



Article

Green Cement Innovations: Use of Pillared Clays to Increase the Environmental Friendliness and Durability of Cement Materials

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Abstract

Cement production is associated with substantial carbon dioxide (CO₂) emissions due to the high material and energy intensity of Portland clinker manufacture. Partial clinker replacement with supplementary cementitious materials is one of the most promising strategies for reducing the carbon footprint of cement; however, the thermal activation of aluminosilicate raw materials does not always yield highly reactive products. In this study, a pillaring approach is proposed as a controlled method for modifying the structure of clays and unlocking their latent reactivity. Different clay types—namely, kaolinitic, montmorillonitic, and illite–chlorite clays—were sequentially treated with an aluminum sulfate solution and calcined at 650 °C. Their phase composition and microstructure were characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM), while specific surface area was determined by BET analysis and pozzolanic activity. The results showed that pillaring doubled the specific surface area of montmorillonitic (2:1) and illite–chlorite (2:1:1) clays. Replacing 30% of clinker with pillared clays and limestone increased the compressive strength to 86.5 MPa and the flexural strength to 34.6 MPa. The developed low-carbon composite cements also exhibited high durability: the density of the hardened cement mortar increased to 2.410 g/cm³, the strength loss after 200 freeze–thaw cycles decreased to ≤5.5%, and the sulfate resistance coefficient (K_s) increased to 0.98 (with minimal expansion of the samples <0.02%). The proposed approach makes it possible to reduce the carbon footprint of cement by 25–30% while enabling the use of locally available raw materials for the production of competitive low-carbon green cements. Reported reductions of this order are broadly consistent with the known effect of lowering clinker content through supplementary cementitious materials in blended cement systems.



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1. Introduction

Cement and concrete production form the foundation of the construction industry [1]. In 2025 alone, global cement production reached 3.8 billion metric tons, while 30 billion tons of concrete are produced and used annually, which is three times more than 40 years ago [2]. Cement production is associated with enormous carbon dioxide (CO₂) emissions—about 4

billion metric tons of CO₂, accounting for approximately 8% of total global emissions [3]. It is well known that greenhouse gases affect climatic conditions [4], and researchers worldwide are seeking ways to reduce greenhouse gas emissions, including those associated with cement production [5].

There are various ways to reduce carbon dioxide emissions in cement production, including the search for alternative fuels for Portland cement clinker burning, the use of carbon capture and storage technologies, the partial replacement of clinker with mineral additives, the reuse of recycled concrete, and others [6–9].

The most promising and straightforward approach to reduce the carbon footprint is to lower the clinker factor of cement by replacing Portland cement clinker with supplementary cementitious materials and complex additives based on them [10].

In addition to the environmental aspect, since the mid-20th century there has been an urgent need to reduce the cost of cements and concretes based on them, as well as to improve their durability [11–14]. In this regard, most modern studies in the field of binding materials are devoted to investigating the properties of composite cements in which the clinker fraction can be replaced with a wide variety of additives, such as metakaolin, silica fume, granulated blast furnace slag, fly ash, and others [15–18]. Although the first references to composite binders date back to around 5000 BC [19,20], the production of such materials is still at the development stage worldwide [21].

Furthermore, modern studies of low-carbon cements produced using the LC3 technology prove the wide applicability of these binders [22–24]. Composite cements have proven highly effective in earthquake-resistant construction due to their increased fracture toughness and ability to restrain the propagation of main cracks [25,26]. Low-carbon cements can be successfully used in the construction of transport infrastructure facilities and hydraulic structures, where sulfate resistance and durability in aggressive environments are critically important [27,28].

A distinct environmental advantage of LC3 systems is their ability to immobilize heavy metals [29]. The high pozzolanic activity of the heat-treated clay promotes the formation of additional C–A–S–H-type hydrates, which effectively bind lead, cadmium, and zinc ions into insoluble hydroxo- and carbonates. This process prevents their migration into the environment from construction structures or during the disposal of man-made waste [30].

Among the many possible additives, thermally treated aluminosilicates have gained considerable attention due to their high pozzolanic activity [31–34]. Owing to this, it is possible to reduce the clinker factor of cement to 0.4–0.5 while maintaining the required physical and mechanical characteristics of the final product [35–37]. Conventional thermal treatment does not always make it possible to achieve maximum activity for all clay types [38]. This is because aluminosilicates represent one of the largest groups of silicates, whose properties and structure vary significantly even within a single deposit [39,40]. Therefore, each clay type requires an individual approach to selecting the optimal thermal treatment regime [19,34,41,42]. The pozzolanic activity of clays is often evaluated against a reference material—metakaolin, which is known for its high pozzolanic activity [43–45]. Nevertheless, reproducing such activity in another clay, for example, montmorillonitic clay, is extremely difficult because of differences in structure and composition. If a producer were to rely exclusively on kaolin clays in the manufacture of composite cements, this would create serious difficulties and lead to a sharp increase in resource costs, making the process economically unjustified. Therefore, studies are being conducted worldwide to determine the optimal thermal treatment regimens for various aluminosilicates—both natural and industrial—in order to broaden the range of applicable additives [40,46–49].

According to the structure of the elementary layer, all aluminosilicates can be divided into three major subgroups [50–52]: the kaolinite group 1:1, in which the structural layer

of the clay mineral consists of one tetrahedral sheet and one octahedral sheet (Figure 1a); the bentonite or montmorillonite group 2:1, consisting of two tetrahedral sheets and one octahedral sheet (Figure 1b); and the chlorite group 2:1:1, consisting of two tetrahedral sheets and two octahedral sheets (Figure 1c).

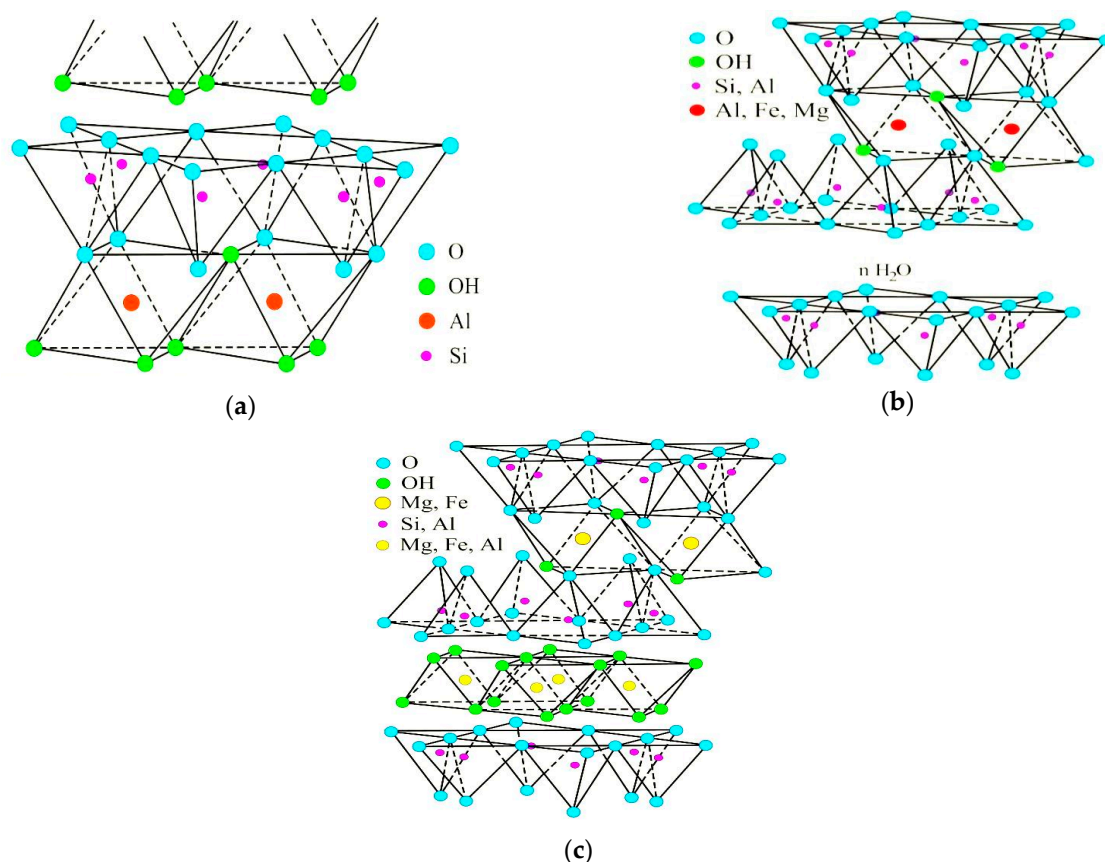


Figure 1. Structure of clay minerals: (a) Kaolinite; (b) Montmorillonite; (c) Chlorite.

In addition, so-called mixed-layer aluminosilicates are widespread in nature (accounting for about 70% of all natural clays) [53–55], the structure of which is formed by the ordered or disordered alternation of two or more layer types.

The diversity of the structure, morphology, and properties of aluminosilicates requires an individual approach in each case, including careful selection of the calcination temperature and duration, as well as the use of special activators, such as salt and hydroxide solutions of different nature and concentration. In addition, 1:1 aluminosilicates, i.e., kaolinitic clays, are not suitable for certain applications, although until a certain time they were considered the most active and highly efficient pozzolanic additives [56–59].

One of the promising methods for treating aluminosilicates, both natural and industrial, is pillaring [60,61]. Pillaring is a method for modifying the structure of clays at high temperatures that makes it possible to introduce inorganic compounds into the interlayer space [62–64]. This process makes it possible to expand the interlayer space of the aluminosilicate and increase its sorption capacity, which should positively affect its pozzolanic activity. At the same time, clays with a 1:1 structural type (kaolinitic clays) are in fact not susceptible to this process because of their strong interlayer bonds [65–67]. Pillaring of bentonitic, montmorillonitic, and illitic clays is used to produce catalyst-adsorbents [68–71]. However, to date, this method has not been applied in the construction industry to obtain supplementary cementitious materials.

The mechanism for increasing the reactivity of clays using the pillaring method is based on three successive physicochemical processes [63–67]:

1. Intercalation and the formation of polynuclear hydroxo complexes (PHC). When clay is mixed with a solution of a transition metal salt (for example, aluminum sulfate), intercalation occurs—the insertion of cations into the interlayer space. In an aqueous medium with controlled pH, Al^{3+} cations undergo hydrolysis and polymerization, forming stable multinuclear clusters—polynuclear hydroxo complexes $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. These large “supermolecules” mechanically push apart the layers of the clay mineral.
2. Interlayer expansion (“nano-reinforcement”). Subsequent heat treatment (650 °C) leads to the dehydroxylation of these complexes and the natural clay. The PAGCs are destroyed, forming metal–oxide clusters that are firmly bound by oxygen bridges within the clay. These bridges (“pillars”) act as molecular spacers, preventing the layers from coming back together. For swelling clays (Figure 1b,c) of the 2:1 type (bentonite, montmorillonite), this is critically important: without pillars, their specific surface area decreases during firing due to irreversible aggregation of the flakes, while with pillars it nearly doubles due to the opening of the internal basal planes [62–64].
3. Overcoming the limitations of kaolinite (group 1:1). For the production of classic low-carbon cements LC3, metakaolin (heat-treated kaolinite) is used. Kaolinite (Figure 1a) has a rigid structure of hydrogen bonds between layers, which hinder the intercalation of large cations. Pillaring allows this limitation to be bypassed. By applying the method to mixed-layer clays of the 2:1 type (montmorillonite) or 2:1:1 (illite–chlorite), raw materials that were previously considered unsuitable for producing highly active pozzolanic additives are activated. The high charge density of the Al^{3+} cation ensures the formation of stronger oxygen bridges, creating a thermally stable microporous structure.

