

STRUCTURAL COMPOSITE MATERIALS BASED ON ANTHROPOGENIC RAW STUFF AND CLINKERLESS BINDERS OF ALKALINE TEMPERING

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ABSTRACT

The importance of the performed studies is stipulated by increasing the annual production of Portland cement; the by-produced carbon dioxide and harmful emissions of sulfurous compounds, dioxins, and other substances exert a negative impact on the environment of both individual countries and the world. Thus, the leading construction companies of Russia and the world are interested in conversion to clinkerless binders and structural composite materials on their basis. To solve the highlighted problems, the authors have attempted to develop binders and concretes of alkaline tempering using finely dispersed aluminosilicate additives aiming at the further substitution of rather an expensive Portland cement at least in such fields where high engineering properties are not necessary. This work studies mineral powdered additives of both natural and anthropogenic origin, such as quartz sand, limestone, volcanic tuff, siliceous marl, wastes of cement industry in the form of precipitator clinker and aspiration dust. After determination of the surface activity of the powders, it was established that the highest activity was characteristic for mineral additives based on volcanic tuff and siliceous marl annealed at 700°C. Optimum recipes and properties of clinkerless binders of alkaline activation based on highly dispersed mineral components have been determined, efficient compositions of fine concrete based on the proposed clinkerless cement of alkaline activation have been developed. The obtained experimental results are of practical value for the construction industry since the developed recipes of clinkerless cement make it possible to substitute expensive and energy-intensive Portland cement in the production of concrete and reinforced concrete structures.

Keywords: Portland Cement, Clinkerless Binders, Mineral Powders, Alkaline Tempering Agent, Liquid Glass, High Dispersity, Precipitator Clinker Dust.

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INTRODUCTION

The concept of steady development of structural materials industry adopted by the world community is based on resource and energy saving of natural raw stuff and improvement of environmental safety of the Earth. First, such a strategy would address the most energy and material-intensive productions, including the cement industry. This will solve the most important environmental issues since increasing production of Portland cement is accompanied by high consumption of mineral and energy resources, significant emissions of carbon dioxide and dust into the atmosphere.¹⁻³

A promising approach to the solution to the mentioned problem is the use of clinkerless cement of alkaline tempering, which can be produced both based on available wastes of fuel industry in a given region, and using high dispersive additives of aluminosilicate origin, with chemical composition characterized by an increased content of aluminum and silicon.^{1,2,4-6}

Significant experience of production and implementation supported by commercial approbation of structural clinkerless composite materials of alkaline activation characterized by rather good engineering and operational properties was gained both in Russia and in well-developed countries, such as Ukraine,

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Germany, Poland, Czech Republic, Japan, France, China, US, and others. It has been demonstrated by numerous studies¹⁻⁶, that the product of clinkerless technology, slag–lime composites, are widely and successfully applied in hydraulic engineering, under conditions of high temperatures, for production of high temperature concretes, upon urgent repair operations due to short maturing time, upon production of massive items and structures, for operation under conditions of negative temperatures and aggressive media. The importance of further development of this clinkerless approach to alkali cement has been proved by modern global trends of a growing number of studies in this field.

The theoretical substantiation of production and application of binders of alkaline activation is based on the formation of numerous mineral formations, which are similar to the processes observed upon hydration solidification of structural materials. For instance, natural zeolites, such as phillipsite, analcime, mordenite, chabasite, heulandite, epidesmine, natrolite, harmotome, and others were generated in earth crust upon weathering, during reactions under hydrothermal conditions at low temperatures.

The material composition of minerals varied as a function of the chemical composition of hydrothermal solutions. This is especially true for aluminosilicates when plagioclase is decomposed under the action of alkali solutions: $\text{Me} \cdot \text{Al}_2\text{O}_3 \cdot n\text{SiO}_2$ – sericitization – the substitution of plagioclase with muscovite^{1,2,4,5}, that is, conversion of anhydrous modification of aluminosilicates into aqueous alkali modification of aluminosilicates. Sodium-potassium feldspars $\text{Me} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ are decomposed into alkali compounds of sericite–muscovite type with the ratio of $\text{SiO}_2 : \text{Al}_2\text{O}_3 : \text{K}_2\text{O} : \text{H}_2\text{O}$.

The formation of silicate minerals can be compared with the hydration of Portland cement clinker minerals and it is quite possible^{2,5} that alkali binders of the systems would be solidified exactly according to this mechanism.

According to to⁶⁻⁸, the highest reactivity and resistance during weathering are characteristic for alkali and alkaline earth elements in such sequence: calcium, sodium, magnesium, and potassium. Therefore, it has been established that the considered processes are characterized by the following consecutive stages with a variety of medium acidity:

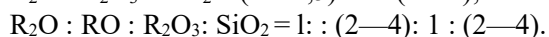
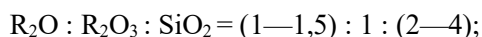
- i. Hydration of alkali and alkaline earth compounds;
- ii. Partial substitution of alkali and alkaline earth minerals with hydrogen ions or hydroxyl group;
- iii. Conversion of aluminum from tetrahedral site to hexahedral site leading to the formation of nearly insoluble hydraulic aluminosilicates of $\text{RO} \cdot (1-3) \cdot \text{Al}_2\text{O}_3 \cdot (2-6) \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ of lower basicity, alkaline earth poorly soluble hydrosilicates of $\text{R}_2\text{O} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ type, as well as soluble hydrates of $\text{R}(\text{OH})_2$; ROH ; $\text{R}_2\text{O} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$ or $\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ type in submicron or amorphous state⁶.

Metamorphism, condensation, and dispersion of residual and metamorphic silicate minerals, running continuously in the earth crust, promote the mutual transformation of aqueous and anhydrous mineral systems with the participation of alkali and alkaline earth oxides leading to the synthesis of stone-like formations, crystallization of feldspars, zeolites, micas, orthoclase, plagioclase, feldspathoid, etc.^{9,10} Creation of alkaline medium is the required condition for the formation of alkali aluminosilicate substance upon the synthesis of rocks.

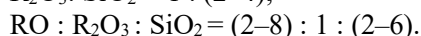
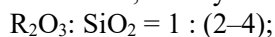
Alkaline medium also presents upon hydration of conventional mineral binders: lime, Portland cement, Portland Pozzolana cement, Roman cement, hydraulic lime, the resultant reaction products provide a stronger alkaline reaction in comparison with alkaline earth metals. These statements evidence that alkaline medium combines all mineral binders and is the main hydraulic property of substances.^{10,11,12}

According to Glukhovskii^{1,4}, alkaline binders can be presented by the system of the following oxides: alkali, alkaline earth, and amphoteric (Fig.-1).

Pure binders obtained by milling of product annealed not to sintering have the following oxide ratio:



Binders comprised of a mixture of alkali metals, interacting with high dispersive and mechanically activated substances, both synthesized and natural, are known as mixed, herewith, the following ratio should be valid:



Krivenko⁵ classified hydraulic binders depending on the chemical and material composition of binder, hydration products as summarized in Table 1. Hydraulic binders are mainly tempered with water except for alkali cement, which is tempered with alkalis, soda, or liquid glass binder.

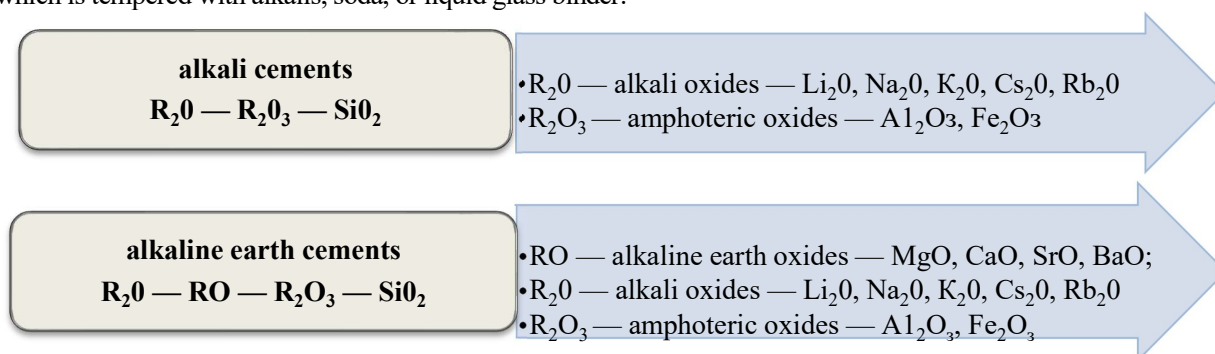


Fig.-1: Alkaline Binders

The process of solidification and structure formation of alkali cement is very similar to the structure formation of lime silica binders. Alkalis react with silicon dioxide as follows: during crystallization, sodium hydroxide is dehydrated and forms crystal hydrates while coating filler grains, then interacts with carbon dioxide: $2NaOH + CO_2 = Na_2CO_3 + H_2O$, simultaneously bonding silicon dioxide: $2NaOH + nSiO_2 = Na_2O \cdot nSiO_2 \cdot H_2O$, with the formation of a bond of alkali hydraulic silicates of sodium or potassium.

