Journal of
Composites Science

MDPI

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Influence of the Chemical Activation of Aggregates on the Properties of Lightweight Vibro-Centrifuged Fiber-Reinforced Concrete

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Abstract: One of the most essential building materials for sustainable development is concrete. However, there is a problem with a lack of inexpensive, efficient ways to make it high-strength and ultra-dense. A promising direction is the additional processing or activation of the cheapest component of the concrete mixture—inert aggregate. The article is devoted to a promising method for the simultaneous activation of both large and small aggregates using vibro-centrifuge technology. It has been established that the activation of concrete aggregates with aqueous solutions of natural bischofite at a concentration of 6 g of dry matter per 1 L of water is the most rational and contributes the maximum increase in strength characteristics and the best values of strain characteristics. Strength characteristics increased up to 16% and ultimate strains increased to 31%, respectively, and the modulus of elasticity increased to 9%. A new improved lightweight fiber-reinforced concrete was created and an innovative technology is proposed that makes it possible to achieve savings in manufacturing due to a significant improvement in structural properties and reducing the working sections of reinforced concrete elements. Regularities between the fundamental chemical processes of the surface activation of aggregates and the physical processes of structure formation of compacted and hardened concrete were revealed. An improvement in the structure of concrete at the micro- and macro-levels was recorded due to a point decrease in crack formation at the interfaces of the "cement matrix-aggregate" and "cement matrix-fiber" phases, and a decrease in the number of micropore defects was also found. Economic efficiency reached 25–27%.

Keywords: lightweight fiber-reinforced concrete; aggregates; chemical activation; centrifugation; vibro-centrifugation; concrete; properties

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Citation: Beskopylny, A.N.; Stel'makh, S.A.; Shcherban', E.M.; Mailyan, L.R.; Meskhi, B.; Beskopylny, N.; El'shaeva, D. Influence of the Chemical Activation of Aggregates on the Properties of Lightweight Vibro-Centrifuged Fiber-Reinforced Concrete. *J. Compos. Sci.* **2022**, *6*, 273. https://doi.org/10.3390/jcs6090273

Academic Editor: Mourad Nachtane

Received: 7 August 2022
Accepted: 12 September 2022
Published: 16 September 2022

1. Introduction

1.1. Relevance and Background of the Study

The urgent issue of materials science in construction engineering is the need for improved building materials due to the constant increase in the responsibility of buildings and structures. Based on the conditions of the global agenda for the greening of construction, there is a need to reduce resources, labor, energy, and material costs in the manufacture of building materials, products, and structures. To achieve these indicators, it is necessary to improve the recipe–technological and design solutions for reinforced concrete elements and structures, and first, such indicators as the bearing capacity of the element and its operational reliability, depending on the properties of the concrete used [1,2].

There are many technological and recipe ways to improve the quality of concrete. Most of them are aimed at controlling the properties of concrete by adjusting the composition with the help of binders, which is quite effective, but it has a significant problem—it is costly in terms of economic efficiency [3–5]. At the same time, it is crucial to understand that small and large aggregates which are presented in concrete, in principle, have a cumulative function. However, due to the scale factor, differences in dispersion, and specific properties, they must be processed or activated using different technologies. Therefore, even more promising are the methods of processing the aggregate, that is, the combined processing by simultaneously activating both the coarse aggregate, which forms the main concrete frame, and the fine aggregate, which acts as a dense packing structure shaper, achieves the required properties.

The modern global trend in the development of concrete science is the expansion of application areas to develop and improve the quality of lightweight concrete [6–8]. Currently, they are used not only in housing construction but also in transport, maritime, and other areas. Moreover, reducing the weight of the structural elements of buildings also makes it possible to solve complex architectural problems. At the same time, despite the obvious prospects and advantages, this concrete has disadvantages, the elimination of which requires the use of various physical and physicochemical methods. In particular, the expansion of the field of application requires more careful control over "the processes of structure formation both in the initial period of formation of the parameters of the structure and properties of the cement stone during hardening and during the operation of products made of lightweight concrete" [9–14].

The problems of managing the processes of the early structure formation of concrete are becoming increasingly important due to the widespread use of multicomponent composite materials based on binders, including fillers from various finely dispersed components and various fibers, with the use of modifying additives and technogenic raw materials [15–19].

The level of the current fundamental sciences, reflecting the essence of physical, chemical, hydrodynamic, thermal, diffusion, and other processes and phenomena that form the basis of building materials science, provides significant additional reserves for improving the technologies to produce building products and individual technological processes. Some of the promising areas for enhancing the properties of building products and structures made of composite materials are technologies based on the control of processes occurring at interphase boundaries. The high energy potential characteristic of interfacial boundaries makes it possible, with the application of minor external influences, to significantly change the course of structure formation processes and the characteristics of the resulting object. Some of the most effective influences on the processes occurring at interfacial boundaries are the various physical, physicochemical, and chemical methods of influencing both individual components and their compositions, leading to the intensification of structure formation processes and the modification of the structure and properties of composite materials [5,20].

A graphic conditional block diagram of these activations is presented in Figure 1.

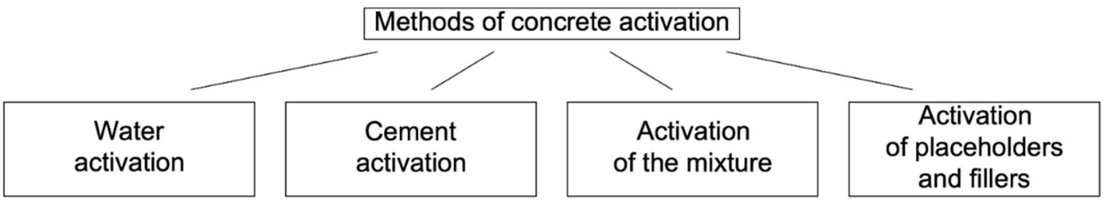


Figure 1. Graphical flowchart of known concrete activation methods.

1.2. Ways to Activate Concrete Aggregates

Let us consider the known methods of activating aggregates while noting the separation of their methods with respect to coarse and fine aggregates. Such methods include electrical, physical, and chemical methods, which are presented in more detail below. For ease of perception, the most effective methods are presented in Figure 2, which have proven themselves in construction practice.

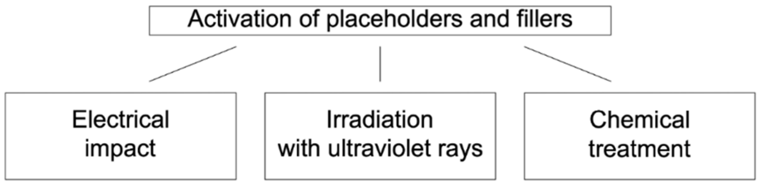


Figure 2. Known activation technologies for concrete aggregates.

1.2.1. Treatment with High-Voltage Electrical Discharges

The activation of mineral components under conditions of the pulsed electrical breakdown of rock pieces in various liquid media predetermines the improvement of the properties of artificial conglomerates. Low-temperature plasma, formed as a result of a high-voltage spark discharge and the rapid release of electrical energy, acts in the electric pulse technology of the destruction and processing of solids by a working fluid. It has been established that the use of filler obtained by electro pulse technology leads to a noticeable increase in mechanical strength (up to 26.5%). The main reason for increasing the strength of concrete, according to the authors, is the activation of the filler surface by a pulsed discharge. In addition, the electric pulse technology provides a given granulometric composition of the aggregate. The state of the surface determines the physical and chemical processes at the border of the aggregate with the cement stone and ultimately affects the composition and properties of the contact zone. A tendency to hardening of the contact layers of aggregates on electro pulse crushing during hardening, regardless of their mineralogical composition, has been established. This is explained by "the penetration of cement hydration products into numerous pores and microcracks located on the surface of the material activated in the process of electric pulse grinding, followed by the coalescence of this surface with the cement stone" [21–26].

1.2.2. Chemical Activation

Chemical treatment was carried out by the alkaline activation of various types of aggregates to optimize the structure formation and improve the physicomechanical characteristics of composites [27–30]. In [27], "fly ash, bottom ash from municipal solid waste incineration (MSWI BA), and Sidoarjo volcanic silt (Lusi) were used in the manufacture of lightweight aggregates (LWA)", which were activated using NaOH 6M and Na_2SiO_3. The impact of the filler type on the physical properties of the resulting LWAs was studied. "The compressive strength of the mortar was reduced by 6% when replacing 16% by volume of natural fine aggregate with fly ash based LWA. Compared to expanded clay LWA, the properties of the alternative LWAs in this study were slightly, but not significantly, worse. The alternative to LWA becomes attractive when considering that expanded clay LWA requires more energy during sintering" [27]. The study in [28] proposed a new methodology for "the production of LWA by alkaline activation of two different waste powders: digested spent bentonite clay and basalt powder. The results were compared with those obtained for commercial lightweight expanded clay concrete, which is one of the most common LWAs in the construction industry" [28]. Following the presented results, the application of alkali-activated waste powders makes it possible to obtain high-quality environmentally friendly LWA and process waste and save energy during their production [28]. A series of studies in [31–35] were devoted to the use of the mineral bischofite and its influence in the manufacture of cement [31], cement-sand mortar [32], processing of quartz sand [33], as a protection of building structures from biocorrosion [34], as well as the technology processing of bischofite and the prospects for its development on the example of specific deposits [35]. Conclusions have been made about the prospects of using bischofite in construction and its positive effect on the characteristics of the final construction materials and structures [31–35].

