the silicon dioxide according to the reaction: $2\text{NaOH} + n\text{SiO}_2 = \text{Na}_2\text{O} \cdot n\text{SiO}_2 \cdot \text{H}_2\text{O}$, thereby forming a bunch of alkali sodium or potassium hydro silicates.

II. METHODS AND MATERIALS

This paper presents the results of research on the development of formulations and the study of the properties of alkali activated binders using natural raw materials with the subsequent design of the compositions of fine-grained concretes.

To conduct research, we used prepared mineral powders from rocks of sedimentary and magmatic origin: quartz sand, limestone powder, volcanic tuff and silicified marl.

The energy dispersive microanalysis of the powders studied using a Quanta 3D 200 i scanning electron microscope showed a significant difference in the chemical composition of natural additives (Table 1 and Figure 2).

TABLE I. CHEMICAL COMPOSITION OF HIGH-DISPERSE POWDERS, %

Oxide composition	Silicified marl	Volcanic tuff	Limestone powder	Quartz sand
MgO	1.64	0.20	0.72	6.32
Al ₂ O ₃	6.42	13.57	1.55	14.99
SiO ₂	28.6	73.67	5.05	73.83
K ₂ O	1.33	6.00	0.6	1.83
CaO	16.9	1.79	90.1	0.6
Fe ₂ O ₃	1.08	1.52	1.4	0.97
TiO ₂	0.47	2.85	-	1.32
SO ₃	0.29	-	0.49	0.14
P.P.P.	43.2	0.40	-	-

Analysis of the results showed that volcanic tuff and quartz sand have higher silica content, silicified marl is characterized by a more uniform silica and calcium oxide content, and calcium oxide is predominant in limestone powder. The obtained chemical analysis made it possible to predict the properties of the proposed clinker-free binders using the powders under study [1, 4, 6, 7].

To prepare highly dispersed powders from the studied rocks, they were pre-crushed in a jaw crusher, and then subjected to fine grinding for 1 hour in a VM-20 vibratory ball mill. The crushed silicified marl was subjected to heat treatment in a muffle furnace at a temperature of 700 °C, and after heat treatment it was again crushed for 3 minutes to activate the surface. Studies have shown that the technological factor significantly affects the activation process of mineral additives [8-12], grinding in a vibratory ball mill gives a fairly high result on the specific surface at almost all sampling intervals.

The best indicators of grindability from the studied additives were limestone powder and silicified marl. Moreover, their specific surface was at the level of 990 - 1150 m²/kg.

III. RESULTS

At the next stage, the number of oxidizing acid active crystallization centers on the surface of the mineral powder was investigated by the method [7, 13-16] of determining the exchange capacity with respect to calcium ions. Figure 3 shows the results of tests to determine the number of active crystallization centers, which showed that the surface concentration of ion-exchange centers of mineral powders varies unevenly and depends on the degree of grinding.

It should be noted that mineral powders based on volcanic tuff and silicified marl, calcined at 700 °C, are the most active. This can be explained by the presence on the surface of these mineral highly dispersed powders of a large number of exchange sites, a significant part of which are oxidizing acids [1,7,17-22].

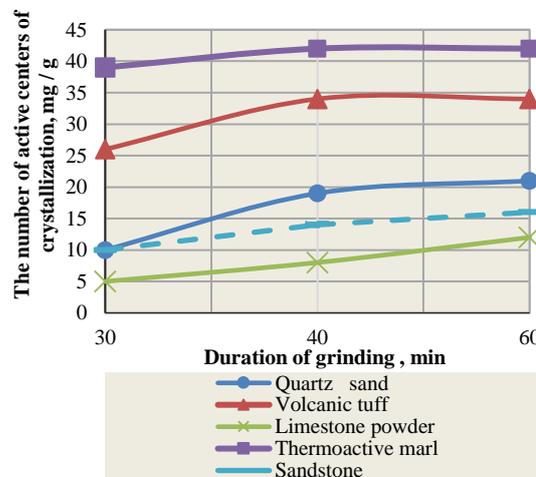


Fig. 2. The dependence of the number of active crystallization centers on the duration of activation