The properties of the first alkali binders were studied in^{1,2,4,5} using the mixtures of caustic alkalis with various active mineral additives: opus signinum, anhydrous kaolinite, fuels ashes, granulated slags. Synthesized alkali binders demonstrated high strength, ultimate compression strength was in a wide range from 50 to 110 MPa.

The researchers in¹³⁻¹⁷ obtained alkali and alkaline earth binders: $R_2O-Al_2O_3-2SiO_2$ and $R_2O-2RO-Al_2O_3(2-4)SiO_2$, comprised of the mixture annealed not to sintering of sodium carbonate and sodium with kaolinite; after tempering with water, the activity of these binders upon natural solidification was quite moderate: from 20 to 35 MPa; however, after modification of solidification conditions by hydrothermal treatment, it was possible to increase the strength up to 56 MPa.

It was established in^{13,14,16} that application of sodium silicate soluble glass as alkali activator in combination with granulated slag would allow, similar to Portland slag cement, to produce slag-lime binders with the strength of 50–120 MPa; and similar to Portland cement and alumina cement, the alkali analogs in the form of annealed mixtures of aluminosilicates of $R_2O-Al_2O_3-(2-4)SiO_2$ and $R_2O-(2-4)RO-Al_2O_3(2-4)SiO_2$ type also demonstrated high activity under various conditions of ossification.

Therefore, the application of alkali components as activators allows synthesizing analogs of conventional mineral hydraulic binders and will provide the required alkaline medium with sufficiently high pH for hydration of silicate and aluminosilicate constituents of the considered binding combination.

EXPERIMENTAL

Material and Methods

The experiments were carried out with prepared mineral powdered additives made of sedimentary and magmatic rocks: quartz sand, limestone, volcanic tuff, and siliceous marl. Also, wastes of the cement industry in the form of clinker and aspiration precipitator dust were used. The considered powders were produced by fine milling of rocks for one hour; the mineral powder of siliceous marl was thermally treated in the furnace at 700°C. Energy dispersive microanalysis of the considered powders was performed using a Quanta 3D 200i scanning electron microscope. The procedure of ion exchange with calcium hydroxide¹⁸ was used for the determination of a cumulative number of active Bronsted acid sites. Standard procedures were used for the development and analysis of properties of binders and concrete of alkaline tempering.

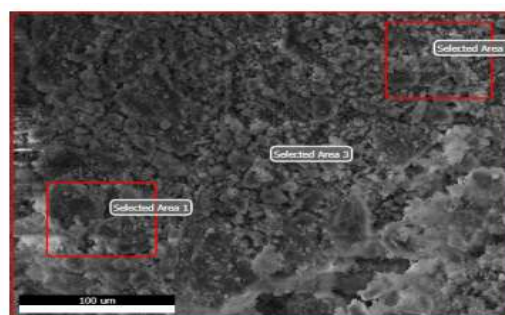
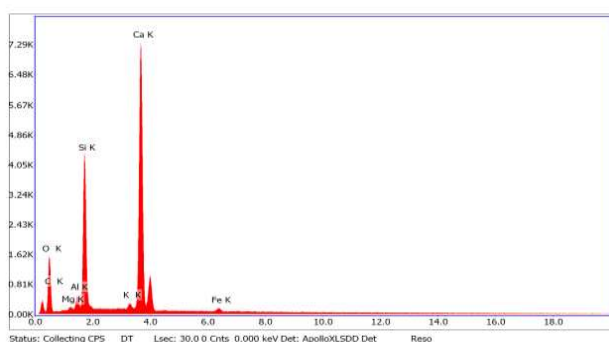
RESULTS AND DISCUSSION

This work presents experimental results on the development of recipes and analysis of properties of binders of alkaline tempering with the use of natural raw stuff and further design of recipes of fine concretes using

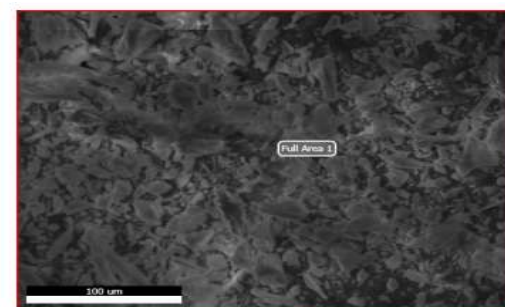
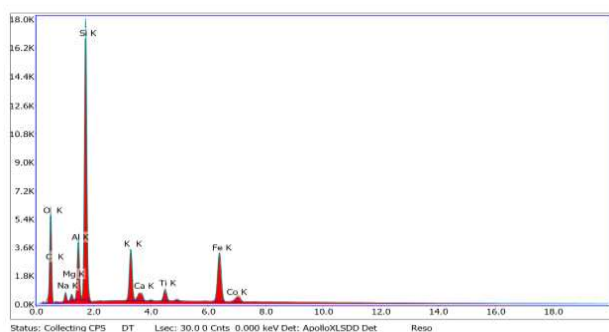
the obtained clinkerless cement. Energy dispersive microanalysis of the considered powders performed by a Quanta 3D 200i scanning electron microscope revealed significant variation in the chemical composition of natural additives (Table-2 and Fig.-2).

Table-1: Classification of Hydraulic Binders

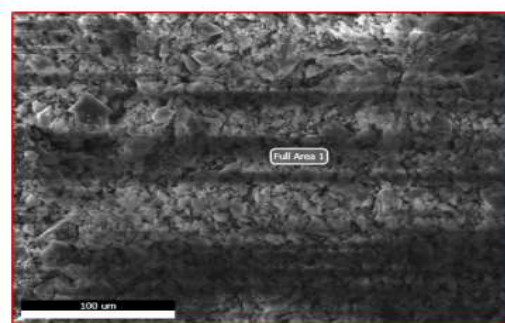
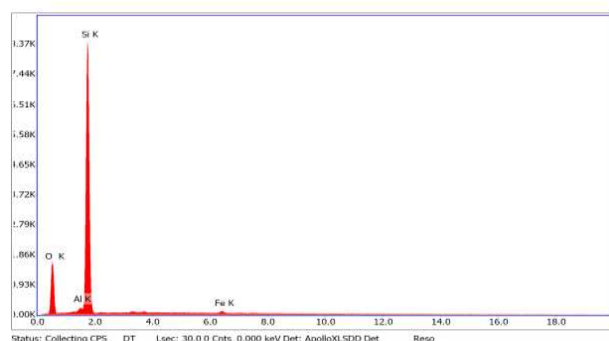
Cement	Phase Composition	Content of Alkali Metal Oxides	Hydration Products
Portland cement (PC)	PC clinker	< 0.6%	$\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$
Alkali PC	PC clinker + R_2O	1–5%	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ $\text{R}_2\text{O} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$
Alkali cement: – slag – ash – high dispersive powdered aluminosilicates	Slag + R_2O Ash + R_2O $\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O} + \text{R}_2\text{O}$	2–8% 5–10% 10–15%	$\text{R}_2\text{O} \cdot \text{RO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$
Geopolymer cement	Kaolinite + R_2O	10–20%	



(a)



(b)



(c)