1.2.3. UV Activation

Under the action of UV irradiation on the surface of fillers, the number of exchange centers more than doubles, which determines the activity of adsorption interactions in the contact zone of the “filler-binder” system. At the same time, the maximum concentration of adsorption centers does not depend on irradiation parameters. The nature of the change in the hydrophilic–hydrophobic properties of the surface of dispersed materials under the influence of UV irradiation is expressed in a slowdown in the rate of rehydration and a decrease in moisture absorption compared to untreated materials. The dependence of the activity of the surface of the fillers on the time of their exposure after UV irradiation showed that over a period of 45–90 min, the number of active adsorption centers on the surface of the fillers decreases to a minimum value, after which the surface stabilizes [36]. In [37], an analysis was made of the effect of “ultraviolet irradiation of construction sand, which is a filler in a concrete mixture, on the dependence of the strength of concrete on the content of the filler. Ultraviolet irradiation leads to dehydration of the surface of sand particles and the appearance of hydrophobic centers. With an increase in the hydrophobicity of sand in the concrete mixture, the content of free water available for cement hydration increases, and the strength of the cement stone increases” [37]. It was noted in [38] that when replacing 10% of the mass of cement with a modified filler, it is possible to obtain concrete with strength parameters 30–40% higher than those of composites without filler. In addition, due to the influence of UV-modified fillers on the processes of structure formation with an inorganic and organic binder, a more durable composite structure is formed, which significantly improves its physical and mechanical characteristics and increases durability [39].

1.3. Conclusions from the Literature Review

After analyzing the existing known methods of activating placeholders, we note two deficits:

- Firstly, aggregates are activated by separate technologies, which is economically and technologically less feasible when compared with the activation of the total and simultaneous;
- Secondly, most existing methods for activating aggregates, even if they are effective, are costly in terms of labor consumption, material extension, energy intensity, and resource intensity.

In this regard, the most promising way seems to be the chemical activation of concrete aggregates, without dividing them into large and small. Therefore, analyzing the known activation methods, the chemical activation of aggregates using a bischofite solution is more promising. Furthermore, this method is low-resource-intensive, fast enough and convenient in terms of technology, affordable in terms of the raw material base, and effective in pioneering research conducted in this area by previous researchers.

1.4. Main Aim, Research Tasks, and Scientific Novelty

The main aim of this research was to investigate the possibility of activating aggregates with bischofite for new generation concrete. At the same time, it was essential to study the effect of such activation not only on the concrete of a simple structure obtained by vibrating technology but also on more promising modern concrete with a variotropic complex structure, obtained using centrifugal compaction.

Thus, the objectives of the study were:

- Identification of the most effective solutions in the field of technology for the activation of concrete aggregates with bischofite solutions;
- Determination of the prescription–technological concept of such activation, optimal dosages, and the identification of the most rational combinations of initial activation parameters;

- Determination of the most influential technology, in which the activation of the filler with bischofite will give the best increments and increase the performance of not only concrete but the entire reinforced concrete element;
- Determination of the nature of the bischofite influence on aggregates and its influence on the final concrete properties;
- Establishing application dependencies and offering practical recommendations for the construction industry and the construction industry as a whole.

The scientific novelty of this research is the first applied chemical activation of aggregates for concrete with a variotropic structure, made using centrifugal compacting concrete mix technology. The synergistic effect of activating the surface of aggregates and creating a variotropic improved structure of heavy concrete with annular sections can be achieved. Moreover, for the first time, we applied a complex method for improving the properties of concrete by activating inert components, namely concrete aggregates, and, in addition, we applied the technology of dispersed reinforcement, that is, improving the performance characteristics of the element and improving the properties of the concrete itself. Thus, a complex effect was achieved, expressed in improving all composition components and technology.

2. Materials and Methods

2.1. Materials

The experimental stage comprised Portland cement of the CEM I 42.5N brand produced by JSC Novoroscement (Novorossiysk, Russia). The physical and mechanical characteristics of Portland cement are shown in Table 1. Table 2 shows the chemical composition of Portland cement.

Table 1. Physical and mechanical characteristics of Portland cement.

Properties	Units	Values
Residue on a 45 μm sieve	%	3.5
Specific surface area (by Blaine)	cm^2/g	3635
Normal cement paste density	%	27.7
The start of setting	min	138
Setting end	min	187
Compressive strength at the age of 28 days	MPa	52.2
Strength in bending at the age of 28 days	MPa	8.5
Uniformity of volume change	mm	0

Table 2. Chemical composition of Portland cement.

Title of Indicator	Actual Value
Silicon oxide content (SiO_2), %	20.89
Content of aluminum oxide (Al_2O_3), %	4.72
Iron oxide content, (Fe_2O_3), %	4.32
Content of calcium oxide (CaO), %	63.27
Magnesium oxide (MgO), wt. %	2.45
Sulfuric anhydride (SO_3), wt. %	2.81
Alkali oxides (Na_2O), wt. %	1.302
The content of free calcium oxide (CaO_{sv}), %	0.00
Chloride ion (Cl^-), wt. %	0.038
Insoluble residue, %	0.20

Quartz sand produced by Arkhipovsky Quarry JSC (Arkhipovskoye village, Belorechensky district, Krasnodar Territory, Russia) was used as a fine aggregate. The grain composition of sand is shown in Table 3. Table 4 shows the physical and mechanical characteristics of sand.

Granite crushed stone produced by Pavlovsknerud JSC (Pavlovsk, Russia) was used as a large dense aggregate, and expanded clay gravel produced by BELKERAMZIT LLC. (Moscow, Russia) was used as a porous aggregate. The physical and mechanical characteristics of large dense and porous aggregates are presented in Tables 5 and 6.

Table 3. Grain composition of sand.

Residues on Sieves, %	Sieve Diameter, mm						Size Modulus
	2.3	**1.25**	**0.63**	**0.315**	**0.16**	**<0.16**	
Partial	1.52	4.02	26.16	62.05	5.84	0.22	2.32
Full	1.52	5.54	31.7	93.75	99.59		

Table 4. Sand properties.

The Content of Dust and Clay Particles, %	Clay Content in Lumps, %	Bulk Density, kg/m^3	True Density, kg/m^3	Content of Organic and Contaminants
1.2	0.1	1682	2670	Absent

Table 5. Physical and mechanical characteristics of crushed stone.

Fraction	Bulk Density, kg/m^3	True Density, kg/m^3	Crushability, wt. %	The Content of Lamellar and Acicular Grains, wt. %	Void, %
5–20	1430	2.66	11.4	9.5	47

Table 6. Physical and mechanical characteristics of expanded clay gravel.

Fraction	Bulk Density, kg/m^3	True Density, kg/m^3	Strength According to GOST 32496, MPa	Void, %
5–20	480	0.88	2.1	46

Basalt fiber produced by Stroykompozit LLC. was used as dispersed reinforcement. Table 7 presents the physical and mechanical characteristics of the fibers used.

Table 7. Physical and mechanical properties of fibers.

Basalt Fiber	Tensile Strength, MPa	Diameter, m	Fiber Length, mm	Elasticity Modulus, GPa	Density, g/cm^3	Elongation Coefficient, %
	3200	16×10^{-6}	12	70	2.6	3.2

To activate the aggregates, we used aqueous solutions of bischofite produced by Alliance LLC. (Noginsk, Russia), prepared from natural bischofite (see Figure 3) with a density of 1320 kg/m^3. The chemical composition of the dry residue of natural bischofite is presented in Table 8.

Figure 3. Natural bischofite crystals.

Table 8. Chemical composition of bischofite ($MgCl_2 \cdot 6H_2O$).

Name of Indicator	Value
Mass fraction of magnesium ions (Mg^{2+}), %	11.8
Mass fraction of magnesium ions (Mg^{2+}), in terms of $MgCl_2$ $6H_2O$, %	97
Mass fraction of calcium chloride in terms of calcium oxide (CaO), %	0.1
Mass fraction of sulfate ions $(SO_4)^{2-}$, %	1.1
Alkali metal ions, wt. %	0.8
Water-insoluble residue, wt. %	0.2

2.2. Methods

Activation of concrete aggregates with aqueous solutions of natural bischofite was preliminarily performed before other operations for preparing concrete mixtures. First, fine and coarse aggregates were thoroughly mixed with aqueous solutions of natural bischofite for 3 min at room temperature, and the amount of solution taken to activate the aggregates was 4% of their mass. Then the required amount of binder was added, and the resulting mixture was thoroughly mixed until a homogeneous mass was obtained for 3 min.