After confirming the reactivity of the proposed powders, samples-beams were prepared with a size of 20x20x100 mm from the mixture: highly dispersed component, Volsky quartz sand (added in a 1: 3 ratio), sodium liquid glass with a silicate module of 2.8 and density of 1.24 g /sm³, sodium hydroxide. The prepared samples were hardened in normal conditions at a temperature of 20 ± 2 ° C, but after 2 days some of the twin samples were placed in a drying cabinet at a temperature of 40 ° C for several days. The formulations and properties of clinkerless binders are shown in Table 2 and Figure 4.

The test results of the investigated compositions based on alkali activated binders showed rather high strength results for the samples using powders of thermo-activated marl and volcanic tuff and it was found that with increasing temperature the strength parameters increase.

It should also be noted that in addition to temperature, the dosage of sodium silicofluoride and the presence of sodium hydroxide affect the rate of activity. Alkali activated binder with the use of a fine powder of thermally activated marl showed the best results of 46.5 MPa for hardening at a temperature of 40 ° C and 42.1 MPa for hardening under natural conditions

To study the properties of fine-grained concretes, samples of cubes measuring 10 cm in size were prepared using a mixture: highly dispersed component (table 2), fractionated sand obtained by mixing in the ratio of 55:45% sifting of the Argunsky field and fine sand of the Chervlensky field. The gauging was carried out with liquid glass, sodium hydroxide and accelerator of the precipitation of silica gel with sodium silico fluoride in predetermined proportions.

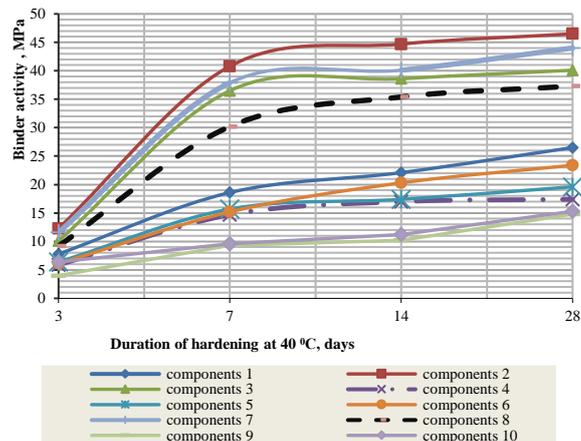


Fig. 3. The dependence of the activity of clinkerless binders on the duration and conditions of hardening

The prepared samples were hardened in normal conditions at temperature of 20 ± 2 ° C, but after 2 days the samples were placed in an oven at temperature of 40-50 ° C for several days. The test results of the investigated fine-grained concretes based on alkali activated binders are shown in Table 3. High strength results of fine-grained concrete using clinker-free binders on an alkali gauging on the base of thermally activated marl is due to the formation of durable geopolymer stone (Figure 5), represented by a frame aluminosilicate with alkali gauging with the formation of a three-dimensional aluminosilicate hydrogel [1,10].

TABLE II. FORMULATION AND PROPERTIES OF BINDENING MATERIALS OF ALKALI ACTIVATION

№ composition	Components of alkali activated binders, %					
	Quartz sand	Thermoactive marl	Volcanic tuff	Limestone powder	Na ₂ SiO ₃	NaOH
1	80	-	-	-	12.0	8.0
2	-	80	-	-	12.0	8.0
3	-	-	80	-	14.0	6.0
4	-	-	-	80	10.0	10.0
5	80	-	-	-	20.0	-
6	-	80	-	-	20.0	-
7	-	-	80	-	20.0	-
8	-	-	-	80	20.0	-

^a. Note : QS – Quartz sand ; TM – Thermoactive marl at 700°C; VT Volcanic tuff; LP – Limestone powder ; Na₂SiO₃ – sodium liquid glass; NaOH – sodium hydroxide.