In this regard, the aim of this work is to establish the fundamental relationships between the microstructure of a cement matrix modified with pillared aluminosilicates, its macroscopic performance characteristics, and the environmental profile of the material.

The authors believe that the use of pillared clays as supplementary cementitious materials will make it possible to reduce the clinker factor of cement and improve its physical and mechanical properties, such as strength, durability, corrosion resistance, and frost resistance. In addition, it will be possible to expand the raw-material base for the production of supplementary cementitious materials.

Based on this, the following scientific hypothesis is proposed. The incorporation of optimally selected pillared aluminosilicates into the cement matrix will lead to a synergistic strengthening effect due to two mechanisms:

1. Physical nano-reinforcement, in which clay pillars act as nucleation centers that hinder the growth of microcracks and their coalescence.
2. Chemical pozzolanic activity, in which the amorphous phases of the clay actively react with calcium hydroxide ($\text{Ca}(\text{OH})_2$), forming an additional amount of calcium silicate hydrates (C–S–H) and calcium aluminate hydrates (C–A–H), which will result in structural densification and a reduction in total porosity.

2. Materials and Methods

2.1. Raw Materials

Three types of natural aluminosilicates were selected as raw materials for the synthesis of pillared clays: kaolinitic clay (Zhuravliny Log deposit, Plast, Chelyabinsk Oblast, Russia), montmorillonitic clay (Gurovsky quarry, Aleksinsky District, Tula Oblast, Russia), and

illite–chlorite clay (mixed-layer clay, Bolshevik field, Volsk, Saratov Oblast, Russia), the chemical compositions of which are presented in Table 1.

Table 1. Chemical composition of natural clays.

Marking	Content	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	R ₂ O
Clay K	Kaolinite	69.45	29.84	0.66	-	-	0.05	-
Clay M	Montmorillonite	57.79	26.21	5.42	6.32	1.93	-	2.33
Clay I	Illite–chlorite	71.57	17.86	4.30	4.01	1.43	0.18	0.65

Sample preparation included several successive stages of thermal and mechanical treatment. Primary drying of all clay materials was carried out in a Binder drying oven at 80–90 °C for 1 h in order to remove physically bound moisture. The dried samples were then mechanically ground until complete passage through an 80 µm sieve to ensure a homogeneous particle size distribution. After this, a thermal activation stage (firing) was carried out at T = 650 °C for 1 h. Thermally activated powders (pillared clays) were then introduced into the cement systems.

Commercial metakaolin (LLC “Geostyle”, Moscow, Russia) was used as the reference material for the comparative evaluation of the pozzolanic activity of the clays under study. The chemical composition of this sample is presented in Table 2.

Table 2. Chemical composition of metakaolin.

Aluminosilicate	The Content of Oxides, %						
Metakaolin	SiO ₂ 57.09	Al ₂ O ₃ 40.5	Fe ₂ O ₃ 0.9	CaO 0.5	MgO 0.7	SO ₃ 0.15	R ₂ O 0.16

The use of commercial metakaolin as the control sample is justified by its well-known high reactivity toward calcium hydroxide, which makes it possible to objectively assess the activation efficiency of the clay minerals under study.

To produce low-carbon cements, additive-free Portland cement (pure ordinary Portland cement, HeidelbergCement Rus LLC, Moscow, Russia) corresponding to strength class 52.5 N (EN 197-1:2011 “Cement—Part 1: Composition, specifications and conformity criteria for common cements” [72]; class CEM I 52.5 N) was used. This type of cement does not contain mineral additives; it consists of 97.1% Portland cement clinker and 2.9% gypsum stone (for regulating the setting time of cement). The mineralogical composition of the clinker used is presented in Table 3.

Table 3. Mineralogical composition of cement.

Type of Cement	Content of Clinker Minerals, %				
CEM I 52.5 N	C ₃ S 65.2	C ₂ S 13.5	C ₃ A 5.2	C ₄ AF 13.2	CaSO ₄ ·2H ₂ O 2.9

To produce a “green” composite cement (Figure 2), natural limestone was used. This material is characterized by a high calcite (CaCO₃) content, the mass fraction of which in the raw material was 98%.

Cement with pillared clays without limestone was obtained in a similar manner.

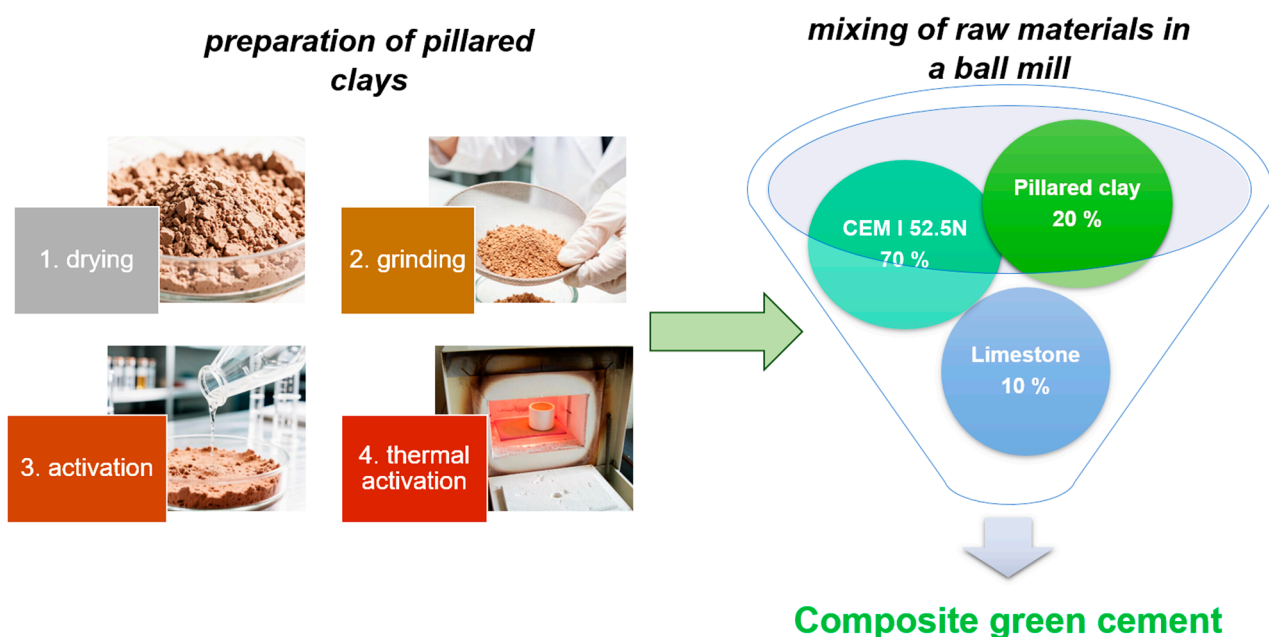


Figure 2. Production of composite «green» cement.

Modification of Aluminosilicates by the Pillaring Method

Aluminosilicates were subjected to both classical heat treatment and pillaring using various salt solutions. The studied samples are presented in Table 4.

Table 4. The studied clay compositions.

Clay	Type and Conditions of Processing	Marking
Kaolinite	Natural	Clay K
	Heat treatment at 550 °C	Clay K-550 °C
	Heat treatment at 600 °C	Clay K-600 °C
	Heat treatment at 650 °C	Clay K-650 °C
	Pillaring with aluminum sulfate	Pillared Clay K or Pillared Clay K- $\text{Al}_2(\text{SO}_4)_3$
	Pillaring with aluminum chloride	Pillared Clay K- AlCl_3
Montmorillonite	Pillaring with iron sulfate	Pillared Clay K- $\text{Fe}_2(\text{SO}_4)_3$
	Natural	Clay M
	Heat treatment at 600 °C	Clay M-600 °C
	Heat treatment at 650 °C	Clay M-650 °C
	Heat treatment at 700 °C	Clay M-700 °C
	Pillaring with aluminum sulfate	Pillared Clay M or Pillared Clay M- $\text{Al}_2(\text{SO}_4)_3$
Illite–chlorite	Pillaring with aluminum chloride	Pillared Clay M- AlCl_3
	Pillaring with iron sulfate	Pillared Clay M- $\text{Fe}_2(\text{SO}_4)_3$
	Natural	Clay I
	Heat treatment at 650 °C	Clay I-650 °C
	Heat treatment at 700 °C	Clay I-700 °C
	Heat treatment at 750 °C	Clay I-750 °C
	Pillaring with aluminum sulfate	Pillared Clay I or Pillared Clay I- $\text{Al}_2(\text{SO}_4)_3$
	Pillaring with aluminum chloride	Pillared Clay I- AlCl_3
	Pillaring with iron sulfate	Pillared Clay I- $\text{Fe}_2(\text{SO}_4)_3$

The pillarization process was optimized by varying intercalating solution concentration, kiln holding time, and firing temperature. These parameters were determined in a series of preliminary studies.

The pillaring method was used to modify the structure of the aluminosilicates (Figure 3).

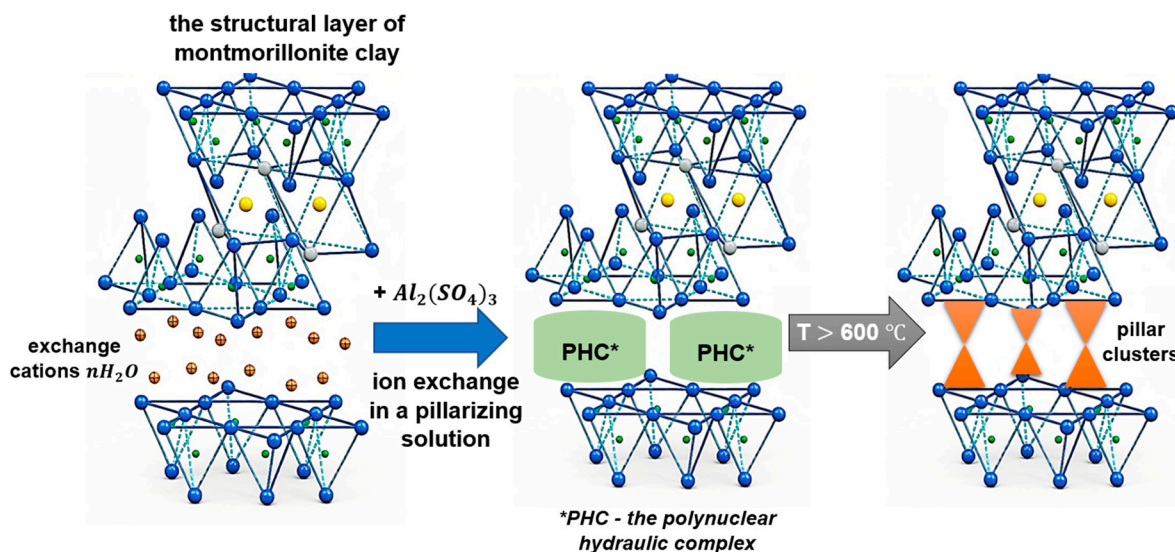


Figure 3. Pillaring scheme showing the formation of pillar clusters during the calcination of aluminosilicates.