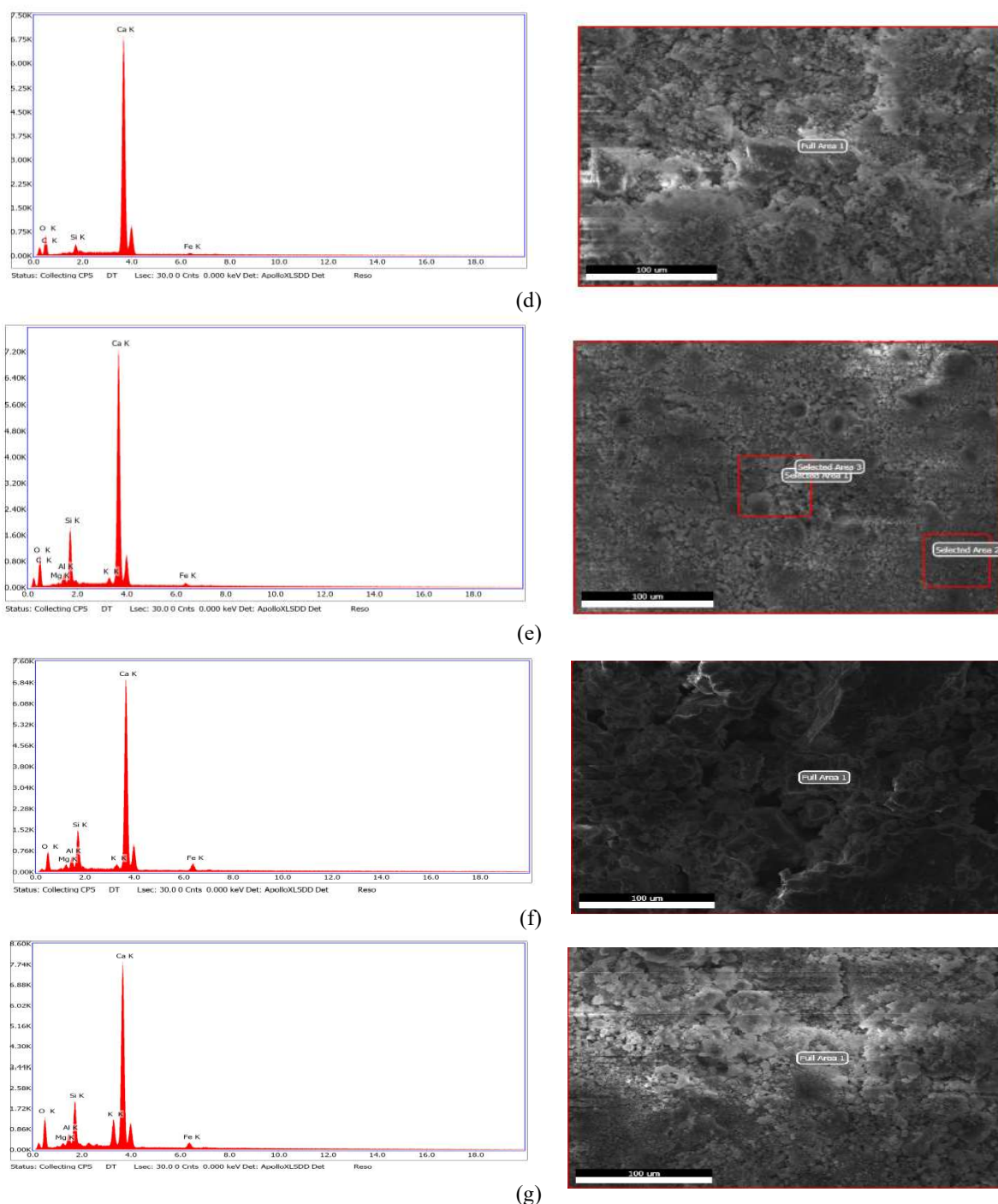


Fig.-2: Energy Dispersive Microanalysis of Mineral Powders: (a) Marl, (b) Volcanic Tuff, (c) Quartz Sand, (d) Sandstone, (e) Limestone, (f) Clinker Dust, (g) Aspiration Dust

Analysis of the presented data has demonstrated that volcanic tuff and quartz sand (Figs.-1b, c) is characterized by a higher content of silica; siliceous marl (Fig.-1a) is characterized by more uniform content of silica and calcium oxide; limestone and sandstone (Figs.-1d, e) are characterized by a higher content of calcium oxide. Analysis of precipitator dust has demonstrated the similarity of chemical compositions of clinker and aspiration dust (Figs.-1f, g) with Portland cement clinker and initial raw mixture, respectively; however, it should be mentioned that the content of oxide K_2O in aspiration dust is 6.43%, whereas in

clinker dust it decreases to 1.57%. This can be attributed to the fact that clinker dust was formed in a hot area of solid-phase synthesis of the rotary furnace at 1,300°C and above, alkali metal oxides were burnt out and decomposed in this area^{7,9,10}. The obtained results of the chemical analysis will allow forecasting properties of the proposed clinkerless binders of alkaline activation using the considered high dispersive powders.^{1,2,4,5,10}

Table-2: Chemical Composition of High Dispersive Powders, %

Description	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Fe ₂ O ₃	TiO ₂	SO ₃	L.O.I.
Quartz sand	6.32	14.99	73.83	1.83	0.60	0.97	1.32	0.14	-
Volcanic tuff	0.20	13.57	73.67	6.00	1.79	1.52	2.85	-	0.40
Limestone	0.72	1.55	5.05	0.60	90.14	1.40	-	0.49	-
Siliceous marl	1.64	6.42	28.6	1.33	16.90	1.08	0.47	0.29	43.2
Sandstone	-	-	2.62	-	57.99	0.79	-	-	38.6
Clinker dust	1.49	4.11	16.89	1.57	71.64	4.30	-	-	-
Aspiration dust	0.97	4.68	20.31	6.43	64.15	3.47	-	-	-

The high dispersive powders of the considered rocks were produced by preliminary crushing in jaw crusher and then fine milling for one hour in mills of different design:

- LMR-15 roller mill
- VM-20 vibratory ball mill.

From time to time samples were taken from the mills to determine the specific surface area of the powders and to perform comparative analysis (using a PSKh-12 instrument). The powdered siliceous marl was thermally treated in the furnace at 700°C, after the treatment, it was additionally milled for three minutes to activate the surface. As demonstrated by the studies (Figs.-3a, b), the engineering factor exerts significant influence on the activation of mineral additives.^{12,19-22}

Milling in a vibratory ball mill provides a higher specific surface area nearly at all sampling stages. It could be mentioned that during a further increase in milling duration this is the vibratory activation that can increase the specific surface area of powdered particles of mineral additives. It should be mentioned that in a roller mill with the increase in milling duration over one hour, the specific surface area did not vary; we suppose that this can be attributed to the features of the milling unit.

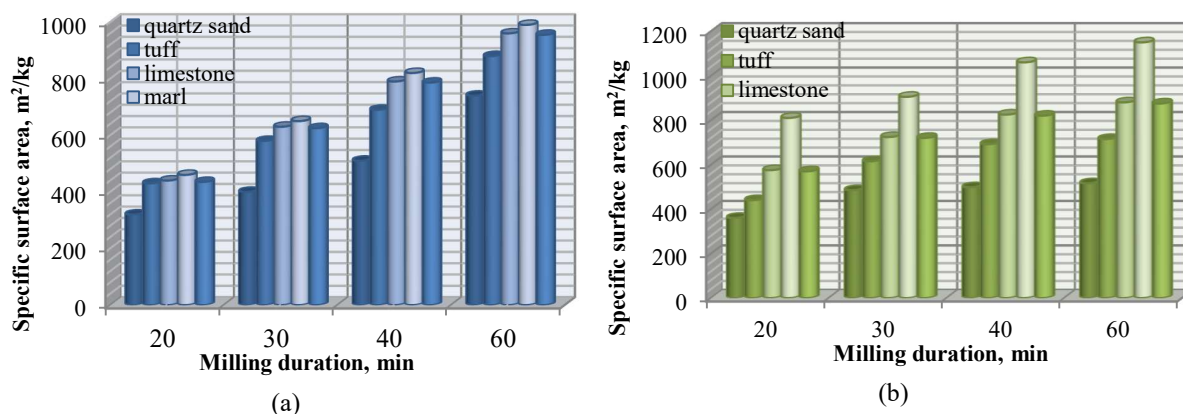


Fig.-3: Specific Surface Area of Mineral Powders As A Function of Activation Time in A (a) Roller Mill and (b) Vibration Mill

The mineral additive of quartz sand was characterized by the lowest performances of milling, which evidences increased hardness of rock-forming sand minerals. For volcanic tuff, the higher grindability can be attributed to the existence of quartz of greenschist facies metamorphism with imperfect structure.