TABLE III. PROPERTIES OF FINE-GRAINED CONCRETES BASED ON ALKALI ACTIVATED BINDERS

№ composition	Material consumption kg per 1 m ³				Density concrete, kg/m ³	Water absorption %	Compressive strength, MPa days	
	Highly-disperse powders	Fractional sand	Na ₂ SiO ₃	NaOH			7	28
1	480	1700	72.0	48.0	2240	5.7	11.8	24.7
2	480	1700	72.0	48.0	2250	4.5	31.4	40.5
3	480	1700	84.0	36.0	2246	4.8	25.3	34.2
4	480	1700	60.0	60.0	2235	6.1	5.9	14.1
5	490	1620	120	-	2110	5.5	12.1	25.8
6	490	1620	122	-	2232	4.3	33.9	45.1
7	490	1620	124	-	2234	4.5	26.7	38.4
8	490	1620	121	-	2230	5.8	7.8	15.9

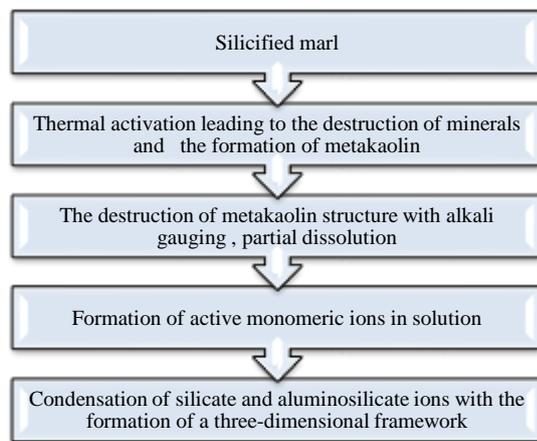


Fig. 4. Geopolymer stone formation process.

IV. CONCLUSION

Thus the compositions were obtained and the properties of the clinker-free binders on an alkali gauging were studied using highly dispersed mineral components.

It has been theoretically substantiated and practically proved that Brønsted acidic sites on the surface of highly active powders accelerate the process of synthesizing silica gel, promote the polymerization of silicon-oxygen anions, enhance ion exchange reactions, and stabilize intergranular contact formation. The obtained effective compositions of fine-grained concretes based on the proposed alkali activated clinker-free cements significantly expand the scope of the clinker-free binders on the liquid glass binder and can enable partial replacement of expensive and energy-intensive portland cement in the construction industry.

References

[1] S-A.Y. Murtazaev, T.S-A. Murtazaeva, "Prospects for the use of thermoactivated aluminosilicate raw materials", *Privolzhsky scientific journal*, vol. 46, no. 2, pp. 65–70, 2018.

[2] J. Davidovitz, *Geopolymer. Chemistry and applications*. Saint-Quentin: Institute Geopolymer, 2008, 592 p.

[3] P. Duxson, A. Fernandez, "Provis Geopolymer technology: The current state of the art", *J. Mater. Sci.*, vol. 42, pp. 2917–2933, 2007.

[4] E.A. Nikiforov, V.I. Loganina, E.E. Simonov, "Effect of alkali activation on the structure and properties of the diatomite", *Bulletin of BG TU*, no. 2, pp. 30–32, 2011.

[5] V.T. Erofeev, A.D. Bogatov, S.N. Bogatova et al., "Bioresistant building composites on the basis of glass wastes," *Biosciences Biotechnology Research Asia*, vol. 12, no. 1, pp. 661–669, 2015.

[6] S-A.Yu. Murtazaev, M.Sh. Salamanova, R.G. Bisultanov, "High-quality modified concretes using a binder based on a reactive active mineral component", *Construction Materials*, no. 8, pp. 74–80, 2016.

[7] V.V. Strokova, I.V. Zhernovsky, A.V. Maksakov, "Rapid method for determining the activity of silica raw materials for the production of granular nanostructuring aggregate", *Construction Materials*, no. 1, pp. 38–39, 2013.

[8] R. Javaherdashti, *Microbiologically Influenced Corrosion an Engineering*. UK: Insight Springer-Verlag, 2008, 164 p.