Salts of almost any transition metals with a charge of Me^{2+} and higher can serve as precursors for the pillaring solution, since all of them are capable of polymerization as a result of hydrolysis. This article examines the activity of clays with solutions (Russia, LLC “MCEC”, Moscow, Russia) of aluminum sulfate ($Al_2(SO_4)_3$), iron sulfate ($Fe_2(SO_4)_3$), and aluminum chloride ($AlCl_3$).

The choice of the precursor and its concentration (0.25 M), as well as the duration of calcination (1 h at 650 °C) was not random—it was based on the results of a series of preliminary tests that were carried out to determine the optimal balance between the cost of reagents and the pozzolanic activity of the material.

The aluminum sulfate concentration ranged from 0.1 to 0.5 M in 0.05 M increments (at a liquid-to-solid ratio of 20). A concentration of 0.25 M provided the maximum increase in pozzolanic activity (+32% lime binding relative to the control fired clay) with minimal chemical reagent consumption. The solution had a strictly controlled pH in the range of 3.8–4.2, which is optimal for stabilizing polynuclear aluminum hydroxo complexes.

The resulting suspension was continuously stirred with a magnetic stirrer for 6 h at room temperature. After the chemical step was completed, the samples were repeatedly washed with distilled water until the soluble sulfates were completely removed and a neutral pH was reached. They were then dried at 90 °C for 24 h to maintain the hydrated state of the precursors.

Heat treatment durations were tested ranging from 30 min to 2 h, followed by rapid air cooling to stabilize the active phase. A one-hour heat treatment was found to be optimal, as it ensured complete dehydroxylation. In some cases, further heat treatment resulted in sintering of the samples.

The prepared clay powders were treated with an intercalating solution; namely, a 0.25 M aqueous solution of aluminum sulfate ($Al_2(SO_4)_3$). The treated samples were placed in corundum crucibles and subjected to conventional thermal treatment in a muffle furnace at a fixed temperature of 650 °C. The holding time in the furnace was 1 h. Upon completion of calcination process, the samples were removed from the furnace and subjected to rapid cooling at room temperature, 21 ± 2 °C, for 30 min. This cooling procedure was intended to stabilize the amorphous dehydroxylated phases and clusters of polynuclear hydroxo

complexes, thereby ensuring the maximum pozzolanic activity of the material. Control samples without the addition of the activator (the pillaring solution) were subjected to the same heat treatment for comparison of their properties.

It should be noted that salts of virtually any transition metals with a charge of Me^{2+} and higher can serve as precursors for the pillaring solution, since all of them are capable of polymerization as a result of hydrolysis.

With the given parameters, it was possible to achieve maximum pozzolanic activity with minimal production costs.

2.2. Instrumental Methods of Analysis

The structural characteristics of the materials were studied using XRD, FTIR, SEM, and BET. The performance properties of the cements were assessed based on compressive and flexural strength, frost resistance, and corrosion resistance. True density and porosity were also measured. Pozzolanic activity was determined according to GOST R 56593-2015 [73] and the classical Butt method [74] based on $\text{Ca}(\text{OH})_2$ absorption. A roadmap for the entire experiment is provided in Table 5.

Table 5. Overview of the experimental methods and characterization techniques used in the study.

Property Studied	Method/Standard	Instrumentation and Parameters
Mineral composition	XRD	D2 Phaser (Bruker AXS GmbH, Karlsruhe, Germany); U = 30 kV; I = 10 mA; 2θ range: 5–70°
Elemental composition	Energy-dispersive X-ray fluorescence spectroscopy (XRFA/EDS)	SSD X-Max Inca Energy (Oxford Instruments, Abingdon, Oxfordshire, UK), integrated with JEOL 1610LV SEM (JEOL, Tokyo, Japan); Resolution for Mn K: 127 eV
Functional groups	FTIR	Nicolet 380 (Thermo Fisher Scientific Inc., Waltham, MA, USA); Resolution: 4 cm^{-1} ; Range: 4000–400 cm^{-1}
Microstructure	SEM	JSM-6510LV (JEOL Ltd., Tokyo, Japan); Accelerating voltage: 20 kV
Specific surface area	Nitrogen adsorption at low temperature (BET method)	ASAP 2020MP (Micromeritics Instrument Corp., Norcross, GA, USA); Pressure ratio range: 0.05–0.30
Density	Helium pycnometry	AccuPyc 1340 (Micromeritics Instrument Corp., Norcross, GA, USA); Accuracy: $\pm 0.00001 \text{ g/cm}^3$
Pozzolanic activity	Accelerated method	GOST R 56593-2015 [73]; Titration after pre-heat treatment at $T = 85\text{--}90^\circ\text{C}$; $\text{Ca}(\text{OH})_2$ consumption
	Classical Butt's method	Titration over 30 days
Compressive and flexural strength	Cement testing standards	EN 196-1/GOST 30744-2001 [75,76]; W/C ratio: 0.50; Slump cone spread: $115 \pm 5 \text{ mm}$; Mortar:sand ratio: 1:3; Specimen size: $40 \times 40 \times 160 \text{ mm}$
Sulfate resistance	Sulfate resistance coefficient, visual inspection, change in mass	GOST R 56687-2015 [77]; Medium: 5% Na_2SO_4 solution
Frost resistance	Freezing and thawing cycles	GOST 10060-2012 [78]; $-18^\circ\text{C} \dots +18^\circ\text{C}$

2.2.1. X-Ray Diffraction Analysis (XRD)

The phase composition of the raw materials was investigated by XRD using a D2 Phaser diffractometer under the following conditions: voltage 30 kV, current 10 mA, scanning angle range 2θ from 5° to 70°, and scanning step 0.01°. Qualitative phase analysis

was carried out by comparing the obtained diffraction patterns with reference data from the PDF4 and ICDD databases.

2.2.2. Elemental Analysis of the Surface Using Energy-Dispersive X-Ray Fluorescence Spectroscopy (EDS/XRFA)

The elemental composition of the sample surfaces was analyzed using an SSD X-Max Inca Energy energy-dispersive spectrometer integrated into a JEOL 1610LV scanning electron microscope at the Shared Research Center of D. Mendeleev University of Chemical Technology of Russia.

The analyzer provided qualitative and quantitative determination of the elemental composition at the microlevel, with visualization of the elemental distribution over the sample surface (elemental mapping). The range of elements determined ranged from sodium (Na) to uranium (U).

For each sample, at least three measurements were performed at different points (mapping) to ensure statistical reliability of the results.

2.2.3. Infrared Spectroscopy (FTIR)

Qualitative determination of the composition of functional groups in the aluminosilicate materials was carried out by FTIR at the Shared Research Center of D. Mendeleev University of Chemical Technology of Russia. The spectra were recorded using a Nicolet 380 FTIR spectrometer equipped with an attenuated total reflectance (ATR) accessory made of diamond and zinc selenide (ZnSe).

2.2.4. Determination of Specific Surface Area by BET

The specific surface area (S_{BET}) of the studied materials was determined by low-temperature nitrogen (N_2) adsorption–desorption using a fully automated ASAP 2020 MP gas adsorption analyzer at the Shared Research Center of D. Mendeleev University of Chemical Technology of Russia.

The specific surface area was calculated from the adsorption isotherm in the linear relative pressure range P/P_0 from 0.05 to 0.30 using the multipoint Brunauer–Emmett–Teller (BET) method.

2.2.5. Scanning Electron Microscopy (SEM)

The morphology and microstructure of the initial aluminosilicates, thermally treated samples, and the structure of the hardened cement paste containing additives were investigated by SEM. The analysis was carried out using a JSM-6510LV low-vacuum electron microscope equipped with an energy-dispersive X-ray microanalysis system (EDS/EDX) at the Shared Research Center of D. Mendeleev University of Chemical Technology of Russia.

The studies were carried out at an accelerating voltage of 20 kV and a working distance of 10–15 mm.

2.2.6. Cement Mortar Strength Testing

The mechanical properties of the composite cements were evaluated in terms of compressive and flexural strength. The tests were performed on standard hardened cement mortar specimens measuring $40 \times 40 \times 160$ mm in accordance with GOST 30744-2001 “Cements. Methods of testing with using polyfraction standard sand” [75], which is harmonized with the European standard EN 196-1:2016 “Methods of testing cement—Part 1: Determination of strength” [76].

Compressive strength was determined using a hydraulic press, while flexural strength was measured using a testing machine. The loading rate of the press during compressive strength testing was 2.4 ± 0.2 kN/s until specimen failure.

For each composition, at least three identical specimens were prepared to determine flexural strength. The remaining six half-prisms from each specimen were tested in compression. The final value was taken as the arithmetic mean of the obtained results. All experimental data were subjected to standard statistical processing with determination of the confidence interval at a significance level of 95%.

To create composite cements, Portland cement CEM I 52.5 N was mixed with pillared clay (20% of the clinker weight) and natural limestone (10%). The dry components were mixed in a laboratory mixer for 2 min until homogenized. They were then mixed with water of normal consistency, which was calculated individually for each composition according to GOST 30744-2001. Mixing was performed according to the standard procedure: 2 min at low speed, 1 min pause, 2 min at high speed. The fresh mixture was poured into $40 \times 40 \times 160$ mm steel molds, compacted on a shaking table (60 strokes), and covered with glass plates to prevent moisture evaporation.

All specimens were cured in a normal curing chamber (20 ± 2 °C, humidity > 95%). Strength tests were performed at the following checkpoints: 28 days (to assess early activity), 90 days, 180 days, and 360 days (to assess the kinetics of the slow pozzolanic reaction).

The authors note that GOST 30744-2001 does not require workability assessment outside of strength sample preparation; consistency control was performed exclusively using the cone flow method. The water–cement ratio was adjusted individually for each composition to compensate for the internal adsorption capacity of pillared clays, ensuring comparable hydration conditions.

2.2.7. Sulfate Corrosion of Hardened Cement Mortar

The resistance of the hardened cement mortar to sulfate attack was evaluated based on changes in its strength characteristics and integrity after prolonged storage in an aggressive medium. The testing procedure was based on GOST R 56687-2015 “Protection of concrete and reinforced concrete structures against corrosion. General technical requirements” [77].