Special equipment was used for the centrifuged and vibrocentrifuged concrete samples manufacture [39]. In [40–42] the order of molding pieces of concrete is described. The technique for samples produced for determining the integral strength characteristics of centrifuged and vibrocentrifuged concrete is described in [41,42]. The experimental research program is shown in Table 9.

Table 9. Experimental research program.

Composition Number	The Content of Bischofite in 1 L of Solution, g	Concrete Manufacturing Technology	Controlled Parameters
1V	0	Vibration	Cubic compressive strength, MPa ($R_{b,cub}$); Axial compressive strength, MPa (R_b); Tensile strength in bending, MPa (R_{btb}); Axial tensile strength, MPa (R_{bt}); Ultimate strains under axial compression, mm/m $\times 10^{-3}$ (ε_{bR}) Ultimate strains in axial tension, mm/m $\times 10^{-4}$ (ε_{btR}) Elastic modulus, MPa $\times 10^3$ (E_b)
2V	2		
3V	4		
4V	6		
5V	8		
6V	10		
1C	0	Centrifugation	
2C	2		
3C	4		
4C	6		
5C	8		
6C	10		
1VC	0	Vibro-centrifugation	
2VC	2		
3VC	4		
4VC	6		
5VC	8		
6VC	10		

A total of 18 series of samples were manufactured and tested. In each series, a total of 3 cube samples and 9 prism samples were tested. A total of 54 cube samples and 162 prism samples were tested in the study (Figure 4).

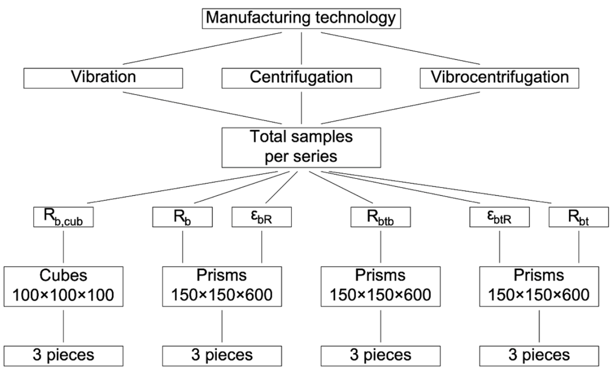


Figure 4. Experiment plan.

"Heavy concrete of class B30 (according to GOST 18105 "Concretes. Rules for control and assessment of strength") was also designed as a control composition for the manufacture of vibrated lightweight fiber-reinforced concrete (LFRC) and the parameters of the composition of the concrete mixture obtained as a result of calculations are given in Table 10" [43].

Table 10. Composition of the concrete mixture.

Parameter	W/C	C, kg/m^3	W, L/m^3	CS, kg/m^3	S, kg/m^3	ρ_{cm}, kg/m^3
Value	0.58	327	190	1315	573	2405

Note: W/C—water-cement ratio, C—cement consumption, W—water consumption, CS—crushed stone consumption, S—sand consumption, ρ_{cm}—concrete mix density.

For the manufacture of centrifuged and vibrocentrifuged LFRC, a composition of heavy concrete of class B30 was developed. "The parameters of the composition of the concrete mixture, obtained as a result of the calculations, are reflected in Table 11" [44].

Table 11. Composition of the concrete mixture parameters.

Parameter	W/C	Absolute Volume of Cement Paste, L	The Absolute Volume of Fillers, L, at the Ratio r = S/CS = 0.4	C, kg/m^3	CS, kg/m^3	S, kg/m^3
Value	0.38	319	1805	400	1290	515

In the manufacture of LFRC using three different technologies, a part of the dense aggregate volume was replaced with the same volume of porous aggregate in an amount of 30% by volume. The density of LFRC ranged from 2070 kg/m^3 to 2180 kg/m^3. The inclusion of basalt fiber in an amount of 3% by weight of cement was applied. Mechanical characteristics under compression, tension, and bending were carried out following the requirements of "GOST 10180. Concretes. Methods for strength determination using reference specimens" [45]. Axial compression tests were carried out following the requirements of "GOST 24452. Concretes. Methods of prismatic, compressive strength, modulus of elasticity and Poisson's ratio determination" [46]. Microstructure analysis was carried out on a microscope ZEISS CrossBeam 340 (Carl Zeiss Microscopy GmbH (Factory), Jena, Germany).

3. Results

The results of the experimental studies of the influence of manufacturing technology and bischofite concentration on the strength and strain characteristics of LFRC are shown in Figures 5–8 and in Tables 12 and 13. The results obtained from testing prototypes of vibrated, centrifuged, and vibrocentrifuged LFRC made on non-activated aggregates are shown in Table 12.

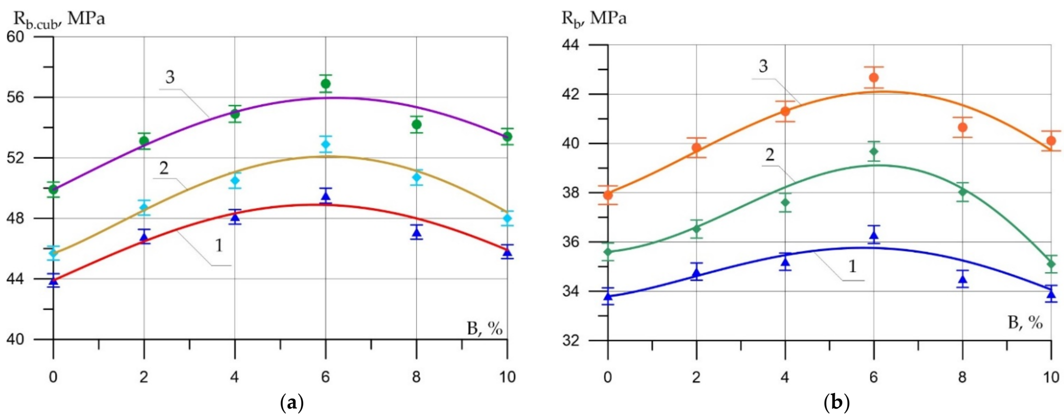
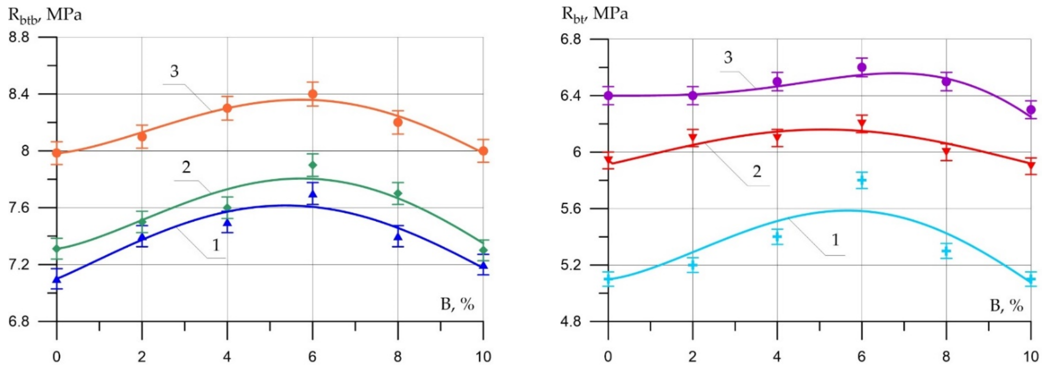
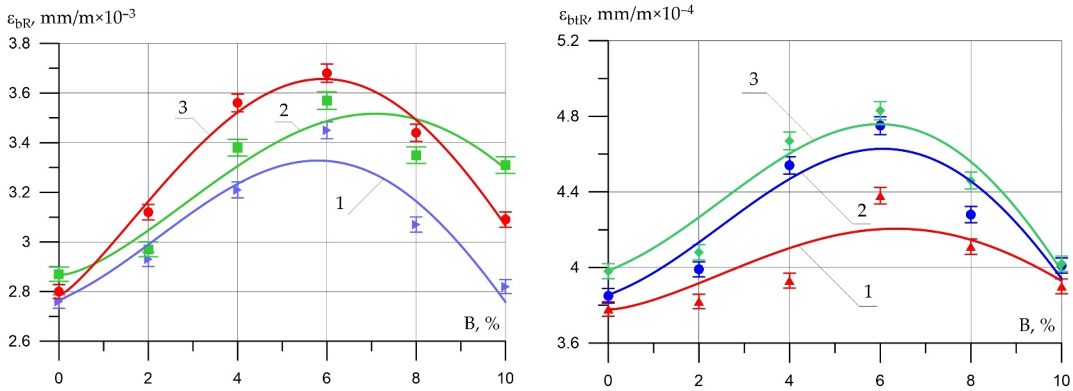


Figure 5. Dependence of (**a**) the cubic strength and (**b**) axial compressive strength of LFRC on the concentration of bischofite (B, %): 1—vibration, 2—centrifugation, 3—vibro-centrifugation.