The best grindability performances for the considered additives were demonstrated by limestone and siliceous marl. Herewith, their specific surface area was in the range of 990–1,150 m²/kg. Such high grindability is stipulated by the organic chemical oolitic genesis of mineral in the form of spherical or ellipsoidal calcite oolites, minor amount of quartz and dolomite cemented by cryptocrystalline carbonate substance; as is known, carbonate rocks due to their softness are milled finer than other mineral additives and clinker. The specific surface area of cement production wastes is moderate in comparison with other

considered powders, clinker dust: 210 m²/kg, aspiration dust: 280 m²/kg.

According to the classification in^{9,10}, the high dispersive mineral powders in terms of the energy potential of active sites on their surface are subdivided into the following groups:

- i. fine additives of acid rocks characterized by high negatively charged potential, since the surface contains particles with a significant amount of adsorptive active sites in the form of O²⁻ ions (quartz, garnet, syenite, and others);
- ii. fine additives of average igneous rock characterized by high negatively charged potential, since the surface contains particles of O²⁻ adsorption sites and univalent cations K⁺, Na⁺ (albite, orthoclase, and others);
- iii. fine additives of average, basic, and ultra-basic magmatic rocks characterized by lower negatively charged potential due to the existence of particles of the high amount of adsorption sites in the form of O²⁻ and cations of different activity K⁺, Na⁺, Ca²⁺, Al³⁺, Fe³⁺ (basalt, anorthite, diabase, and others);
- iv. fine additives of basic sedimentary rocks with high positively charged potential due to the existence of a high amount of adsorption sites in the form of Ca²⁺, Mg²⁺ (dolomite, limestone, marl, and others);
- v. fine additives of neutral surface (talc, graphite, and others).

The properties of fine additives for the production of binders are determined by their surface state. The surface of solids at the molecular level is the main factor of crystalline structure. Gibbs² established that the contact surface of phases was determined by the layer of minimum thickness characterized by composition and thermodynamic conditions of the phase boundary.

It has been established that application of high dispersive mineral powders of various essence promoted an increase in strength of Portland cement concrete by several times at constant water to cement ratio. This is attributed to the fact that ultrafine particles of the mineral component with the sizes close to colloidal, being located between or near the grains of Portland cement, promote the formation of new crystallization sites, intensify structure formation, and improve physicomechanical properties of cement stone and concrete.^{6,9,18,23} Also, the ultra-filling effect takes place, which increases the volumetric concentration of mineral powder and decreases the porous space of cement stone²⁰. However, to increase the ultra-filling effect, it is required that the additive particles would not prevent new phases on the surface and synthesis of crystalline hydrates. This is possible upon determination of the optimum degree of system saturation with fine additive taking into account its pozzolanic activity, the volume of capillary pores, voids, and micro defects.

It has been proved that on the surface of high dispersive mineral additives, two acid and base sites can exist: Lewis and Bronsted. The existence of these activity sites in the presence of water determines the reactivity of mineral additive as a catalyst of solidification and maturing, increases corrosion resistance, participates in electrochemical processes, including electron transfer to surfaces, etc.

It has been established that the surface of mineral material can contain:

- i. Lewis acid site (L⁺) with free orbital, which is the acceptor of electron pair;
- ii. Lewis base site (L⁻) with electron pairs of higher energy on orbitals, which is the donor of electron pair;
- iii. Bronsted acid site (B⁺) capable to lose a proton (H⁺);
- iv. Bronsted base site (B⁻) acting as acceptor.

In the presence of water, the Lewis acid sites can transfer to the Bronsted acid sites and vice versa. It has been established in¹⁰ that on the surfaces of fine filler and silica filler there exist active sites of crystallization, which to some extent promote interaction with Portland cement. The surface of solid mineral material is a combination of Lewis and Bronsted sites of both acid and base type.

The Lewis centers on the surface of silica and aluminosilicate oxides interact with nonsaturated aluminum atoms. There is no unique explanation of the behavior of Bronsted sites. Some researchers assign proton-donor functions to proton surface hydroxyl groups, others – to coordinate bonded water molecules.

Lewis acid site is the free level of metal atom electron, which can accept electron pair. The Lewis sites are obtained because of two-electron orbitals of the oxygen atom on the surface, which chemically interact with electron loss to energy acceptor level of atom or molecule.

Bronsted acids and bases are generated because of the adsorption of a water molecule or its fragments on respective Lewis sites, being, respectively, proton donors.¹⁸

Acidic–basic properties of surfaces are manifested only in the presence of acids and bases, that is, compounds, capable to be acid, become such only in the presence of a base and vice versa (Fig.-4).

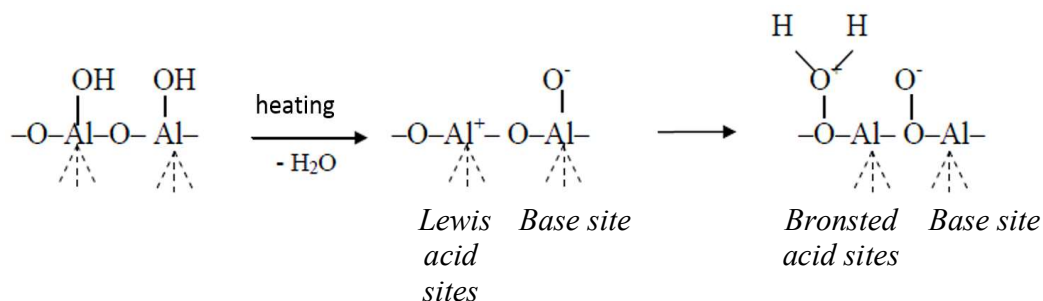


Fig.-4: Acid-base Properties of Surface Sites

The determination of the activity of high dispersive mineral powders is comprised of detection of the cumulative amount of active Bronsted acid sites using the procedure of ion exchange with calcium hydroxide. It is known¹⁸ that this is accompanied by rapid equivalent ion exchange of H^+ ions of silica silanol groups with Ca^{2+} .

The surface activity of mineral components is determined by the ion-exchange method because chemical interaction with cement strongly depends on Bronsted acid sites.^{9,10,18}

Surface properties of material grains are manifested from the time of formation of the obtained surface because of milling and mechanical activation. Upon the formation of a new surface, various structural heterogeneities appear at molecular and submolecular levels. The Molecular-level (crystalline structure of rock-forming minerals) determines mutual position, composition, and atom ratio on the surface. It has been mentioned in^{8,18} that significantly strong adhesive bonds in cement–filler composition can be created only when the surface energy of filler is by far higher than that of cement.

An increase in the reactivity of mineral additive upon its mechanical activation is promoted by its amorphization, the thickness of the amorphized layer can reach 150–400 Å. Exactly this layer of powders is rapidly deactivated in the air since it possesses high adsorption ability and mutual compensation of charges occurring during mechanical activation.

It is confirmed theoretically that the use of activated filler in the system would allow to adjust properties, structure formation of cement stone, and to decrease binder consumption. Also, with a known degree of activity of the applied high dispersive mineral additives, it is possible to improve the effectiveness of their use in concretes^{9,10}, to optimize binder consumption, to control the rheology of concrete mixtures, etc.

To analyze the amount of Bronsted active sites of crystallization on the surface of mineral powder using the procedure of determination of exchange capacity concerning calcium ions¹⁸, saturated calcium hydroxide solution was prepared by mixing milled quicklime with distilled water. The solution was stored for 7 to 10 days in a sealed vessel at 18–20°C. During several days, the activity stability was determined by titration with 0.1 N solution of hydrochloric acid.

At the next stage, 1–2 g of the powder was placed into a conical flask, and then 40 ml of saturated calcium hydroxide solution was added. Herewith, the vessel should be sealed with a plug to prevent air penetration. The obtained mixture was agitated for several hours. The agitation duration depends on the exchange reaction and powder milling fineness.

Then the solution was washed with distilled water and filtered. Methyl orange indicator was added to water extracts, the solution was discolored to yellow, and then it was titrated with 0.1 N solution of hydrochloric acid until it was discolored to pink. The difference in volumes of acids consumed for titration of the saturated calcium hydroxide solution and the solution after interaction with mineral powder determined the degree of surface activity.