For the experiment, two groups of specimens were prepared: the main (test) specimens and the control specimens. The main specimens were immersed in a 5% sodium sulfate (Na_2SO_4) solution simulating a highly aggressive sulfate environment, while the control specimens were stored in distilled water. The duration of the tests was up to 12 months under stable environmental conditions.

At the end of the exposure period, the specimens were removed from the solutions and visually inspected to record defects such as cracks, chips, and visible damage. After that, the compressive strength of all specimens was determined. For quantitative assessment of resistance, the sulfate resistance coefficient (K_S) was calculated as the ratio of the strength of a specimen stored in the Na_2SO_4 solution to the strength of a similar specimen stored in distilled water.

2.2.8. Determination of Frost Resistance of Cement Mortar

The frost resistance of the hardened cement mortar was determined according to GOST 10060-2012 “Concretes. Methods for the determination of frost-resistance” [78] using the accelerated method in a sodium chloride (NaCl) solution. For the tests, two groups of specimens were prepared: the main group subjected to freeze–thaw cycles and the control group.

Before testing, all samples that had reached the design strength within 28 days were saturated in a 5% aqueous solution of NaCl . The control group was tested in compression to determine the initial strength. The specimens of the main group were subjected to alternating freezing at -18 °C for 4 h and thawing in the same solution at a temperature not lower than $+18$ °C for 4 h.

After completion of the prescribed number of cycles (according to the requirements of GOST), the specimens were removed from the solution, residual water was removed using paper or a cloth, and the specimens were weighed. The criterion for frost resistance was the change in specimen mass. The material was considered to have passed the test if the total mass loss after all cycles did not exceed 2%. After that, the specimens were also tested in compression to determine the residual strength.

The experimental data were subjected to standard statistical processing with the determination of the confidence interval at a significance level of 95%. The standard deviation for the compressive strength was on average ± 2.3 MPa.

2.2.9. Determination of Density

The density of the hardened cement paste specimens was determined using an automatic helium pycnometer AccuPyc 1340 at the Mendelev University of Chemical Technology Collective Use Center (Moscow, Russia). This method is based on the principle of gas displacement from a sealed chamber of known volume.

Before measurement, the samples were ground to a fine powder and degassed in a desiccator to remove adsorbed air and moisture. The analysis was carried out under controlled laboratory conditions under standard conditions. The instrument measurement error is ± 0.00001 g/cm³, which ensures high accuracy of the obtained data. The density of the hardened cement paste specimens was calculated as the ratio of the specimen mass to the volume of gaseous helium displaced by it; helium penetrates all open pores of the material (from several angstroms to hundreds of micrometers), making it possible to determine its true volume without taking porosity into account.

2.2.10. Determination of Porosity

The total (open and closed) porosity of the hardened cement paste specimens was determined by a calculation method based on data on their true density (ρ) and volume weight of cement (ρ_0).

To determine the volume weight of cement, geometric measurements of each specimen were first carried out using a caliper, measuring the length (l), width (w), and height (h). The specimen mass (m) was determined using high-precision analytical balances. The volume weight of cement was calculated as the ratio of the specimen mass to its volume, calculated from the measurement results according to Equation (1):

$$\rho_0 = \frac{m}{l \cdot w \cdot h} \quad (1)$$

For each composition, three identical samples were prepared (according to GOST 30744-2001). The standard deviation for calculating ρ_0 was less than ± 0.015 g/cm³.

To determine the true density of cement samples, a pycnometric method was used [74], for which the samples, after preliminary drying at $T = 95 \pm 5$ °C, were ground in a mortar until passing through a sieve with a mesh size of 80 μ m.

The pycnometers and samples were weighed on a technical scale, then kerosene was added until it completely covered the cement powder and reached 1/3 of the volume below the neck of the pycnometer. The pycnometers were then connected to a jet vacuum pump for 60 min, after which the samples were weighed again.

Based on the obtained values, the total porosity (P) was calculated as a percentage using Equation (2):

$$P = \frac{\rho - \rho_0}{\rho} \cdot 100\% \quad (2)$$

2.2.11. Pozzolanic Activity

The pozzolanic activity of the aluminosilicate additives under study was determined by two methods: an accelerated method, according to GOST R 56593-2015 [73], and a classical Butt's method [74]. Both methods are based on evaluating the ability of the mineral additive to absorb calcium hydroxide ($\text{Ca}(\text{OH})_2$, portlandite) from its saturated aqueous solution, which is a key indicator of the reactivity of pozzolanic materials.

The accelerated method, unlike the classical one, allows for a preliminary assessment of pozzolanic activity in just 24 h by titrating unreacted calcium hydroxide. The method is extremely sensitive to the presence of active sites (silicate and aluminate groups) on the clay surface immediately after thermal activation. It is important to note that there is virtually no systematic data in the literature on the correlation between the results of these two methods for modified columnar clays.

Classical Butt's Method

The classical procedure involves a long-term experiment lasting 30 days. During the test, the concentration of $\text{Ca}(\text{OH})_2$ in the solution was measured every two days by sampling followed by titration with a hydrochloric acid (HCl) solution according to Equation (3).

$$C_{\text{Ca}(\text{OH})_2} = \frac{C_{\text{HCl}} \cdot V_{\text{HCl}}}{V}, \quad (3)$$

where $C_{\text{Ca}(\text{OH})_2}$ is the molar concentration of calcium hydroxide in the collected sample (mol/L); C_{HCl} is the exact molar concentration of the standard hydrochloric acid solution (mol/L); V_{HCl} is the volume of HCl solution used for the titration of the given sample (L); V is the aliquot of the test solution taken for analysis (L).

The resulting molar concentration was converted to a mass of calcium oxide (m_{CaO}), equivalent to the amount of reacted portlandite at the time of sample collection. The mass of CaO in one sample was calculated using Equation (4):

$$m_{\text{CaO}}(t_i) = C_{\text{Ca}(\text{OH})_2}(t_i) \cdot M_{\text{CaO}} \cdot V_f \quad (4)$$

where M_{CaO} is the molar mass of the oxide (56.08 g/mol); V_f is the total working volume of the expanded vessel (L); t_i is the corresponding time of sampling.

At the end of the experiment, the total amount of absorbed portlandite (expressed as CaO) over the entire period was calculated using Equation (5):

$$M_{\text{total}} = \sum_{i=1}^n m_{\text{CaO}}(t_i) \cdot \Delta t \quad (5)$$

where n is the total number of measurements; M_{total} is the total amount of portlandite absorbed over the entire period of the experiment and is expressed in grams of CaO.

Accelerated Method

The accelerated procedure makes it possible to obtain results within a significantly shorter time. A saturated $\text{Ca}(\text{OH})_2$ solution containing the thermally treated clay additive was heated at 85–90 °C for 8 h. After thermal treatment, the system was cooled to room temperature.

In both cases, the concentration of calcium hydroxide remaining in the solution was determined by acid–base titration. The solution sample was titrated with a standard hydrochloric acid (HCl) solution in the presence of methyl orange indicator until the color changed from yellow to tea rose, corresponding to the endpoint of the titration. The amount of absorbed calcium oxide (CaO) was calculated from the difference between the initial CaO

concentration in the control (initial) solution and its final concentration after interaction with the additive Equation (6):

$$\text{CaO} = 1.4 \cdot 2 \cdot \frac{V_0 \cdot (V_2 - V_1)}{V_2} \quad (6)$$

where 1.4 is the titer of a 0.05 mol/L HCl solution with respect to CaO (differential correction coefficient), $\text{mg} \cdot \text{mL}^{-1} \cdot \text{g}^{-1}$; V_0 —the volume of HCl consumed for the titration of 50 mL of saturated $\text{Ca}(\text{OH})_2$ solution without the mineral additive that was tested, mL. This sample was not heated in the drying oven (“cold” solution); V_1 —the volume of HCl consumed for the titration of 50 mL of the test solution containing the tested mineral additive, mL; V_2 —the volume of HCl consumed for the titration of 50 mL of saturated $\text{Ca}(\text{OH})_2$ solution without the mineral additive, mL. This sample was heated in the drying oven, as were the samples of additives tested (“hot” solution).

Since the accelerated and classical methods differ in temperature and duration of the test, therefore their absolute results are not directly comparable. Both methods are used for mutual verification of the obtained results.

3. Results

3.1. Structure and Composition of Natural and Pillared Clays

The investigation of the initial aluminosilicate clays by XRD and SEM revealed significant differences in their mineral composition and morphology, which directly correlate with their crystallochemical type.

Figure 4 shows the X-ray diffraction patterns of three types of aluminosilicates: kaolinitic clay (Clay K), montmorillonitic clay (Clay M), and illite–chlorite clay (Clay I). The plot is presented as intensity versus diffraction angle (2θ , degrees). It can be seen that each clay has a unique set of peaks corresponding to different minerals.

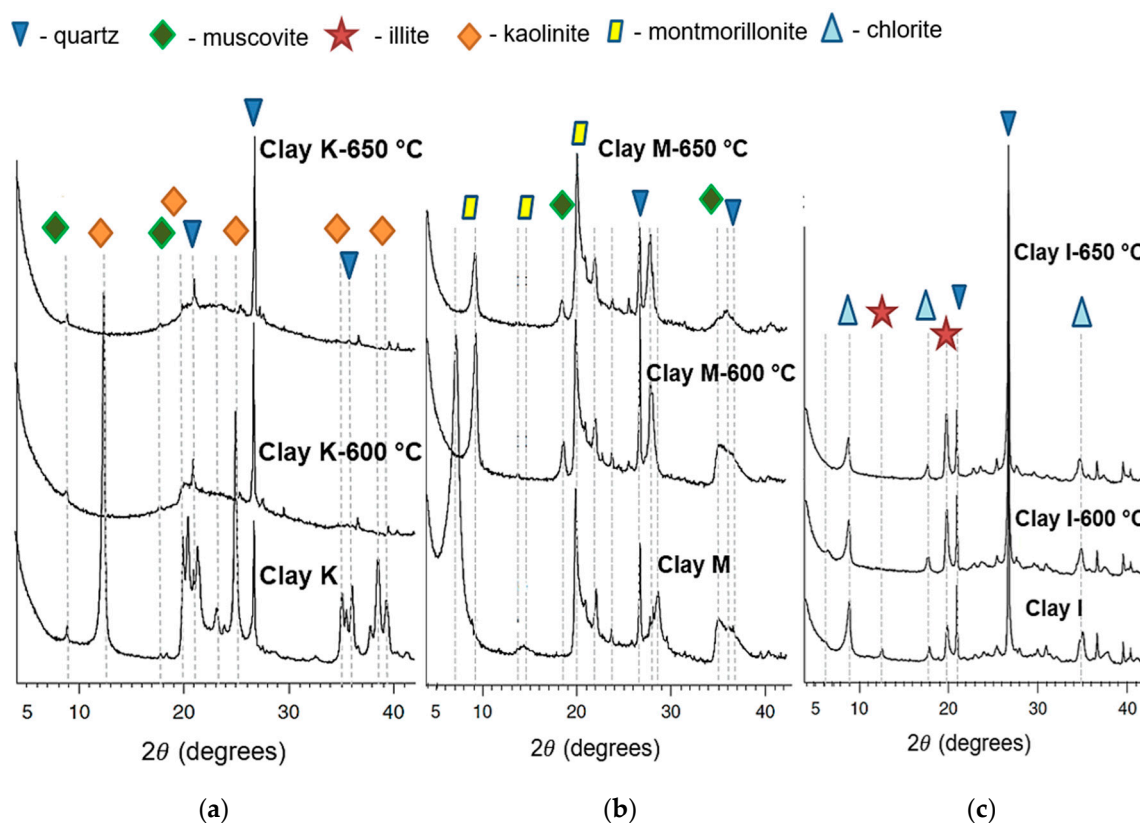


Figure 4. XRD patterns of: (a) kaolinite clay; (b) montmorillonite clay; (c) illite–chlorite clay.