(**a**) (**b**)

Figure 6. Dependence of (**a**) tensile strength in bending and (**b**) axial tensile strength of LFRC on the concentration of bischofite (B, %): 1—vibration, 2—centrifugation, 3—vibro-centrifugation.



(**a**) (**b**)

Figure 7. Dependence of (**a**) ultimate strains in axial compression and (**b**) ultimate strains in axial tension of LFRC on the concentration of bischofite (B, %): 1—vibration, 2—centrifugation, 3—vibro-centrifugation.

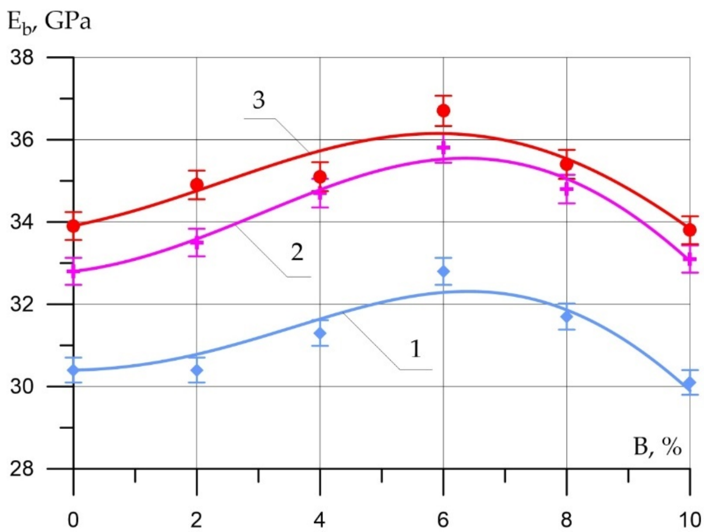


Figure 8. Dependence of the elastic modulus of LFRC on the concentration of bischofite (B, %): 1—vibration, 2—centrifugation, 3—vibro-centrifugation.

Table 12. Values of strength characteristics of prototypes of various types of concrete technology on non-activated aggregates.

Concrete Characteristics	Manufacturing Technology Vibration	Centrifugation	Vibro-Centrifugation
$R_{b.cub}$, MPa	43.9	45.7	49.9
R_b, MPa	33.8	35.6	37.9
R_{btb}, MPa	7.1	7.3	8.0
R_{bt}, MPa	5.1	5.9	6.4
ε_{bR}, mm/m × 10^{-3}	2.76	2.87	2.80
ε_{btR}, mm/m × 10^{-4}	3.78	3.85	3.98
E_b, GPa	30.4	32.8	33.9

Table 13. Values of strength characteristics of prototypes of vibrated, centrifuged, and vibrocentrifuged concrete on activated aggregates.

Concrete Characteristics	Manufacturing Technology														
	Vibration					Centrifugation					Vibro-Centrifugation				
	The Content of Bischofite in 1 L of Solution, g														
	2	4	6	8	10	2	4	6	8	10	2	4	6	8	10
$R_{b,\,cub}$, MPa	46.8	48.1	49.5	47.1	45.8	48.7	50.5	52.9	50.7	48.0	53.1	54.9	56.9	54.2	53.4
R_b, MPa	34.8	35.2	36.3	34.5	33.9	36.5	37.6	39.7	38.0	35.1	39.8	41.3	42.7	40.7	40.1
R_{btb}, MPa	7.4	7.5	7.7	7.4	7.2	7.5	7.6	7.9	7.7	7.3	8.1	8.3	8.4	8.2	8.0
R_{bt}, MPa	5.2	5.4	5.8	5.3	5.1	6.1	6.1	6.2	6.0	5.9	6.4	6.5	6.6	6.5	6.3
ε_{bR}, mm/m × 10^{-3}	2.93	3.21	3.45	3.07	2.82	2.97	3.38	3.57	3.35	3.31	3.12	3.56	3.68	3.44	3.09
ε_{btR}, mm/m × 10^{-4}	3.82	3.93	4.38	4.11	3.90	3.99	4.54	4.75	4.28	4.01	4.08	4.67	4.83	4.46	4.02
E_b, GPa	30.4	31.3	32.8	31.7	30.1	33.5	34.7	35.8	34.8	33.1	34.9	35.1	36.7	35.4	33.8

The results obtained from testing prototypes of vibrated, centrifuged, and vibrocentrifuged LFRC made on aggregates activated with an aqueous solution of bischofite are presented in Table 13.

The dependences of the characteristics of concrete on the content of bischofite are shown in Figures 5–8.

All graphs show an approximation by the synergistic saturation function:

$$Y = C_0 + A\,x^b\,\sin(\omega\,x + \varphi) \tag{1}$$

where Y is the characteristic of concrete; C_0 is the value of the characteristic by saturation at level B = 0, %; A, b and ω are constants; φ is the phase angle.

Dependences of strength and strain characteristics of vibrocentrifugated concrete on saturation with bischofite, obtained as a result of approximation by function (1) using the least squares method, have the form:

$$R_{b.cub} = 49.9 + 5.94\,x^{0.0114}\,\sin(0.254\,x + 0.0) \tag{2}$$

$$R_b = 37.9 + 2.33\,x^{0.333}\,\sin(0.265\,x + 0.12) \tag{3}$$

$$R_{btb} = 37.9 + 0.187\,x^{0.415}\,\sin(0.314\,x + 0) \tag{4}$$

$$R_{bt} = 6.4 + 0.0031\,x^{2.22}\,\sin(0.348\,x - 0.04) \tag{5}$$

$$\varepsilon_{bR} = 2.8 + 0.63\,x^{0.176}\,\sin(0.29\,x - 0.044) \tag{6}$$

$$\varepsilon_{btR} = 3.98 + 0.2\,x^{0.822}\,\sin(0.275\,x + 0.39) \tag{7}$$

$$E_b = 33.9 + 0.586\,x^{0.822}\,\sin(0.273\,x + 0.428) \tag{8}$$

All expressions are presented for vibrocentrifuged concrete, since it has the best characteristics and is of greater interest. Units for strength indicators are MPa, compressive strain

ε_{bR}, mm/m $\times 10^{-3}$, tensile strain ε_{btR}, mm/m $\times 10^{-4}$, elastic modulus GPa. All equations are in good agreement with the experimental data and the coefficient of determination was from 0.9 to 0.98.

From Figures 5–8 it can be seen that with any technology for the manufacture of LFRC—vibration, centrifugation, vibro-centrifugation—the best strength and deformation characteristics were demonstrated by samples of the composition, the aggregates of which were activated with a bischofite solution in an amount of 6 g/L. At the same time, there was a smooth increase to the maximum of the characteristics of LFRC in the range from 0 to 6 g of bischofite, then there was a sharper decrease in the range from 7 to 10 g of bischofite. The maximum focus was in the range of 5.5–6.5 g/L. A further increase in the concentration of bischofite over 8 g/L led to a sharp decrease in the strength and deformation characteristics of LFRC. At values close to 10 g/L, the activation efficiency was 0 or even negative, which indicates the inappropriateness of a further increase in the content of bischofite.

For clarity of comparison of the effect of chemical activation of aggregates with an aqueous solution of bischofite on the deformative characteristics of LFRC, compression diagrams "ε_b-σ_b" and tension "ε_{bt}-σ_{bt}" were plotted for control compositions 1V, 1Ts, 1VTs and experimental compositions 4V, 4Ts, 4VTs with the best deformative characteristics. In addition, stress–strain diagrams are shown in Figures 9 and 10.

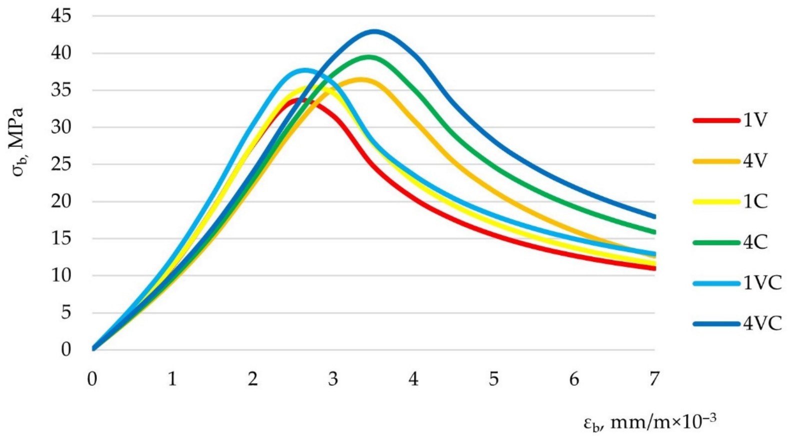


Figure 9. Stress–strain diagram under compression.