[9] N.I. Kozhukhova, I.V. Zhernovsky, M.S. Ocadchaya, "Revisiting a selection of natural and technogenic raw materials for geopolymer binders", *International Journal of Applied Engineering Research*, vol. 9, no. 22, pp. 16945–16955, 2014.

[10] N.I. Kozhukhova, I.V. Zhernovsky, V.V. Strokova, "Evaluational of geopolymer binders biopositivity based on low-calcium fly ash", *International Journal of Applied Engineering Research*, Vol. 10, no 15, pp. 35618–35620, 2015.

[11] V.S. Lesovik, N.I. Alfimova, P.V. Trunov, "Reduction of energy consumption in manufacturing the fine ground cement", *Research Journal of Applied Sciences*, vol. 9, iss. 11, pp. 745–748, 2014.

[12] S-A.Yu. Murtazaev, Sh.Sh. Zaurbekov, A.Kh. Alaskhanov, M.S. Saydumov, T.S-A. Murtazaeva, M.R. Khadzhiyev, "Impact of Technogenic Raw Materials on the Properties of High-Quality Concrete Composites", *International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2018)*. *Advances in Engineering-Ing Research*, vol. 177, pp. 275–279, 2018.

[13] V.S. Lesovik, L.K. Zagorodnyuk, A.E. Mestnikov, A.I. Kudinova, D.A. Sumskoj "Designing of mortar compositions on the basis of dry mixes", *International Journal of Applied Engineering Research*, vol. 10, iss. 5, pp. 12383–12390, 2015.

[14] S-A.Yu. Murtazaev, M.Sh. MintsaeV, S.A. Aliev, M.S. Saydumov, "Strength and Strain Properties of Concrete, Comprising Filler, Produced by Screening of Waste Crushed Concrete", *Published by Canadian Center of Science and Education*. Received, vol. 9, no. 4, pp. 32–44, 2015.

[15] D.K-S. Bataev, A.A. Uzaeva, S.A. Uzaeva, M.A. Uzaev, T.A. Tuzurkaeva "The Study of Shrinking Deformations of Repair Compositions on Barkhan Sands", *International Symposium on Engineering and Earth Sciences (ISEES 2018) Advances in Engineering Research*, vol. 177, pp. 254–257, 2018.

[16] S.A. Udodov, "Re-introduction of plasticizer as a tool for controlling the mobility of a concrete mix", *Scientific works of the Kuban State Technological University*, no. 9, pp. 175–185, 2015.

[17] E.M. Shcherban, S.A. Stelmakh, A.K. Khaliushev, "Development of pozzolan cement composition on the volcanic tuff", *Building. Architecture. Economy*, pp. 110–113, 2018 [International Forum "Victorious May 1945", 258 p., 2018].

[18] S.A. Stelmakh, E.M. Shcherban, K.V. Serdiukov, "The effect of some characteristics of coarse aggregate used on the properties of heavy concrete, intended for the manufacture of centrifuged products and structures", *Bulletin of Belgorod State Technological University*. V.G. Shukhov, no. 10, pp. 15–20, 2017.

[19] Yu.I. Korianova, N.E. Rezantsev, A.S. Shumilova, "Materials and structures used in the construction of high-rise buildings – from tradition to innovation", *Alley of science*, vol. 6, no. 4 (20), pp. 95–99, 2018.

[20] A.A. Soldatov, A.V. Galych, I.V. "Experience of using sodium silicate as a binder in the production of building", *Actual problems of construction, transport, engineering and technosphere safety*, pp. 186–188, 2016 [The 6th Annual Scientific and Practical Conference of the North Caucasus Federal University, 254 p., 2016].

[21] M.I. Afonina, E.V. Kozyreva, "Features of the construction of sports facilities in the territories of former industrial zones", *Days of student science*, pp. 390–392, 2017 [Scientific and Technical Conference on the results of research works of students of the Institute of Construction and Architecture, 488 p., 2017].