Clay K (Figure 4a) is characterized by distinct kaolinite reflections at $2\theta \approx 12.4^\circ$, 20.3° , and 24.8° . A small amount of muscovite is also present. The absence of an intense reflection in the low-angle area ($2\theta < 5^\circ$) indicates low interlayer sorption capacity and the absence of swelling phases, which is characteristic of 1:1 structural-type clays, to which kaolinite belongs. After thermal treatment at $T = 600\text{--}650^\circ\text{C}$, the kaolinite reflections disappear, indicating its complete dehydroxylation and transformation into metakaolin. The intensity of the main basal peak ($2\theta \approx 12.4^\circ$) after heat treatment decreased by approximately 83%. Moreover, the decrease in the integral intensity of the reflection is accompanied by its broadening, which confirms the complete loss of long-range order in the crystal lattice (transition to metakaolin).

Clay M (Figure 4b) has a complex mineralogical composition: montmorillonite predominates ($2\theta \approx 8.1^\circ$, 14.5° , and 20°), while muscovite peaks are also visible ($2\theta \approx 18^\circ$ and 35°). The intensity of the main basal peak ($2\theta \approx 8.1^\circ$) after heat treatment decreased by more than 95%. For montmorillonite, the destruction of the structure is even deeper than for kaolinite—the reflection practically disappears, since the interlayer space is completely destabilized before intercalation.

Clay I (Figure 4c) is mixed-layered, as it contains illite phases ($2\theta \approx 12.5^\circ$ and 20°), which belong to the 2:1 structural type, and chlorite phases ($2\theta \approx 9.1^\circ$, 18° , and 34.9°), which belong to the 2:1:1 structural type.

Mixed-layer clays are the most common in nature. Therefore, they are especially relevant. For the montmorillonitic and illite–chlorite clays, the diffraction patterns differ significantly, both before and after calcination. The montmorillonite reflection shifts from 8.1° to 11° , confirming the release of water. In contrast, the $2\theta \approx 20\text{--}30^\circ$ region changes to a lesser extent. At the same time, changes in the muscovite crystalline phase can be observed; for example, in the $35\text{--}38^\circ$ region, the intensity of the reflections decreases. The diffraction features of illite and chlorite change only slightly before and after thermal treatment. The dehydroxylation that already occurs at these temperatures is not reflected in the crystallinity of the samples.

It should be noted that all three clays contain quartz (SiO_2), while kaolinite and montmorillonite clays contain traces of muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$). Any natural clay, especially polymineral clays, contains impurities, especially quartz. The presence of clearly defined quartz reflections in diffraction patterns can serve as an “internal standard.” Since the amount of this mineral remained unchanged before and after heat treatment (see the lack of change in the intensity of their peaks in Figure 4), we can confidently state that the observed change in the basal reflections of the clays is caused by the activation and amorphization of layered silicates, and not by a sample preparation error or a change in the overall mineral balance.

The structure of the muscovite elemental layer is characterized by a three-layer stack, similar to that of montmorillonite (Figure 1b). Therefore, at firing temperatures above 600°C , the mineral undergoes dehydroxylation, similar to montmorillonite. Therefore, the presence of this impurity is advantageous during intercalation, as it increases the surface area for creating pillars. The subsequent success of pillarization for kaolin clay can also be explained by the presence of muscovite impurity in the aluminosilicate (the specific surface area of kaolin clay with the precursor increases slightly, Table 6).

Thus, it can be concluded that, due to their different structural types, kaolinite becomes amorphous during calcination, whereas montmorillonite, illite, and chlorite lose their hydroxyl groups without obvious changes in the crystallographic arrangement of the other atoms; i.e., any possible amorphization proceeds only due to impurities of 1:1 clay minerals (kaolinite and halloysite).

Table 6. Specific surface area of clays after calcination.

Aluminosilicate/ Calcination Mode	Clay K		Clay M		Clay I	
	Without the Precursor	With the Precursor	Without the Precursor	With the Precursor	Without the Precursor	With the Precursor
S_{BET} , m ² /g	24.8	30.1	25.1	48.2	17.5	33.2

The studied clays exhibited different trends in BET surface area during thermal treatment (Figure 5). These patterns are determined by their crystallochemical structure and the degree of amorphization.

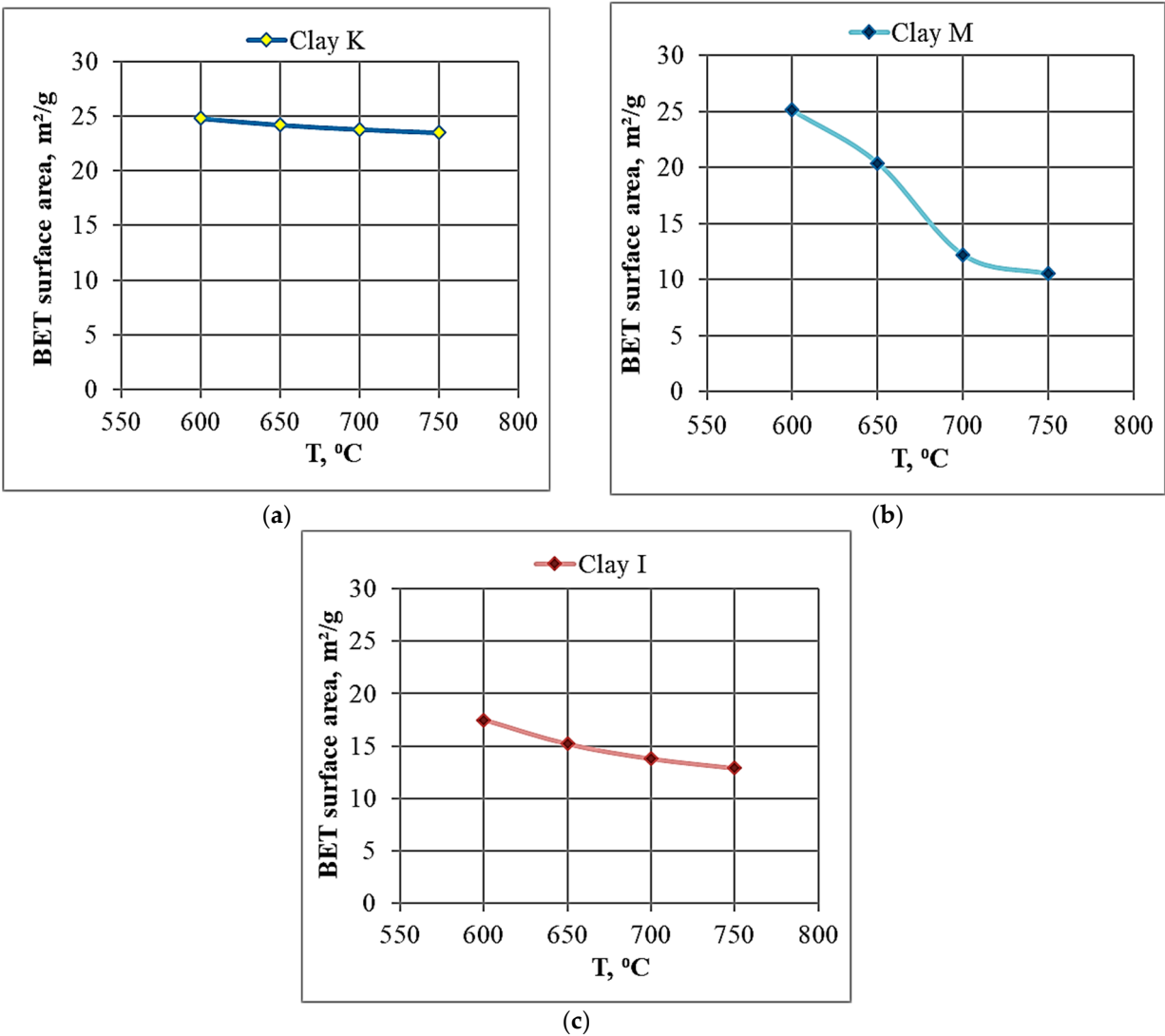


Figure 5. Specific surface area (BET method) as a function of calcination temperature: (a) kaolinitic clay; (b) montmorillonitic clay; (c) illite–chlorite clay.

A decrease in BET surface area after calcination is characteristic of all samples. The higher the calcination temperature, the lower the specific surface area. Montmorillonitic clay (Figure 5b) is more prone to particle agglomeration. After calcination at $T = 600\text{ }^{\circ}\text{C}$, its specific surface area decreases by 23%. At $T = 650\text{ }^{\circ}\text{C}$ the decrease reaches 37%. At $T = 700\text{ }^{\circ}\text{C}$, it reaches 62%, and at $T = 750\text{ }^{\circ}\text{C}$, 68%.

Illite–chlorite clay (Figure 5c) is less prone to particle agglomeration, and its specific surface area decreases overall by 36% compared with the natural sample. The lowest change

in specific surface area is observed for kaolinitic clay (Figure 5a), with a total decrease of 9% at $T = 750\text{ }^{\circ}\text{C}$ compared with the initial sample. The decrease in specific surface area is associated both with the loss of hydroxyl groups and with the structural rearrangement of clays [40,79]. At temperatures above $800\text{ }^{\circ}\text{C}$, sintering occurs and the formation of new crystalline phases form. As a result, the specific surface area may decrease substantially.

Kaolinitic clay belongs to the 1:1 structural type. It also contains fewer hydroxyl groups than montmorillonitic and illite–chlorite clays, which belong to the 2:1 and 2:1:1 structural types, respectively. Therefore, the change in specific surface area is less pronounced than in the other two samples. Thus, the change in specific surface area of the calcined clays can be expressed as follows: $S_{\text{BET}}\text{--Clay K} < S_{\text{BET}}\text{--Clay I} < S_{\text{BET}}\text{--Clay M}$.