The activity of crystallization sites was determined as follows:

$$\frac{(V_1 - V_2) \cdot 0.1 \cdot 1000}{m} = [mg \cdot eq/g] \quad (1)$$

Where V_1 was the volume of acid consumed for titration of 20 ml of the initial calcium hydroxide solution, ml; V_2 was the volume of acid consumed for titration of the solution after interaction with mineral powder, ml; m was the weight of a sample of mineral powdered filler, g.

Then, the activity coefficient of the mineral additives was determined by the procedure proposed by Strokova¹⁸. With this aim, a dried sample of raw stuff milled to screen undersize of 0.315 mm was placed into the conical flask with NaOH solution. The obtained suspension was agitated using a shaker for 10 min, and then it was thermally treated for 2 h at 90°C in a steam chamber or closed water bath. The thermally treated suspension was filtered, the mineral residue was washed three-fold with distilled water, and then it was dried to constant weight and weighed.

The activity coefficient of silica raw stuff was calculated as follows:

$$K_a = \frac{m_1 - m_2}{m_1} \cdot 100 \quad (2)$$

Where m_1 was the weight of initial raw stuff, g; m_2 was the weight of dried mineral residue, g.

The coefficient of hydraulic activity of mineral additive (H_{AMA}) was calculated as follows:

$$H_{AMA} = \sqrt{\ln K_a} \quad (3)$$

Where K_a was the activity coefficient of mineral additive, %.

Table-3 summarizes experimental results of the determination of active crystallization sites, which demonstrated that the surface concentration of ion exchange sites of mineral powders varied heterogeneously and depended on the degree of milling (Fig.-5).

It should be mentioned that the highest activity is observed for mineral powders based on volcanic tuff and siliceous marl annealed at 700°C. This can be attributed to the existence of numerous exchange sites on the surface of the mentioned mineral high dispersive powders; a significant portion of them is presented by Bronsted acids and bases.^{10,18} Concerning electric precipitators, it should be mentioned that clinker dust is reactive; its activity during tempering with water was 24 MPa.

Table-3: Surface Activity of High Dispersive Powders

No.	Mineral Powder	Activity Coefficient K_a , %	Coefficient of Hydraulic Activity H_{AMA}	Number of Active Sites of Crystallization, mg·eq/g	The Specific Surface Area of Powders, m ² /kg
1	Quartz sand	22	1.76	21	810
2	Volcanic tuff	37	1.90	34	905
3	Limestone	8	1.24	12	1,060
4	Marl (700°C)	62	2.03	42	1,150
5	Sandstone	10	1.44	16	1,020
6	Aspiration dust	12	1.45	17	280

Therefore, based on the acquired experimental results, it is possible to state that the activity coefficients, including the number of active crystallization sites, strongly depend on the degree of detection of defects formed upon milling, this promotes an increase in the reactivity of the considered powders applied in binders as high dispersive additives.

After verification of reactivity of the proposed mineral additives, it is required to detect the existence of hydraulic properties of the obtained powders after tempering with an alkaline solution. With this aim, bar-like samples were prepared with the size of 20×20×100 mm made of the mixture: high dispersive component (of 100% of binder weight), commercial sodium liquid glass with the silica module of 2.8 and density of 1.24 g/cm³, sodium hydroxide. The prepared samples were cured on the first day under normal conditions at 20±2°C, however, in two days a portion of twin samples was located from time to time into cabinet dryer at 40°C for a couple of hours, and a portion of thermally treated samples was stored in water. The recipes and properties of clinkerless binders of alkaline tempering are summarized in Table-3 and Fig.-6.

The experimental results of the considered compositions based on binders of alkaline activation, summarized in Table-4 and Figs.-6a, b, c, demonstrated rather scattered results, and this can be attributed to the essence of rock-forming minerals of the considered additives.

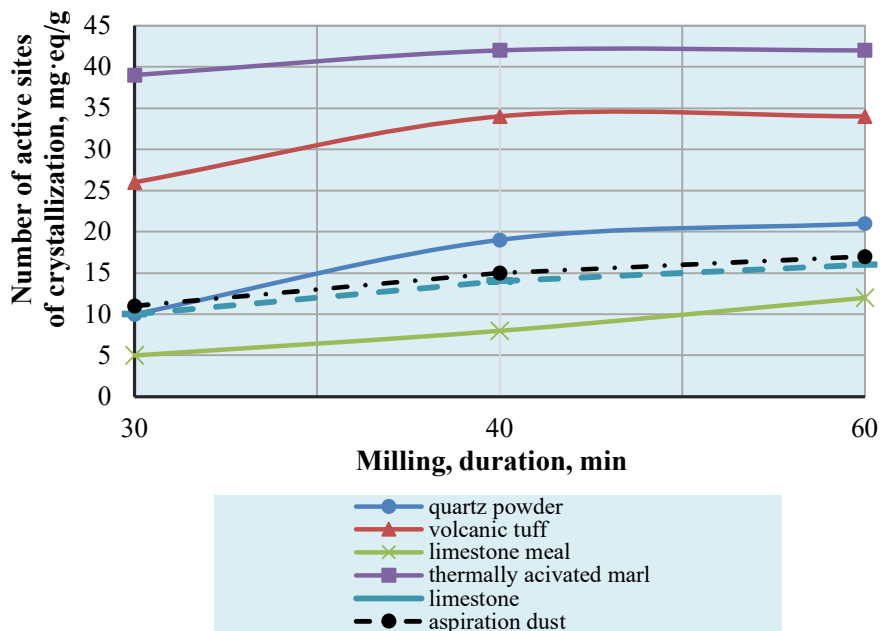


Fig.-5: Number of Active Sites of Crystallization as a Function of Activation Time.

Table-4: Recipes and Properties of Binders of Alkaline Activation

No.	High Dispersive Powders	Alkaline Activator, %		Activity, MPa, 28 days		
				Conditions of Solidification		
		NaOH	Na ₂ SiO ₃	natural	40°C	in water
1	Quartz powder	5.5	20.5	20.3	22.3	23.5
2	Marl (700°C)	5.5	24.0	39.2	42.6	46.5
3	Volcanic tuff	5.5	21.0	33.1	37.6	39.4
4	Limestone meal	5.0	24.0	13.7	16.5	9.0
5	Sandstone	5.5	21.0	14.6	17.3	9.2
6	Clinker dust	5.5	17.5	42.1	44.7	50.5
7	Aspiration dust	5.5	18.5	15.4	15.6	10.1

The maximum strength of samples with precipitator clinker dust can be attributed to the existence of clinker minerals in this additive, and it should be mentioned that the samples stored in water were characterized by intensive leaching in the first days.

The high strength of samples made of thermally activated marl and volcanic tuff can be attributed to aluminosilicate essence of the considered powders; also, it has been detected that temperature increase to 40°C and water storage promotes increase inactivity. Quartz sand with a high content of silica after alkaline tempering was characterized by strength significantly lower than that of thermally activated siliceous marl and volcanic tuff, however, in comparison with limestone, sandstone, and precipitator aspiration dust the activity was higher.

It appears that to form solid cement stone, the existence of cement system is required comprised of fine amorphous and crystalline aluminosilicates dissolved by alkali solution. Binder based on mineral carbonate additives tempered by alkali solution demonstrated minimum compression strength, decrease in activity was observed upon solidification in water. Therefore, the hydraulic properties of these compositions (Nos. 4,5, and 7) were not exhibited properly.

Then, the compositions were developed, and the properties of fine concrete based on the obtained binders of alkaline activation were studied. Cubic samples with the size of 7 cm were prepared using the following components: high dispersive powder (Table-3), graded sand obtained by mixing of screened rocks of Argun

deposit and fine sand of Chervlenskoe deposit in the ratio of 55:45%. Tempering was performed using liquid glass, sodium hydroxide in preset ratios determined experimentally.