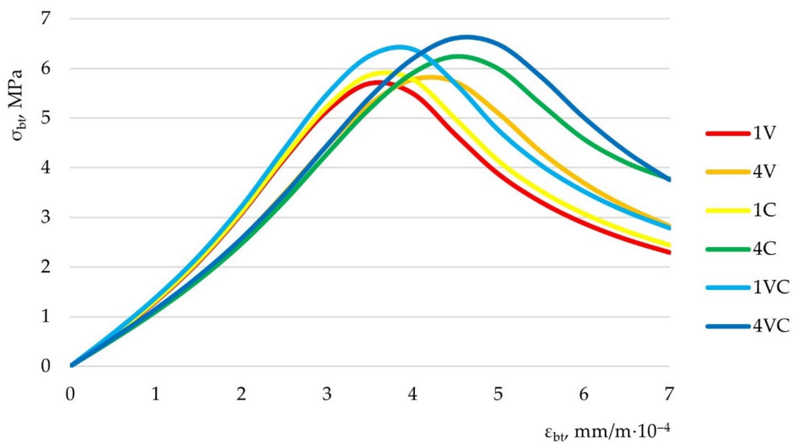


Figure 10. Tensile stress–strain diagram.

It was established that the chemical activation of aggregates with an aqueous solution of bischofite affected the deformation diagrams of LFRC obtained using various technologies, as follows: all peaks of the deformation diagrams of LFRC made on activated aggregates were shifted up and to the right relative to the diagrams of control concrete samples. At the same time, the peak of the deformation diagram of vibrocentrifuged fiber-reinforced LFRC made on activated aggregates was located higher and to the right than the peaks of diagrams of centrifuged and vibrated LFRC containing the optimal concentration of bischofite solution of 6 g/L.

Trends in the strength and strain characteristics of LFB prototypes, manufactured using various technologies, depending on the concentration of bischofite, are shown in Table 14 and are expressed as a percentage compared to control compositions.

Table 14. Change in the strength and strain characteristics of prototypes of LFRC depending on the concentration of bischofite (Δ).

Concrete Characteristics	**Manufacturing Technology**																	
	Vibration						**Centrifugation**						**Vibro-Centrifugation**					
	Change in % (Δ) at the Content of Bischofite in 1 L of Solution, g																	
	0	**2**	**4**	**6**	**8**	**10**	**0**	**2**	**4**	**6**	**8**	**10**	**0**	**2**	**4**	**6**	**8**	**10**
$R_{b.cub}$, MPa	0	+7	+10	+13	+7	+4	0	+7	+11	+16	+11	5	0	+6	+10	+14	+9	+7
R_b, MPa	0	+3	+4	+7	+2	0	0	+3	+6	11	7	−1	0	+5	+9	+13	+7	+6
R_{btb}, MPa	0	+4	+6	+8	+4	+1	0	+3	+4	+8	+5	0	0	+1	+4	+5	+3	0
R_{bt}, MPa	0	+2	+6	+14	+4	0	0	+3	+3	+4	+1	−1	0	0	+2	+3	+2	−2
ε_{bR}, mm/m $\times 10^{-3}$	0	+6	+16	+25	+11	+2	0	+3	+18	+24	+17	+15	0	+11	+27	+31	+23	+10
ε_{btR}, mm/m $\times 10^{-4}$	0	+1	+4	+16	+9	+3	0	+4	+18	+23	+11	+4	0	+3	+17	+21	+12	+1
E_b, GPa	0	0	+3	+8	+4	−1	0	+2	+6	+9	+6	+1	0	+3	+4	+8	+4	0

According to the data on the change in the characteristics of LFRC, shown in Table 14, it was found that the most effective concentration of bischofite was 6 g per liter of solution. As for the solutions made with the bischofite in the amount of 2, 4, and 8 g per liter, their use also increased the strength and deformation characteristics, but they were less effective. The increments were insignificant or absent when using a solution with a bischofite concentration of 10 g per liter. Therefore, it is logical to assume that a further increase in the concentration of the solution would lead to a more significant drop in strength characteristics.

In a quantitative aspect, the improvement in the properties of vibrated LFRC was for cubic compressive strength—13%, for axial compressive strength—7%, for axial tensile strength—14%, for tensile strength in bending—8%, for the modulus of elasticity—8%. The increase in deformation characteristics was for deformation under axial compression—25%, for deformation under axial tension—16%.

The increase in the strength characteristics of centrifuged LFRC was for cubic compressive strength—16%, for axial compressive strength—11%, for axial tensile strength—4%, for tensile strength in bending—8%, for the modulus of elasticity—9%. The strain characteristics increased: for deformation under axial compression—24%, for deformation under axial tension—23%.

Finally, the increase in the strength characteristics of vibrocentrifuged LFRC was for cubic compressive strength—14%, for axial compressive strength—13%, for axial tensile strength—3%, for tensile strength in bending—5%, for modulus elasticity—8%. The strain characteristics increased: for deformation under axial compression—31%, for deformation under axial tension—21%.

Chemical activation of aggregates with an aqueous solution of bischofite of rational concentration promoted an increase in the physicochemical activity of the mineral surface of aggregates in relation to the binder. According to the general theory of conglomerate materials, the structure of concrete is determined by the location of the aggregate grains and the bond energy with the cement stone. At the boundary of their contact, there are microcracks and cavities, which are stress concentrates and contribute to a significant decrease in the strength of concrete. However, the chemical activation of aggregates with an aqueous solution of bischofite provides binding to the surface of the aggregates of polyvalent metal ions, causing an increase in its physical and chemical activity in relation to the cement stone, which contributes to the provision of tighter and stronger contacts, which in turn lead to an increase in the structural strength of concrete.

The effectiveness of adding a bischofite solution of a rational concentration (5.5–6.5 g/L) was experimentally revealed, which correlates with the above. However, the addition of a bischofite solution in excess of a rational concentration, that is, more than 6.5%, led to a negative effect on the characteristics of concrete. This can be explained by the fact that magnesium chloride in high concentrations begins to cause corrosion of the second type. The corrosion process is accompanied by the interaction of magnesium chloride with calcium hydroxide. In this case, the reaction products either dissolve easily or remain at the reaction site in the form of an amorphous mass that does not have astringent properties. At low concentrations of $MgCl_2$ solution, the reaction capacity of the solution is low. Reactions with $Ca(OH)_2$ proceed on the concrete surface. The liberated $Mg(OH)_2$ at the same time forms a film on the concrete surface, which helps to protect the concrete from further destruction.

If we talk about sulfate corrosion, then this is a special type of corrosion that occurs when concrete interacts with water containing sulfates—sulfate compounds (CaSO, NaSO, MgSO, etc.) and destruction manifests itself in the form of swelling and curvature of structural elements. In this case, not only does the removal of components from the volume of cement stone occur, but, on the contrary, as a result of chemical reactions between it and substances coming from the external environment, new compounds are formed, the volume of which exceeds the volume of the solid phase of the cement stone components. A typical example of such corrosion is the formation of a "cement bacillus"—calcium hydrosulfoaluminate. Calcium hydrosulfoaluminates occupy a volume two and a half times larger than the original calcium aluminate. As a result, internal stresses appear, which can exceed the tensile strength of concrete and thereby cause cracking. A feature of the impact of magnesium salt solutions on cement stone is their chemical interaction with hydroaluminates and hydrosilicates that make up the structure of cement stone, which leads to an increase in volume and strong cracking. The low density of concrete, and the presence of cracks and voids can lead to the rapid destruction of concrete with this type of corrosion. However, according to GOST 31384 "Protection of concrete and reinforced concrete structures against corrosion. General technical requirements" water is considered aggressive for this type of corrosion if the content of soluble salts in it exceeds 10 g/L; therefore, the use of a magnesium salt solution with less salt content as an activator of the surface of inert aggregates will not have a negative effect and activate the process of salt crystallization in the pores of concrete.

Figures 11–16 show SEM images of the structure of hardened cement mixtures. For microscopic examination, samples of cement mixtures were taken from the structure of a destroyed concrete composite made using vibrating technology with different concentrations of bischofite additive.