Based on the obtained data, the authors assume that kaolinitic clay is less susceptible to intercalation than the other clay types; i.e., to the incorporation of ions or molecules into the interlayer space. To test this assumption, all three clay types were examined by infrared spectroscopy and scanning electron microscopy after calcination in the presence of the pillaring solution.

FTIR is one of the most informative methods for studying the structure of aluminosilicates. It makes it possible to evaluate changes in silicon–oxygen and aluminum–oxygen bond vibrations before and after calcination. These changes may indicate the extent of the thermal reaction and the pozzolanic activity of the additive.

In the FTIR spectrum of kaolinitic clay (Figure 6—Clay K), two strong bands can be observed at 1032 and 1010 cm^{-1} . These bands correspond to the stretching vibrations of silicon–oxygen groups (Si–O–Si and Si–O, respectively). The quartz-related vibrations partially overlap with the Si–O vibrations of kaolinite. However, quartz shows a characteristic doublet at 796 and 696 cm^{-1} . The band at 550 cm^{-1} corresponds to the bending vibrations of Si–O–Al. The band at 913 cm^{-1} is assigned to the bending vibrations of structural hydroxyl groups associated with Al^{3+} cations in the octahedral sheet of kaolinite.

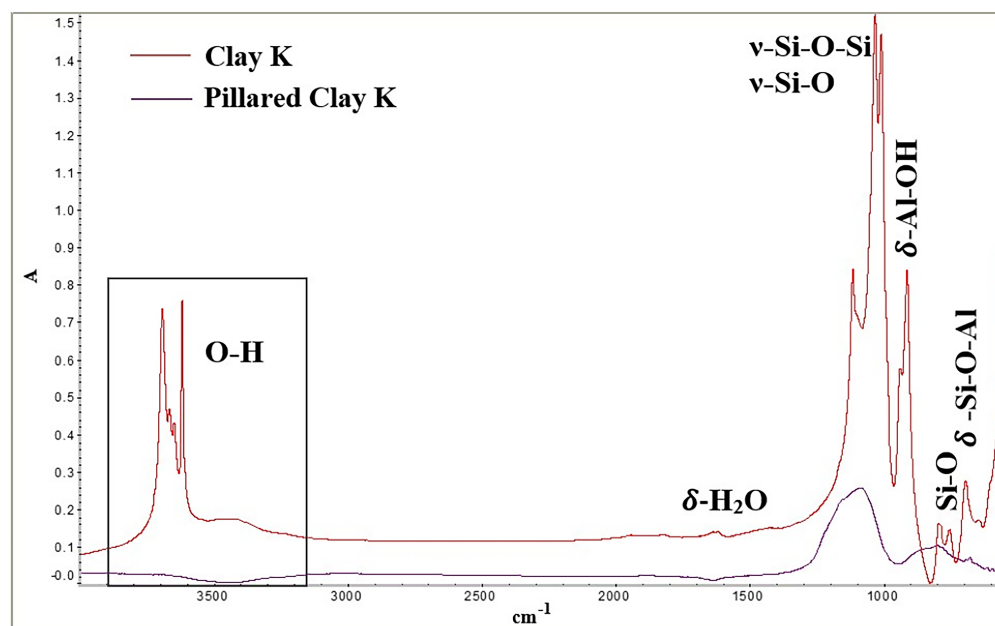


Figure 6. FTIR spectra of kaolinitic clay before and after pillaring (Pillared Clay K).

After pillaring with an aluminum sulfate solution at $650\text{ }^{\circ}\text{C}$ for 1 h (Figure 6, Pillared Clay K), clear dehydration of the sample can be observed. The absorption bands in the $3600\text{--}3700\text{ cm}^{-1}$ region disappear completely. These bands are associated with the stretching vibrations of water molecules adsorbed on the particle surface. A distinct depression also appears near 3500 cm^{-1} , indicating almost complete water removal.

The high growth of the absorption bands in the 900–1100 cm^{-1} region, which are associated with vibrations of quartz and kaolinite crystals, merge into a single broad band with no pronounced maxima. This confirms amorphization of the sample. A similar change is observed in the 650–800 cm^{-1} region: the sharp peaks assigned to Si-O-Si stretching and Si-O vibrations are replaced by a smooth broad band. This also indicates decomposition of the crystalline phase and the formation of an amorphous structure.

In addition, the band at 913 cm^{-1} , assigned to Al-OH bending vibrations, disappears. It should also be noted that the overall height of the absorption bands decreases sharply after pillaring. This is consistent with previous reports showing that 1:1 clays of the 1:1 structural type show only a slight structural change after columnar treatment, which is consistent with its decrease depending on the intercalation of inorganic particles due to strong hydrogen bonds in the interlayer space [33,50]. The structure becomes disordered, but no clear structural rearrangement is observed. The band positions do not shift to lower wavenumbers; instead, they become broadened and less intense. The absorption band heights drop markedly, from 1.5 a.u. to 0.2 a.u. Since the quartz doublet disappears after pillaring, the sample can be considered amorphized, whereas clear evidence of successful pillaring is limited.

The spectral changes observed for 2:1 and 2:1:1 clays before and after pillaring differ from those of kaolinitic clay (Figure 7).

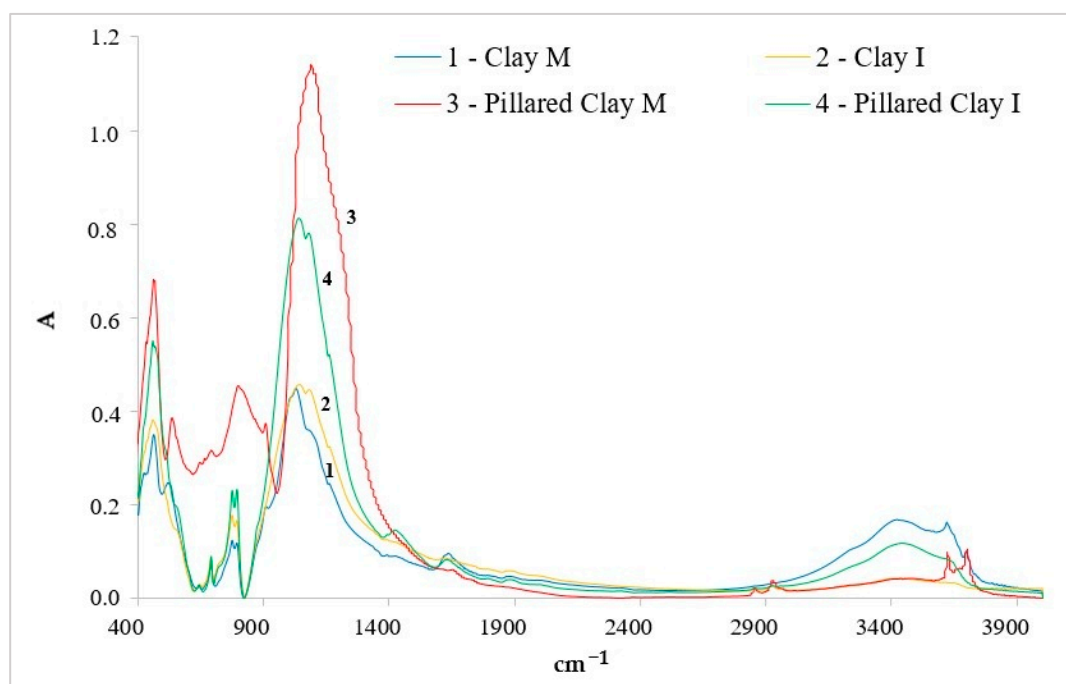


Figure 7. FTIR spectra of montmorillonitic (Clay M and Pillared Clay M) and illite–chlorite clays (Pillared Clay I).

The crystalline phase of montmorillonitic clay is less intense, although it shows distinct maxima in the same regions as kaolinitic clay. The spectrum of natural illite–chlorite clay is very similar to that of montmorillonitic clay [19,40,55,57] and is therefore not shown separately in the figure to avoid spectral overlap. This similarity is related to their comparable structural types; namely, 2:1 and 2:1:1. In contrast, kaolinite is a 1:1 clay mineral. As a result, the absorption bands of kaolinitic clay are sharper than those of the other two clays.

At the same time, montmorillonitic clay shows a distinct low-amplitude (Si)-OH band in the 1400–1500 cm^{-1} region. In addition, the band in the 3000–3500 cm^{-1} range, which is assigned to O-H vibrations, is broader and higher in montmorillonitic clay than

in kaolinite. This may be related to vibrations of bound water rather than adsorbed water. Interestingly, the pillared montmorillonitic clay exhibits two sharp hydroxyl maxima at 3621 and 3698 cm^{-1} . Changes in this region are observed for all three samples, but the pillared sample shows the clearest modification of the band shape, as the broad rounded band becomes less intense and better defined.

After pillaring, the band intensity, i.e., the degree of absorption, increases. It is well known that a higher peak corresponds to stronger light absorption by the molecule [80]. The absorption intensity depends on several factors, including the bond type, bond strength, number of bonds, substance concentration, and the optical path length through the sample.

Because the clays belong to different structural types, their spectral features are also different, although the vibration types themselves are generally similar. This is expected because clay minerals are composed of the same major elements and contain similar bonds, such as O-H, Si-O, and Al-O.

It should be noted that crystalline kaolinite (Figure 6) absorbs a relatively large amount of radiation. In particular, the Si-O-Si bands at 1032 and 1010 cm^{-1} show an absorption of about 1.5 a.u. In contrast, a similar vibration at 1032 cm^{-1} assigned to montmorillonite (Figure 7) shows an absorption of 0.5 a.u. This indicates that the crystalline phase of montmorillonite, and likely illite as well, is less pronounced and less intense than that of kaolinite.

After pillaring, the degree of absorption of the broad band in this region differs among the three clays. For kaolinitic clay (Figure 6, band at 1087 cm^{-1}), the band height is 0.3 a.u. For illite–chlorite clay (Figure 7, band at 1084 cm^{-1}), it is 0.45 a.u. For montmorillonitic clay (Figure 7, band at 1100 cm^{-1}), it reaches 1.15 a.u. These data indirectly support the view that clays with a 2:1 structure, such as montmorillonitic clays, are more suitable for pillaring, whereas kaolinitic clay with a 1:1 structure is only weakly affected by this process. In other words, the interlayer space does not increase significantly, and the pillaring agent is either not incorporated into this clay structure or is incorporated only partially.

This interpretation is supported by the SEM images (Figure 8). The pillared montmorillonitic clay has a loose, sponge-like structure (Figure 8b). The crystalline phase is nearly absent, and no well-defined crystal faces can be observed. The pore size reaches up to 3 nm.

In contrast, pillared kaolinitic clay is characterized by relatively distinct and individually discernible edges with sizes of up to 5 nm (Figure 8a).

Illite–chlorite clay has a morphology different from that of the other two clays (Figure 8c). Its structure resembles cotton-like aggregates. At the same time, a certain amount of crystalline phase can still be observed, with crystal sizes of up to 6 nm.