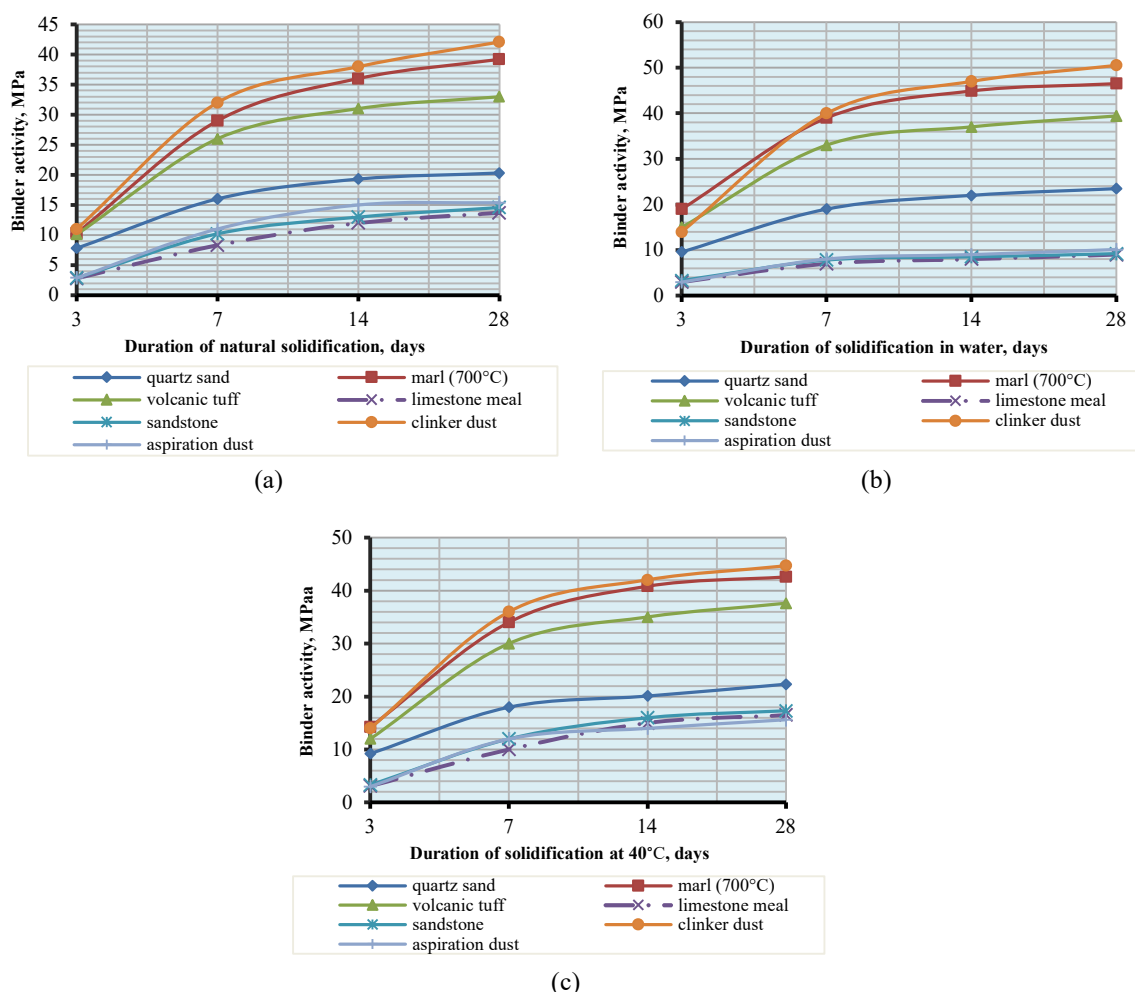


Fig.-6: Activity of Clinkerless Binders as a Function of Duration and Conditions of Solidification: (a) Natural Solidification at 18-20°C; (b) Solidification at 40°C; (c) Solidification in Water Medium

The prepared samples were solidified under normal conditions at $20 \pm 2^\circ\text{C}$; after two days the samples were placed into a cabinet dryer and held at $40\text{--}50^\circ\text{C}$ for several days, then they were solidified in a climatic chamber before testing. The experimental results of the considered fine concrete based on binders of alkaline activation are summarized in Table-5.

The binder of alkaline activation using high dispersive powders in the form of precipitator clinker dust demonstrated 47.6 MPa, however, these were production wastes of Portland cement, the operation lifetime and corrosion resistance of the product should be studied separately. Therefore, concrete samples of thermally activated marl with a strength of 40.5 MPa were analyzed using a Quanta 3D 200i scanning electron microscope equipped with Genesis Apex 2 EDS microanalysis system (EDAX) (Fig.-7). For a more detailed analysis of interphase transformations in cement stone by X-ray phase analysis, the following results were obtained, which are summarized in Fig.-8 and Table-6.

It has been detected that in the contact area, there exists sufficiently solid coalescence of particles of binder and quartz sand, the surface does not contain defects in the form of buildups or cracks, there are some irregularities of various shape and size, some particles are characterized by needle-like fibrous structure, which evidences increased activity of binder. X-ray analysis revealed the existence of quartz, feldspars similar to albite and orthoclase, mica, calcite, zeolites (Fig.-8). Mica corresponds to muscovite; the measured composition of flakes can be in average described as follows:

$(\text{Na}0.14\text{K}0.63)0.8(\text{Fe}^{2+}0.05\text{Mg}0.02\text{Al}^{\text{VI}}2.01\text{Ti}0.01)2.1(\text{Si}3.01\text{Al}^{\text{IV}}0.99)4.0\text{O}10(\text{OH}2.00)2.0$, which reflects enrichment with sodium and aluminum.

Table-5: Properties of Fine Concretes Based on Clinkerless Binders of Alkaline Activation

No.	High Dispersive Powders	Consumption of Materials, kg per 1 m ³					Concrete Density, kg/m ³	Compression Strength, MPa, at the age, Days	
		HSP	GS	Na ₂ SiO ₃	NaOH	AS/HSP		7	28
1	Quartz sand	480	1,700	114	10	0.26	2,240	11.8	24.7
2	Marl (700°C)	480	1,700	115	10	0.26	2,250	31.4	40.5
3	Volcanic tuff	480	1,700	116	9	0.26	2,246	25.3	34.2
4	Limestone meal	480	1,700	121	8	0.27	2,235	5.9	14.1
5	Sandstone	480	1,700	120	8	0.27	2,239	6.6	15.9
6	Clinker dust	480	1,700	114	10	0.26	2,240	35.2	47.6
7	Aspiration dust	480	1,700	120	8	0.27	2,239	5.0	12.4

Remarks: HSP – high strength powders; GS – graded sand; AS/HSP – alkaline solution to high strength powder ratio.

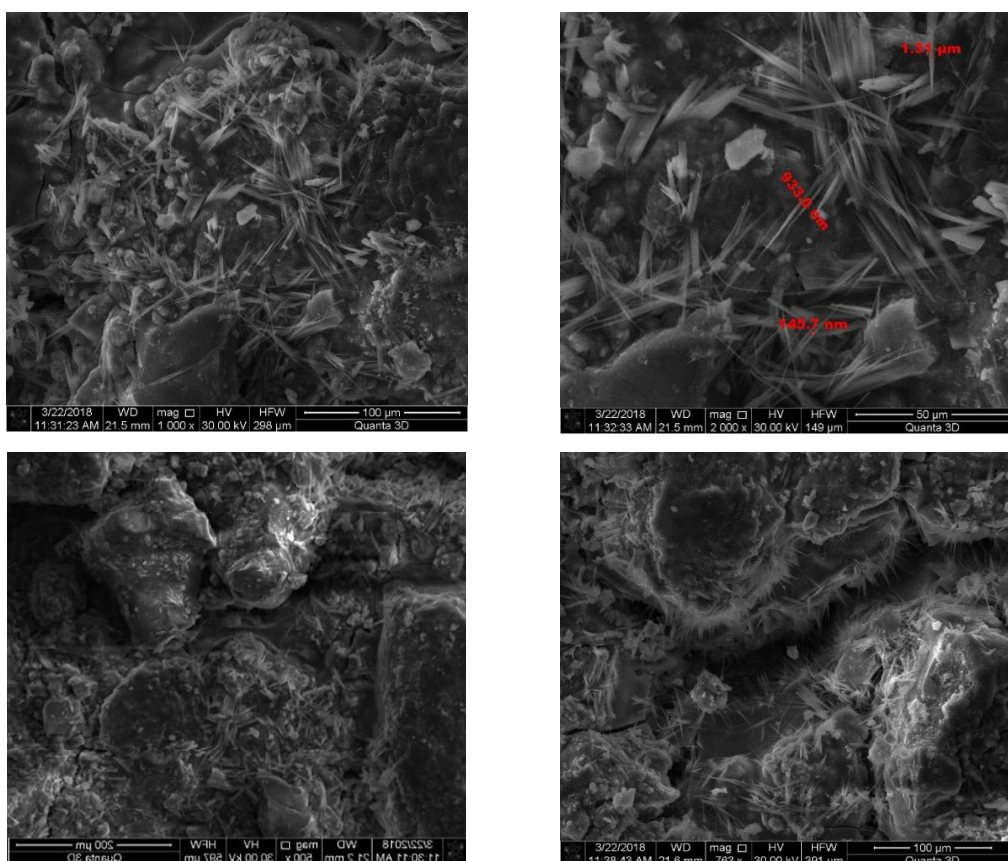


Fig.-7: Micrographs of Concrete based on Thermally Activated Marl of Alkaline Activation