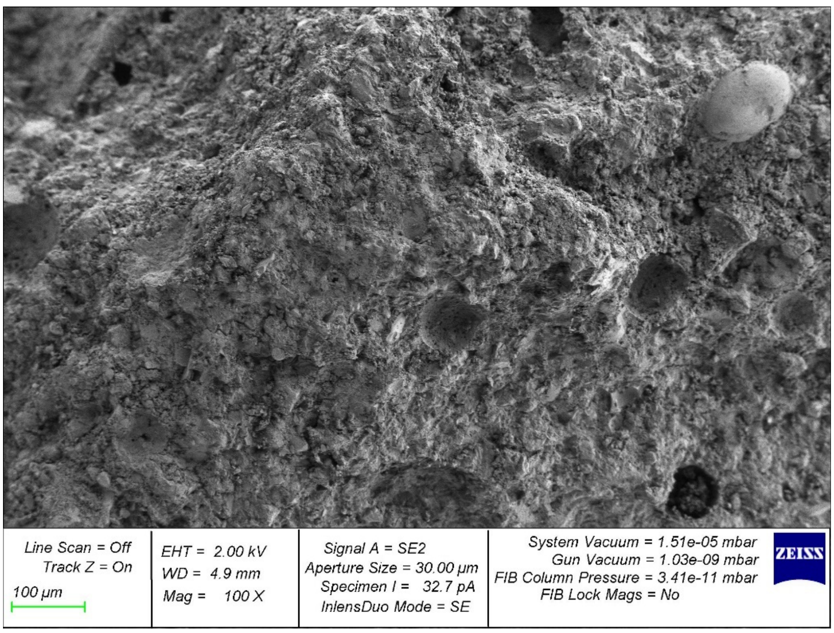


Figure 11. SEM image of the structure of the hardened cement mixture of composition 2V.

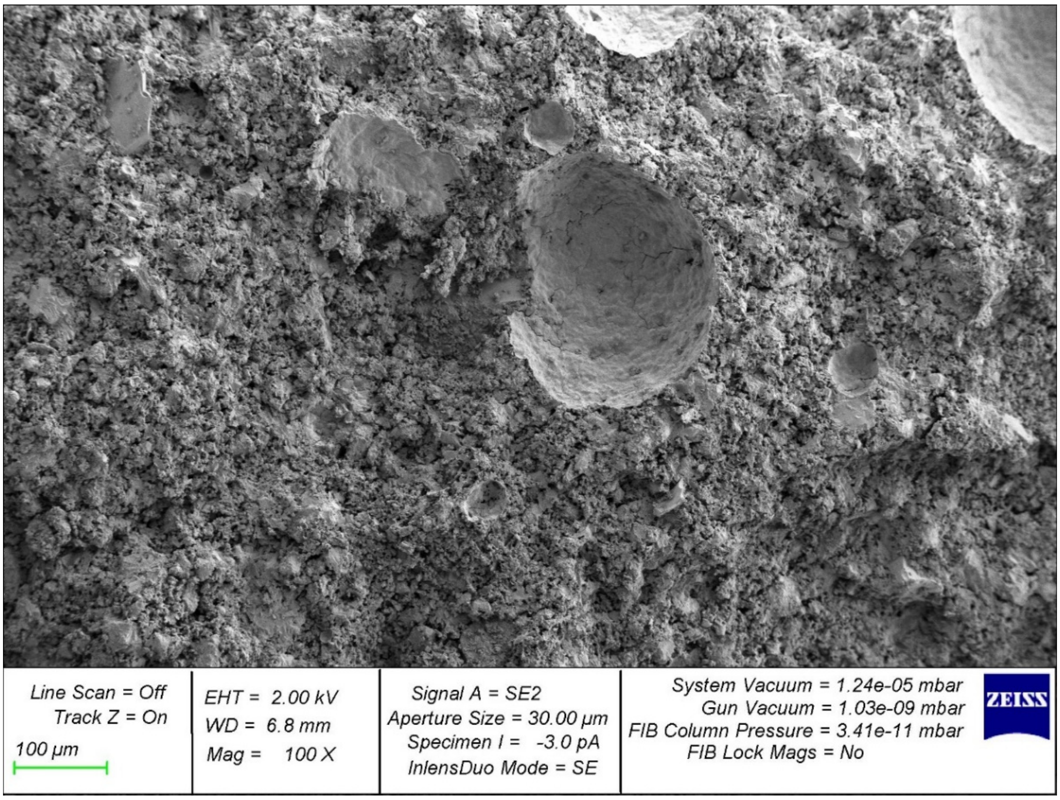


Figure 12. SEM image of the structure of the hardened cement mixture of composition 3V.

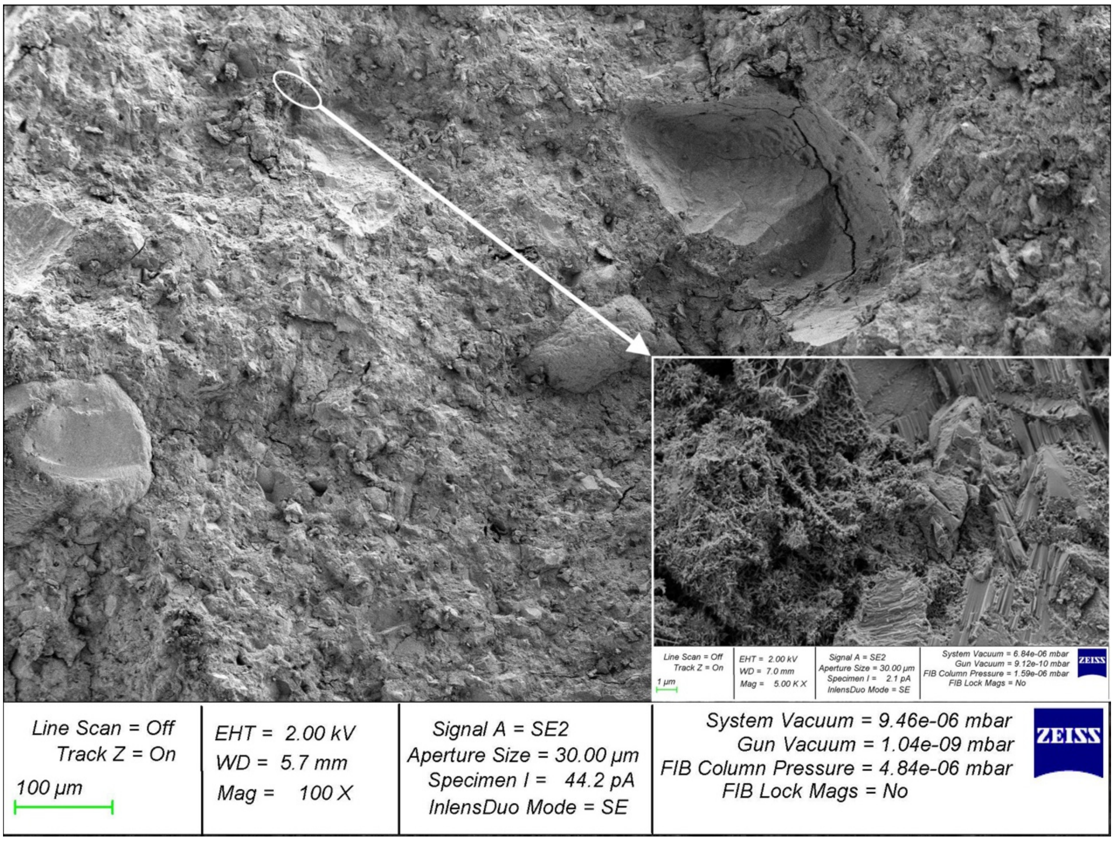


Figure 13. SEM image of the structure of the hardened cement mixture of composition 4V with a fragment of a magnification of 5000 times.