Pillared montmorillonite clay exhibited the highest capacity for incorporating polynuclear hydrocomplexes into its structure. Therefore, it was further studied using XRFA before (Figure 9) and after pillaring (Figure 10).

It should be noted that the classical XRD analysis did not allow for identifying the formation of a new pillared structure. This is due to the specific features of the structure and the method itself. X-ray structural analysis is well suited for identifying well-crystallized phases. If the material is a very fine powder or contains very small particles, the method becomes less informative. In this case, XRD is not an effective research method. The method is primarily sensitive to the bulk crystalline structure, not to local distortions. Metal oxide clusters that form during heat treatment after pilling-back have an amorphous or weakly crystalline structure. Their diffraction peaks are too weak or absent to be detected by a standard X-ray diffractometer.

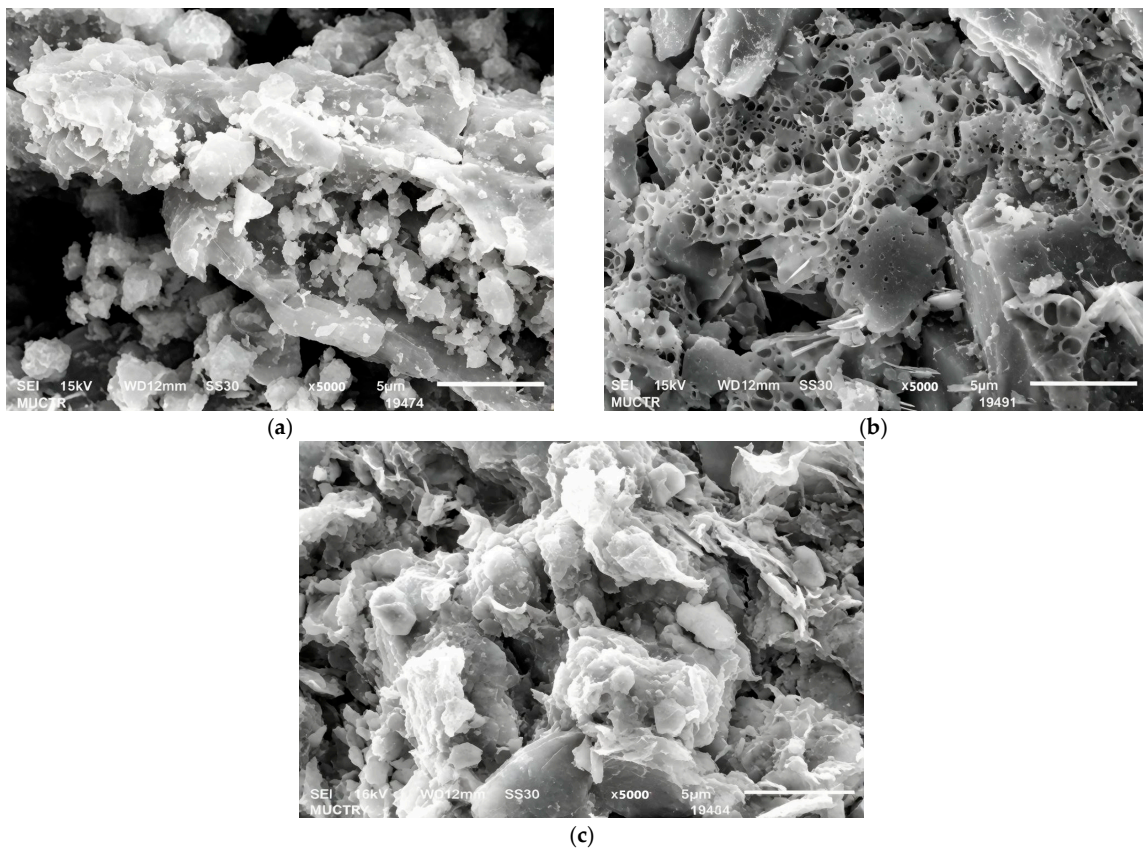


Figure 8. Microstructure of pillared clays: (a) kaolinitic clay; (b) montmorillonitic clay; (c) illite–chlorite clay.

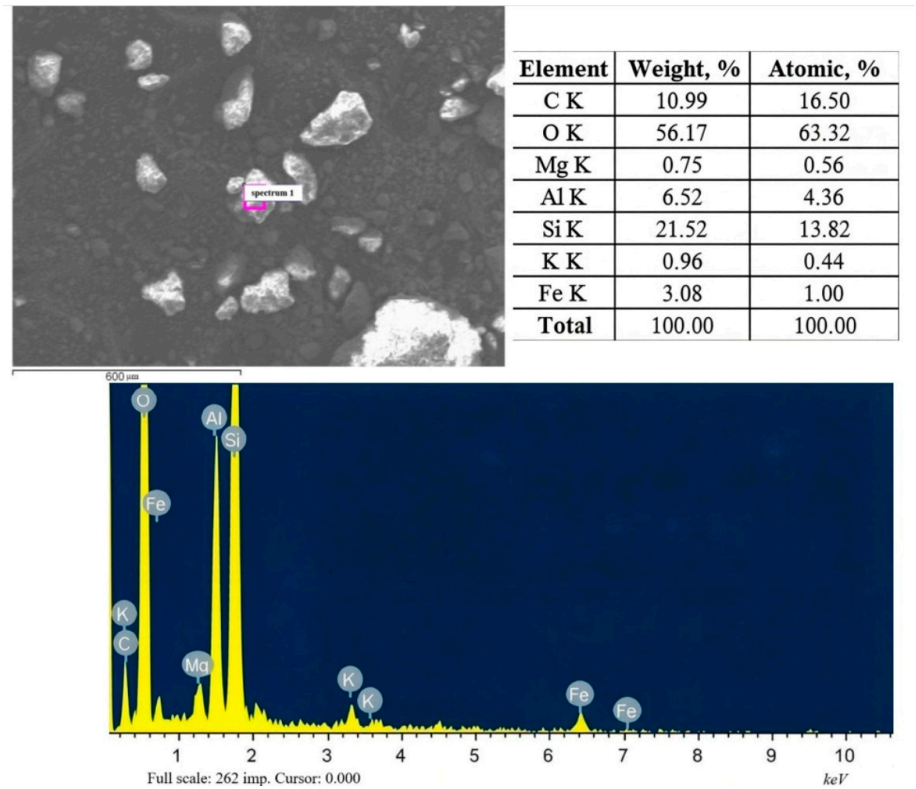


Figure 9. XRF analysis of Clay M.

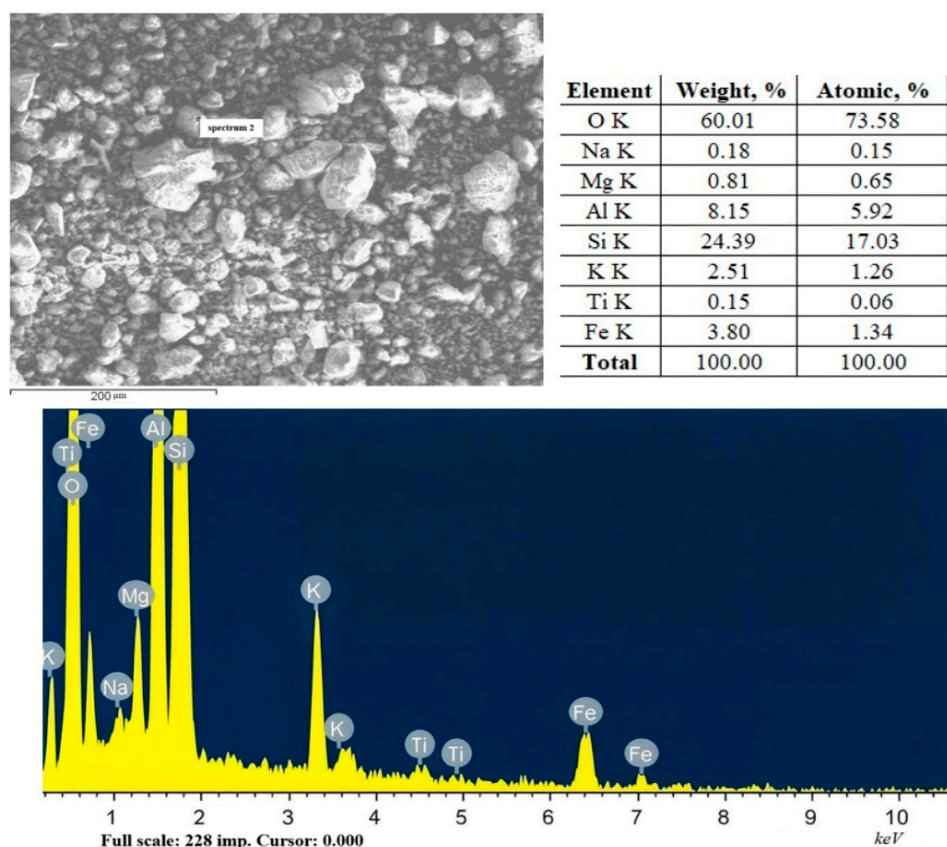


Figure 10. XRF analysis of pillared Clay M.

Analysis of natural montmorillonite clay reveals a typical macroelement profile. The main components are oxygen ($O_2-56.17 \pm 0.76\%$), silicon ($Si-21.52 \pm 1.20\%$), and carbon ($C-10.99 \pm 1.36\%$). The high carbon content indicates a significant proportion of carbonate impurities, as well as adsorbed moisture/volatiles, which contribute to the X-ray fluorescence signal when using standard calibrations without accounting for matrix absorption effects.

The content of structure-forming oxides (Al_2O_3 and SiO_2) corresponds to a moderately aluminous raw material. Iron, magnesium, and potassium impurities are at levels typical of secondary sedimentary rocks of continental origin. Oxygen predominates in atomic terms (63.32%), confirming the oxide nature of the mineral matrix.

Heat treatment at $650^\circ C$ leads to a profound restructuring of the chemical profile of the sample (Figure 10), caused by the processes of dehydroxylation of layered silicates.

The weighted average Si content increases from 21.52% to 24.39%. Removing the constituent water from the smectite lattice (dehydroxylation) reduces the matrix mass, which mathematically overestimates the relative proportion of the remaining elements. Furthermore, partial amorphization of the montmorillonite crystal structure occurs, releasing some silica from the rigid tetrahedral networks.

The aluminum content increases slightly (from 6.52 to 8.15%), as aluminum cations are firmly retained within the octahedral layer structure after heat treatment. The detection of sodium exclusively in the pillared sample is explained by the destruction of interlayer complexes. The hydration shells of exchangeable cations, previously trapped in the interlayer space, are destroyed.

After pillarization, an increase in the iron and aluminum signals is observed, which may indicate the formation of oxides or hydroxo complexes. It is worth noting that X-ray fluorescence analysis does not directly confirm the formation of polynuclear complexes, but

its data can be used as indirect confirmation in combination with other physicochemical analytical methods.