Table-6: Energy Dispersive Microanalysis of Contact Area

Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	SO ₃	K ₂ O	CaO	MnO	FeO	L.O.I.
2.59	0.65	2.85	17.53	0.19	0.36	37.77	0.02	1.22	36.8

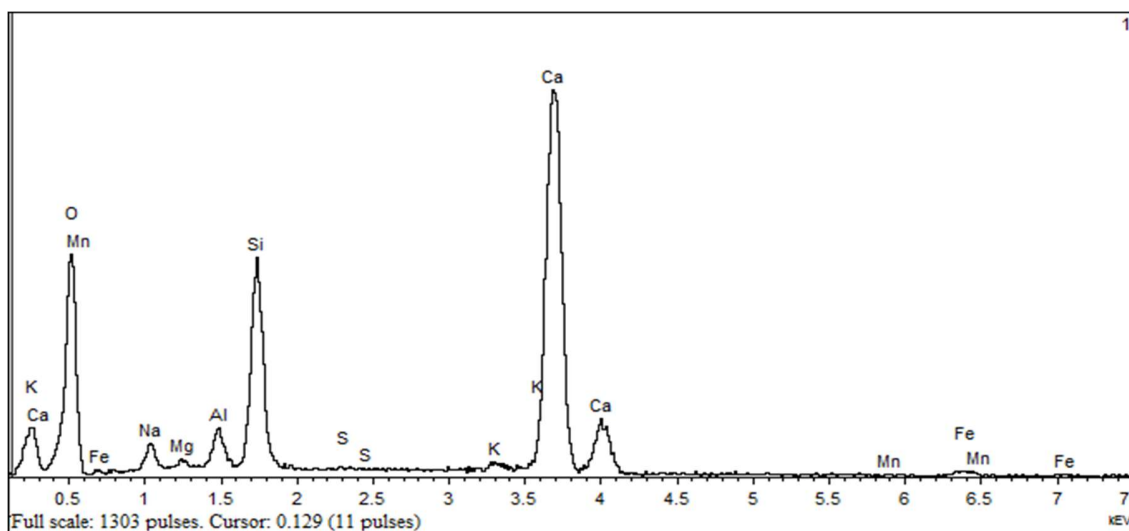


Fig.-8: X-ray Pattern of Cement Stone based on Thermally Activated Marl of Alkaline Activation

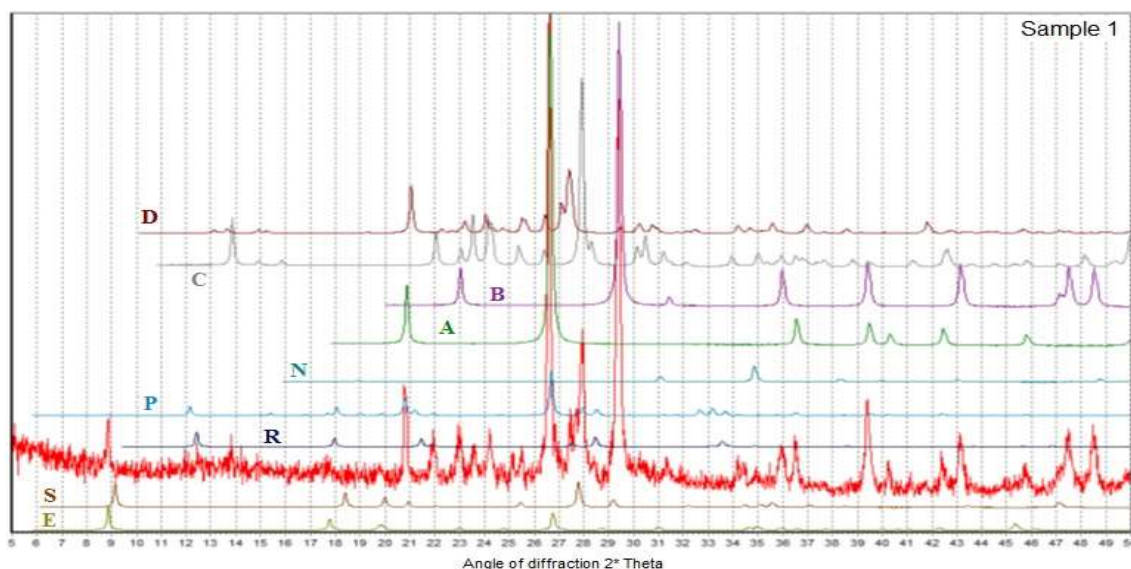


Fig.-9: Diffraction Pattern of Cement Stone based on Thermally Activated Marl of Alkaline Activation. Reference Phases: A – Quartz; B – Calcite; C – Albite; D – K-Feldspar; E – Muscovite; N – Analcime; P – Gismondite; R – Garronite; S – Paragonite

Zeolite is identified as similar to garronite (the composition is described theoretically as $\text{Na}_2\text{Ca}_5\text{Al}_{12}\text{Si}_{20}\text{O}_{64} \cdot 27(\text{H}_2\text{O})$, the main reflex of this phase is distinctly highlighted: $(2\theta - 12.4 (7.10\text{\AA}))$. The sizes of crystals of certain zeolites (up to $50 \mu\text{m}$) make it possible to determine their composition by semi-quantitative elemental analysis (Fig.-9). All considered zeolites are characterized by Ca–Na variable compositions; they are hydrate nonstable compositions similar to zeolites (enriched in terms of Na_2O). The high strength of fine concrete with clinkerless binder of alkaline tempering based on thermally activated marl can be attributed to the formation of strong geopolymer stone. The mechanism of structure formation is time-consuming and complicated. The initial stage of structure formation is characterized by the generation of dispersing–coagulating solutions. Alkali metal cation increases the basicity pH of the tempering medium, breaks the structure of aluminosilicates Si–O–Si and Al–O–Al of thermally treated marl, and promotes the release of slag cation Ca^{2+} . The primary newly formed structures resulting from the cation exchange $2\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$ are of varying types. At the next stage, the primary structure is transformed due to mass exchange processes in the colloidal disperse system and hydrosols are converted into a solid phase, which intensifies the structure crystallization. The cation exchange $2\text{Na}^+ \leftrightarrow \text{Ca}^{2+}$ also promotes

chemical interaction in solid phases with metal ions of alkali hydroxides. This would bind silicates by alkali compounds with simultaneous occurrence of hydration processes²³. At the final stage of structure formation, the primary solid phases of nonstable compositions are developed leading to the formation of solid crystalline aggregate. The crystallization phases are of variable pattern and depend on numerous factors, chemical and mineralogical compositions, system constituents, the essence of alkali solution, dispersity of components, solidification conditions, and others.^{24,25} Alkali medium of high basicity promotes the formation of such compounds as tobermorite-like calcium hydro silicates CSH(B), hydrogarnets of varying composition, silica gel, alkali hydro-aluminosilicates of natural zeolite and hydro-mica type, and other alkali and alkaline earth compounds of variable composition.^{1,2,4,5,24-26}

CONCLUSION

Therefore, the properties of clinkerless binders based on alkaline tempering agents using high dispersive mineral components of various essence have been studied, and their recipes have been obtained together with efficient compositions of fine concretes based on the proposed cement.

It has been theoretically substantiated and practically proven that the Bronsted acid sites on the surface of highly active powders accelerate the synthesis of silica gel, promote polymerization of silicon-oxygen anions, enhance ion exchange, and stabilize the formation of intergranular contacts.