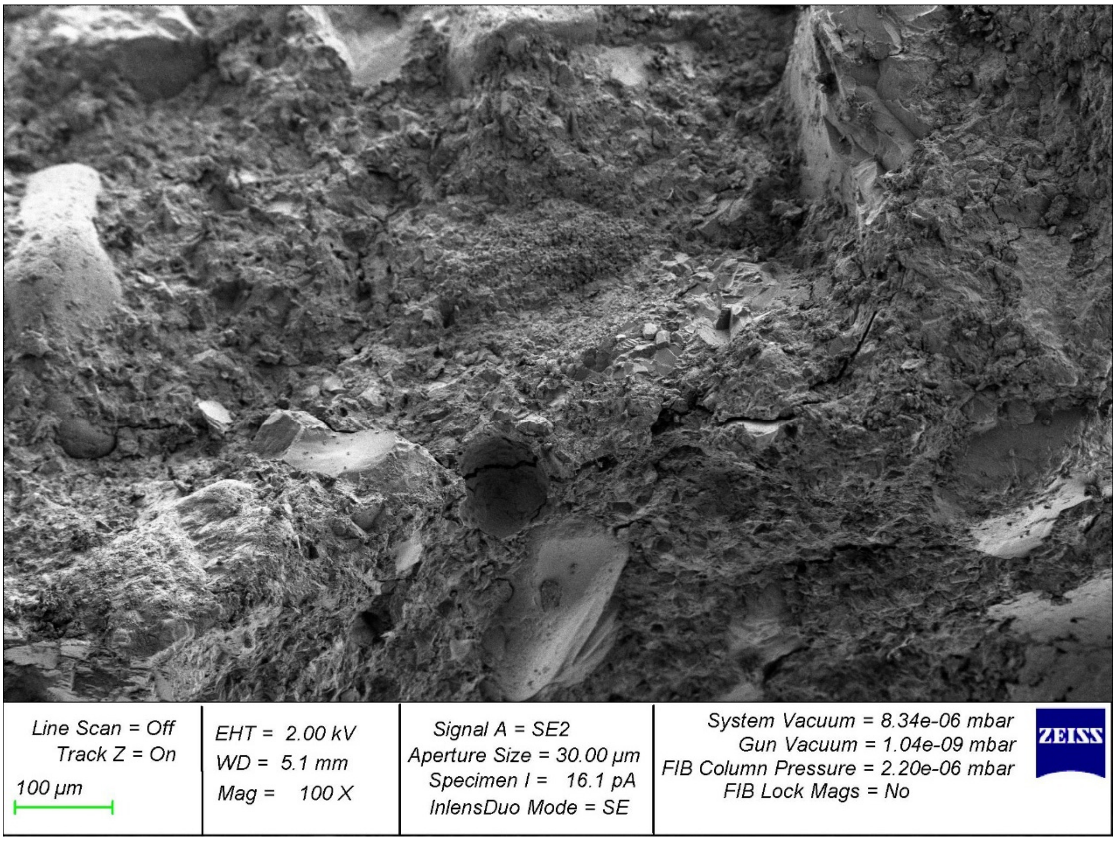


Figure 14. SEM image of the structure of the hardened cement mixture of composition 5V.

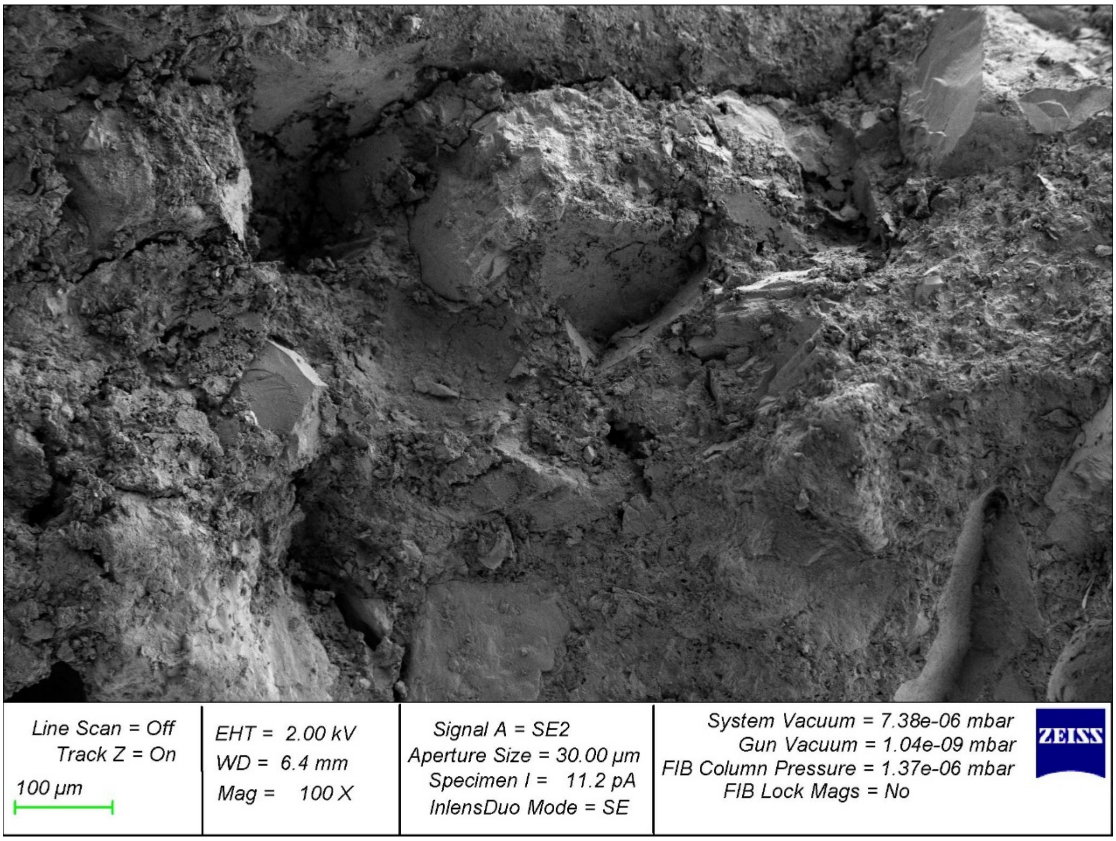


Figure 15. SEM image of the structure of the hardened cement mixture of composition 6V.

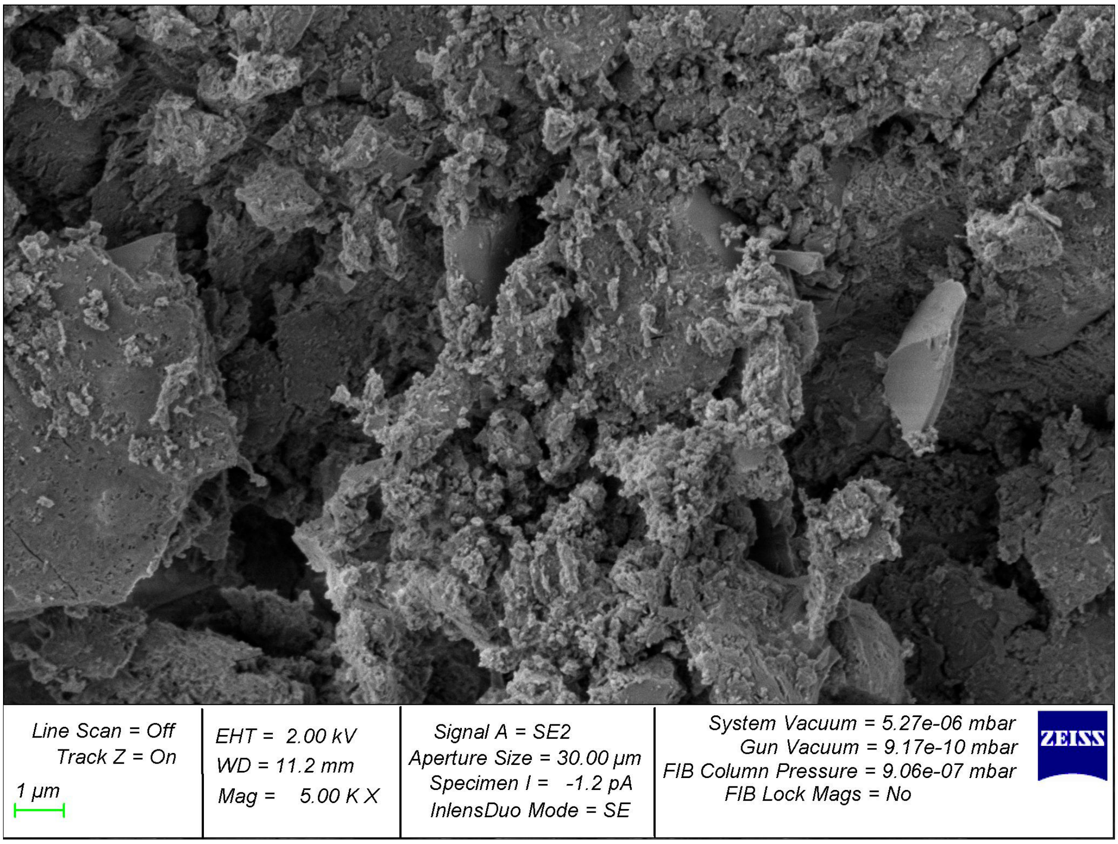


Figure 16. SEM image of the structure of the hardened cement mixture of composition 1V.

These micrographs clearly reflect the structure of the studied experimental compositions. In Figures 11–14, the structure of the hardened cement paste is homogeneous and dense with a small number of pores and microcracks. In Figure 13, at a magnification of 5000 times, the compaction of the structure of the hardened cement paste with a concentration of bischofite solution of 6 g/L is clearly visible in comparison with the structure of the vibrated concrete of the control composition shown in Figure 16.

As for the structure of the sample of composition 6B (Figure 15), it is less dense with a large number of micropores of irregular shape and microcracks. Thus, the processing of aggregates with an aqueous solution of bischofite at its concentration of 2–8 g/L (compositions 2V–5V) is the most optimal. This activation technology provides a more active process of calcium silicate hydrate gel formation at the interfacial boundaries, due to which the composite material becomes stronger. However, when using solutions with a dosage of bischofite that exceeds the optimal value, the opposite effect was observed. Thus, the analysis of the microstructure confirmed the above results of testing concrete for strength and deformation characteristics.

4. Discussion

To determine the scientific and practical significance of our study, it was necessary to compare it with the results of other authors. For greater clarity, we summarize in Table 15 an analytical comparison of previously known and proposed activation methods, noting their advantages and disadvantages.

It should be noted that the chosen method of activating aggregates by treating them with an aqueous solution of bischofite makes it possible to achieve almost the same increase in mechanical characteristics as more traditional methods of concrete modification, for example, the use of various chemical and mineral additives [27,28,43,44,47,48].

Table 15. Comparative analysis of known and proposed methods for activating concrete aggregates.

Fillers Activation Method	Advantages	Disadvantages
Electrophysical influences [21–26]	Improving the strength characteristics of concrete	High energy, resource, material, labor costs Technological complexity
Ultraviolet irradiation [36–38]	Improving the strength characteristics of concrete	Expensive equipment High energy, resource, material, labor costs
Chemical treatment in combination with dispersed reinforcement [27–35]	Improving the strength and strain characteristics of concrete Intensification of hydration processes Low cost	Low degree of knowledge on the criteria of applicability to various technologies

It is necessary to analyze the following main scientific results obtained in the course of theoretical and experimental studies. Firstly, in the development of theories and technologies previously developed by the authors of works [28–32], the effectiveness of the activation of inert concrete aggregates with bischofite solutions was tested and confirmed. Secondly, the optimal value of the concentration of this solution of 6 g/L was phenomenologically set and experimentally proved. Thirdly, we conducted a study of the three-factor influence on the properties of concrete by the recipe, technology, and constructive structure. Thus, the chemical activation of concrete aggregates by bischofite acts as a prescription factor. The method of concrete production is a technological factor. Finally, a structural factor is additional dispersed reinforcement and replacing a part of coarse aggregate from dense to porous. That is, the hypothesis of potential synergetic effects arises when choosing the most optimal technology and the most optimal concentration of bischofite solution for obtaining concrete with the best characteristics was studied.

The following reasons explain the effects on the increase in quality indicators depending on the three-factor influence. As is known and was shown by us earlier in previous works [42,44,47], firstly, manufacturing technology has a considerable influence on the concrete properties. Considering the increasing requirements for the quality and reliability of reinforced concrete products and structures, including increased responsibility, their manufacturing technologies can differ significantly depending on the type of buildings and structures. Thus, our study involved comparing the effectiveness of the proposed activation methods for various initial conditions. Thus, vibrocentrifuged concrete has an improved variatropic structure in comparison with centrifuged and even more so with vibrated concrete. With a rational ratio of recipe–technological factors, such concrete has the best combination of physical–mechanical, strength, strain, and structural characteristics. High indicators of the qualitative characteristics of such concrete are due to its structural features, which have enhanced variatropy in terms of the working outer and middle layers of a conditional three-layer section. In many ways, this variatropy of the structure and properties over the cross-section of the ring element is due to the nature of the drift of aggregates in the body of the concrete mixture. When the aggregates are activated with bischofite, the most active surface of the inert components of the aggregates can be obtained, which provides the best interaction and adhesion of these aggregates with cement stone, which is most important for variotropic structures due to the non-trivial drift of aggregates in such concrete, the concentration of heavy aggregate and large grains in the outer the main layer of an annular section element. Thus, the filling—the frame and the supporting frame of the element—is imparted, and at the same time, the surface and other activity of the fine filler is improved, which is distributed over the entire section of the element, which makes it possible to achieve the perfect structure and the best properties with the most significant increments relative to the base control samples. However, with monolithic concreting and in different conditions, the use of vibrated concrete is the most effective. That is, the study aimed at the maximum universalization of the developed proposals. The mechanism of strengthening and improving the structure of vibrated concrete is similar to that described above.

Secondly, the constructive–structural factor used by us in the study–additional dispersed reinforcement and replacement of part of the coarse aggregate from dense to porous—

allowed us to achieve improved strength and greater operational versatility of concrete by giving it a more ductile fracture pattern and enhancing its ability to work in non-trivial complex conditions [14,40,43,44,48–50]. Thus, with structural and structural improvements in concrete, due to the factors of aggregates, their additional chemical activation contributes to the achievement of a synergistic effect following the mechanism for increasing their surface activity and drift characteristics during concrete structure formation. Thus, the study has demonstrated the theoretical validity and applied prospects for using new improved LFRC with the chemical activation of aggregates.

In our study, the following innovations are proposed: these are conceptual innovations related to formulation and technological factors; namely, the use of the combined activation of fine and coarse aggregates for one type of activation. This is a prescription aspect, expressed in the quantitative and qualitative expression of the components used not only for concrete, but also for the activator itself. This is also a technological aspect, expressed in the development of a methodology for carrying out activation and features of the technological process for the manufacture of concrete, in turn, made using various technologies on activated aggregates; Finally, this is a constructive aspect, expressed in dispersed reinforcement and a significant change in the characteristics of concrete due to additional fiber, which plays the role of dispersed reinforcement in this concrete. Thus, having conducted complex studies and analysis of the experimental and theoretical results we note the following:

- In a qualitative aspect, our study differs from previous studies [21–38] due to the a significant reduction in material, resource, labor, and time costs for activation, reaching 20%;
- From the point of view of formulation and technology, as well as a constructive solution for reinforcing with fiber reinforcement, our results can be evaluated by the difference in increments and changes in the strength and deformation characteristics of the resulting concrete. With a bischofite content of 6 g in 1 L of solution, the strength characteristics increased to 17%. At the same time, concrete obtained using centrifugation and vibro-centrifugation technologies showed the best result. In terms of deformability, vibrocentrifuged concrete demonstrated the best performance. Deformations in compression and tension increased by 31% and 21%, respectively. These acquired properties of activated concrete make it more technological and versatile in terms of operation. In previous works [21–38], the main emphasis was placed exclusively on increasing strength, which simultaneously gave the concrete a more brittle fracture character and reduced its damping capacity, which can be effective under certain and frequently occurring types of loads.
- In terms of applicability and the possibility of introducing the technology into real practice, our results, expressed in the creation of new materials and the receipt of new technologies, significantly exceeded previously known analogues and allows, according to preliminary estimates of industrial partners, to achieve savings in manufacturing due to a significant reduction in defects and an improvement of design properties and, thus, the possibility of reducing the working sections of reinforced concrete elements made of such concrete and the effect of economic efficiency, which reached 25–27%.

5. Conclusions

As a result of the research, several scientific and practical results have been achieved.

An activation technology for variotropic concrete was proposed for the first time by treating aggregates with bischofite. Its optimal qualitative and quantitative parameters were determined and substantiated. As a result, new dependences of the properties of concretes with the use of activated aggregates on the recipe were obtained. In addition, existing theoretical concepts, and practical recommendations on the chemical activation of aggregates in non-traditional centrifugally compacted concrete with a variotropic structure were developed.

New recipes and technological proposals for the manufacturing industry were developed in this research work. It was established that the activation of both fine and coarse aggregates of concrete with aqueous solutions of natural bischofite at a concentration of 6 g (in terms of dry matter) per 1 L of water is the most rational and provides the maximum increase in strength characteristics and the best values of deformation characteristics.

Strength characteristics (compressive strength) increased up to 16%. Strains in compression and tension increased by 31% and 21%, respectively. The modulus of elasticity increased to 9%. The analysis of the microstructure confirmed the effective dosage of the aqueous solution of bischofite.

The achieved results make it possible to solve the technological problem of searching for low energy, resource-, material-, and labor-intensive technology for the activation of inert components of concrete up to 20%.

A new improved LFRC was created, and new technology was proposed that makes it possible to achieve savings in manufacturing by significantly reducing rejects and improving structural properties and, thereby, the possibility of reducing the working sections of reinforced concrete elements made from such concrete, that is, the effect of economic efficiency, reaching 25–27%.

The proposed activation technology with a bischofite solution as applied to the concrete of a complex variotropic structure makes it possible to optimize the production of reinforced concrete products and structures by increasing the strength of the latter or by reducing cement consumption and ensuring the environmental friendliness of the production of concrete and concrete products.

Author Contributions: Conceptualization, S.A.S., E.M.S. and A.N.B.; methodology, S.A.S., E.M.S. and D.E.; software, S.A.S., E.M.S., A.N.B. and N.B.; validation, S.A.S., E.M.S. and A.N.B.; formal analysis, D.E., S.A.S. and E.M.S.; investigation, L.R.M., S.A.S., E.M.S., A.N.B.; resources, B.M.; data curation, S.A.S., E.M.S. and D.E.; writing—original draft preparation, S.A.S., E.M.S. and A.N.B.; writing—review and editing, S.A.S., E.M.S. and A.N.B.; visualization, S.A.S., E.M.S., A.N.B. and N.B.; supervision, L.R.M. and B.M.; project administration, L.R.M. and B.M.; funding acquisition, A.N.B. and B.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The study did not report any data.

Acknowledgments: The authors would like to acknowledge the administration of Don State Technical University for their resources and financial support.

Conflicts of Interest: The authors declare no conflict of interest.

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