Formation of mineral powder-alkaline activator multicomponent system should be thoroughly analyzed, since the features of binder, its essence, degree of dispersity, alkaline tempering agent, the rate of their dissolution, crystallization conditions, interphase contact area, and other factors exert influence on solidification and maturing of cement stone. No doubts that material and quantitative compositions of constituents of this complex system would exert their direct influence at all stages of structure formation.

The obtained experimental results significantly expand the application area of clinkerless binders based on the alkaline binder and would provide partial substitution of expensive and energy-intensive Portland cement in the construction industry. Further studies will be devoted to alkaline tempering agents since in the proposed recipes of clinkerless binders the most expensive constituent is commercial liquid glass.

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REFERENCES

1. V.D. Glukhovskii (ed), *Shchelochnye i shchelochno-shchelochnozemel'nye gidravlicheskie svyazuyushchie i betony* [Alkaline and alkali and alkaline earth hydraulic binders and concretes], Vishcha shkola, Kiev (1979).
2. J. Davidovitz, *Geopolymer. Chemistry and applications*, Institute Geopolymer, Saint-Quentin (2008).
3. A.A. Soldatov, I.V. Sariev, M.A. Zharov, M.A. Abduraimova, *Stroitel'nye materialy na osnove zhidkogo stekla* [Structural materials based on liquid glass], Proceedings of the 4th Annual Conference of North Caucasus Federal University, Urgent Problems of Construction, Transportation, Engineering, and Technogenic Safety, pp. 192-195 (2016).
4. V.D. Glukhovskii, V.A. Pakhomov, *Shlakoshchelochnye tsementy i betony* [Slag-lime Cements and Concretes], Budivel'nik, Kiev (1978).
5. P.V. Krivenko, K.K. Pushkareva, *Dolgovechnost' shlakoshchelochnogo betona* [Lifetime of Slag-lime Concrete], Budivel'nik, Kiev (1993).
6. P. Duxson, A. Fernandez, J. Provis, *Journal of Materials Science*, **42**, 2917(2007).
7. E.A. Nikiforov, V.I. Loganina, E.E. Simonov, *Vliyanie shchelochnoi aktivatsii na strukturu i svoistva diatomita* [The influence of alkaline activation on structure and properties of diatomite], *Vestnik BGTU im. V.G. Shukhova*, **2**, 30-32 (2011).
8. A. Shuisky, S. Stelmakh, E. Shcherban, E. Torlina, *Recipe-technological aspects of improving the properties of non-autoclaved aerated concrete*. Proceedings of MATEC Web of Conferences Ser. "International Conference on Modern Trends in Manufacturing Technologies and Equipment.

- ICMTMTE 2017", pp. 05011(2017), [DOI:10.1051/mateconf/201712905011](https://doi.org/10.1051/mateconf/201712905011)
9. S-A.Yu. Murtazaev, M.Sh. Salamanova, M.S. Saidumov, Z.Kh. Ismailova. Vliyanie aktivnykh tsentrov poverkhnosti na reaktivnost' mineral'nykh dobavok [The influence of active surface centers on reactivity of mineral additives], *Sovremennaya nauka i innovatsii*, **2(18)**, 168(2017).
 10. S-A.Yu. Murtazaev, M.Sh. Salamanova, Perspektivy ispol'zovaniya termoaktivirovannogo syr'ya alyumosilikatnoi prirody [Possible applications of thermally activated aluminosilicates], *Privolzhskii nauchnyi zhurnal*, **2(46)**, 65(2018), [DOI:10.34708/GSTOU.2020.49.91.010](https://doi.org/10.34708/GSTOU.2020.49.91.010)
 11. M.Sh. Salamanova, S.Yu. Murtazayev, Z.H. Ismailova, The Use of Highly Active Additives for the Production of Clinkerless Binders, Proceedings of the International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2018), pp. 355-358 (2018), [DOI:10.2991/isees-18.2018.68](https://doi.org/10.2991/isees-18.2018.68)
 12. M.Sh. Salamanova, S.Yu. Murtazayev. Clinker-free binders based on finely dispersed mineral components. 20. Internationale Baustofftagung. Tagungsbericht, Bauhaus-Universitdt Weimar. Band 1 und 2. Weimar: 2018. -B.2m 707-714 (2018), [DOI:10.34708/GSTOU.2020.19.1.007](https://doi.org/10.34708/GSTOU.2020.19.1.007)
 13. N.I. Kozhukhova, R.V. Chizhov, I.V. Zhernovsky, V.V. Strokova, *ARPN Journal of Engineering and Applied Sciences*, **11(20)**, 12275(2016).
 14. N.I. Kozhukhova, R.V. Chizhov, I.V. Zhernovsky, V.V. Strokova, *International Journal of Pharmacy and Technology*, **8(3)**, 15338(2016).
 15. J.A. Larbi, J.M. Bijen, *Cement and Concrete Research*, **20(4)**, 506(1990).
 16. N.I. Kozhuhova, I.V. Zhernovskiy, M.S. Osadchaya, V.V. Strokova, R.V. Tchizhov, *International Journal of Applied Engineering Research*, **9(22)**, 16945(2014).
 17. S.A. Udodov, M.R. Gish, Vliyanie dozirovki redispergiruemogo poroshka na lokalizatsiyu polimera i deformatsionnye svoystva rastvora [The influence of dosage of re-dispersible powder on polymer localization and deformation properties of mortar], *Nauchnye trudy Kubanskogo gosudarstvennogo tekhnologicheskogo universiteta*, **9**, 164-174 (2015).
 18. V.V. Strokova, I.V. Zhernovskii, A.V. Maksakov. Ekspress - metod opredeleniya aktivnosti kremnezemnogo syr'ya dlya polucheniya granulirovannogo nanostrukturiruyushchego zapolnitelya [Rapid determination of activity of raw silica for production of granulated nanostructured filler], *Stroitel'nye materialy*, **1**, 38-39 (2013).
 19. A.A. Volodchenko, V.S. Lesovik, L.H. Zagorodnjuk, A.N. Volodchenko, Influence of the inorganic modifier structure on structural composite properties, *International Journal of Applied Engineering Research*, **10(19)**, 40617(2015).
 20. V.S. Lesovik, L.K. Zagorodnyuk, A.E. Mestnikov, A.I. Kudinova, D.A. Sumskoi, *International Journal of Applied Engineering Research*, **10(5)**, 12383(2015).
 21. M.Sh. Mintsae. D. K.-S. Bataev. K. Kh. Mazhiev. Adam Kh. Mazhiev. Prospects for Using 3D-Printing Technologies in Construction of Buildings in Seismic Areas. In Proceedings of the International Symposium on Engineering and Earth Sciences (ISEES 2018) «Advances in Engineering Research», 177, pp. 311-315 (2018), [DOI:10.2991/isees-18.2018.60](https://doi.org/10.2991/isees-18.2018.60)
 22. A.A. Volodchenko, V.S. Lesovik, A.N. Volodchenko, L.H. Zagorodnjuk, Y.V. Pukharenko. Composite performance improvement based on non-conventional natural and technogenic raw materials, *International Journal of Pharmacy and Technology*, **8(3)**, 18856(2016).
 23. G. Nesvetaev, Y. Koryanova, T. Zhilnikova, On effect of superplasticizers and mineral additives on shrinkage of hardened cement paste and concrete. In MATEC Web of Conferences 27th Ser. "27th R-S-P Seminar. Theoretical Foundation of Civil Engineering (27RSP), TFoCE 2018", pp. 04018 (2018).
 24. V.A. Matvienko, Studying Slag-lime Binders and Concretes Based on Alkaline Industrial Wastes. Ph.D. Thesis. Kiev (1979).
 25. N.R. Rakhimova. R.Z. Rakhimov, Properties of the slag-alkaline bindings - specific surface and granulometric of ground blast furnace slags relation, 17, Internationale Baustofftagung. Tagungsbericht. Band 1. Weimar, pp. 1-0499-0504 (2009).
 26. I.B.W. Gunam, Y. Setiyo, N.S. Antara, I.M.M. Wijaya, I.W. Arnata, I.W.W.P. Putra, *Rasayan Journal of Chemistry*, **13(2)**, 1022(2020), [DOI:10.31788/RJC.2020.1325573](https://doi.org/10.31788/RJC.2020.1325573)

[RJC-5850/2020]