Since pillaring is intended to increase the interlayer spacing of aluminosilicates, thereby enhancing the sorption properties and, consequently, the activity of the material, the specific surface area of the clays was investigated under different calcination conditions, both with and without the pillaring agent (Table 6).

It was found that clays calcined in the presence of the precursor, i.e., a 0.25 M aluminum sulfate solution, developed a more pronounced specific surface area than clays calcined without the pillaring agent. For montmorillonitic and illite–chlorite clays, the specific surface area increased almost twofold after calcination in the presence of the precursor. In contrast, the specific surface area of kaolinitic clay changed only slightly, increasing from 24.8 m²/g before pillaring to 30.1 m²/g after pillaring.

Other solutions, such as aluminum chloride and iron sulfate, were also used as precursors. For all samples pillared with salts other than aluminum sulfate, a decrease in specific surface area of approximately 15% was observed compared to samples based on Al₂(SO₄)₃. This is due to the less efficient formation of a rigid oxide framework (“pillars”) in the interlayer space. It is the sulfate anion that acts as a stabilizer for polymeric aluminum hydroxocomplexes, ensuring maximum dispersion of clay layers during heat treatment. The use of chlorides and other sulfates leads to partial shielding of active sites or premature agglomeration of particles, which reduces the available surface area for subsequent hydration.

The change in specific surface area (Figure 5 and Table 6) before and after pillaring is due to montmorillonite’s swelling structure with weak van der Waals bonds between the tetrahedral layers. In its natural state, water molecules readily penetrate the interlayer space. Upon heating to 650 °C, rapid dehydroxylation of the octahedral sheet occurs, causing the layers to lose their bonds and move closer together. This leads to strong particle agglomeration (an effect confirmed by increased microporosity according to IR spectra—the disappearance of the OH band in Figure 7), resulting in a decrease in specific surface area (by 37%, from 25.1 to 15.8 m²/g, Figure 5b). However, subsequent introduction of aluminum sulfate as a precursor literally “breaks” these aggregates from the inside, creating rigid inorganic columns. This restores access to the inner surface, increasing the total area by almost 2 times (up to 48.2 m²/g).

Kaolinite has a rigid structure, where the layers are tightly linked by hydrogen bonds through shared oxygen vertices. It is non-swelling. Upon dehydroxylation (approximately 550–600 °C), the structure transforms into metastable metakaolin without significant layer separation. Therefore, the initial loss of specific surface area during firing is minimal (only 9%, from 24.8 to 22.6 m²/g, Figure 5a), as there is no primary process of convergence of large interlayer spaces. Because the layered structure of kaolinite remains relatively compact, the intercalating agent cannot effectively penetrate between the densely packed packets. As a result, the area increase after pillarization is only ~21% (up to 30.1 m²/g, Table 6), which is significantly lower than the values for the 2:1 group.

In the classical sense, a high specific surface area indicates the presence of active sites for chemical reactions. However, in this case, this increase correlates not only with the amorphization of the clay layers but also with their physical stratification (presumably, the formation of pillars). The formation of interlayer cavities 1–2 nm in diameter (Figure 8b) creates conditions for the adsorption of hydration products. With further growth of C–S–H crystals, a nanoreinforcement effect occurs within these spaces: clay particles transform from inert inclusions into a rigid “reinforcing” framework (pillars), which physically blocks the mobility of adjacent phases.

These results indicate that montmorillonitic clay is the most susceptible to chemical activation, whereas kaolinitic clay is the least susceptible. This difference is expected to affect their pozzolanic activity, which is discussed below.

3.2. Pozzolanic Activity of Clays

Pozzolanic activity is one of the most important characteristics of calcined aluminosilicates. It is influenced by many factors, including calcination time and temperature, additive composition and structure, activation method, and specific surface area.

At the first stage, the effect of conventional calcination on the pozzolanic activity of the clays was investigated (Table 7). The holding time in the muffle furnace was 60 min, followed by rapid cooling in air for 30 min at 21 ± 2 °C.

Table 7. Pozzolanic activity of Butt’s method of heat-treated clays.

Clay	T ₁ , °C	Pozzolanic Activity, mg/g	T ₂ , °C	Pozzolanic Activity, mg/g	T ₃ , °C	Pozzolanic Activity, mg/g
Clay K	550	455	600	550	650	480
Clay M	600	395	650	490	700	420
Clay I	650	345	700	440	750	370

The authors [19,34,35,59] previously studied all clays using differential thermal analysis, which made it possible to identify temperature ranges corresponding to the dehydration/dehydroxylation of clay minerals and the formation of active centers.

The optimum calcination temperature for kaolinitic clay (Table 7, Clay K) is 600 °C, at which the activity reaches 550 mg/g of additive. Lowering or increasing this temperature by 50 °C leads to a marked decrease in pozzolanic activity. When the calcination temperature is increased to 650 °C, the activity of the calcined kaolinitic clay decreases from 550 to 480 mg/g of additive. When the temperature is reduced to 550 °C, the activity decreases from 550 to 455 mg/g of additive.

A similar trend is observed for the other samples. For calcined montmorillonitic clay, the optimum calcination temperature is 650 °C (Table 7, Clay M, T₂), and the activity reaches 490 mg/g. For calcined illite–chlorite clay, the optimum temperature is 700 °C (Table 7, Clay I, T₂), and the activity increases from 345 to 440 mg/g.

Since all of the aluminosilicates studied are mixed-layered, their classification into groups is somewhat conditional and is based mainly on the predominance of one mineral over the others. At the same time, it should be noted that the calcination temperature of illite–chlorite clays is higher than that of montmorillonitic clays, whereas the lowest calcination temperature is observed for kaolinitic clays. This relationship can be expressed as follows: $T_{\text{Clay K}} < T_{\text{Clay M}} < T_{\text{Clay I}}$. However, the optimal calcination temperature may vary depending on the deposit and the presence of impurity minerals.

At the second stage, the pozzolanic activity of clays with various precursors was studied: 0.25 M solutions of aluminum sulfate and chloride, and iron sulfate (Figure 11). The firing was carried out at optimal temperatures (Table 7) with an isothermal holding time of 1 h.

The activity of pillared clays activated with aluminum chloride and iron sulfate was lower than that of clays activated with aluminum sulfate. Sulfate ions (SO_4^{2-}) have a high affinity for the positively charged edges of aluminosilicates and the hydroxide groups on the basal planes. They act as “anchors,” holding aluminum polymer complexes near the clay flake surface until dehydroxylation occurs. Chloride ions (Cl^-) bind much more weakly to the surface. As a result, when using AlCl_3 , a significant portion of the aluminum

remains as simple hydrated ions or is washed out or evaporated during drying and firing, preventing the formation of a rigid pillar structure.

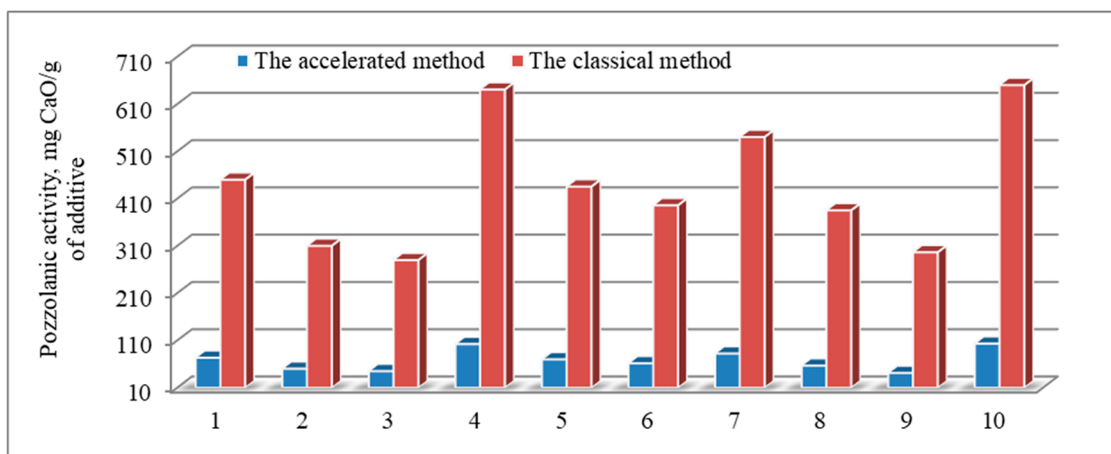


Figure 11. Pozzolanic activity (mg/g of additive) of pillared clays with different precursors: 1—Pillared Clay K-Al₂(SO₄)₃; 2—Pillared Clay K-AlCl₃; 3—Pillared Clay K-Fe₂(SO₄)₃; 4—Pillared Clay M-Al₂(SO₄)₃; 5—Pillared Clay M-AlCl₃; 6—Pillared Clay M-Fe₂(SO₄)₃; 7—Pillared Clay I-Al₂(SO₄)₃; 8—Pillared Clay I-AlCl₃; 9—Pillared Clay I-Fe₂(SO₄)₃; 10—Metakaolin.

Furthermore, stable polynuclear oxocations [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ (Keggin ions) spontaneously form in an aqueous aluminum sulfate solution at certain pH values. These oxocations serve as ideal building blocks (“blanks”) for the pillar. The presence of sulfate ions stabilizes the environment, facilitating the growth of these clusters. Chloride ions are a more chaotic counterion; chloride-based environments often result in the formation of less ordered and less thermally stable polynuclear structures.

At high temperatures, residual chlorine can form volatile aluminum compounds (e.g., subchlorides) or promote undesirable surface sintering of particles, which paradoxically reduces the specific surface area instead of increasing it. The sulfate group decomposes to form gases that readily escape the system, leaving behind a pure oxide framework.

Iron sulfate can be used as a pillaring agent, but it should be noted that its use in this study resulted in a nearly 50% decrease in activity. This was due to the larger ionic radius of Fe³⁺ and the tendency of its oxides to locally sinter the interlayer space at 650 °C. Thus, aluminum sulfate proved to be the only precursor that provided an optimal balance between intercalation depth and preservation of the microporosity of the structure.

At the third stage, the pozzolanic activity of the pillared clays was investigated using both the classical method and the accelerated method according to GOST R 56593-2015 (Figure 12).

A highly reactive commercial metakaolin was selected as the reference material. Its pozzolanic activity was 103.4 mg/g by the accelerated method and 650.2 mg/g by the classical method. Similar values were obtained for montmorillonitic clay; namely, 102.5 and 640.8 mg/g, respectively.

The lowest activity was observed for pillared kaolinitic clay: 73.5 mg/g by the accelerated method and 450.1 mg/g by the classical method. Illite–chlorite clay showed higher activity than kaolinitic clay, reaching 82.4 mg/g by the accelerated method and 540.3 mg/g by the classical method, but its activity remained lower than that of montmorillonitic clay. This difference is related to the lower content of the amorphous phase, according to the IR spectroscopy data, as well as to the less developed specific surface area after pillaring.

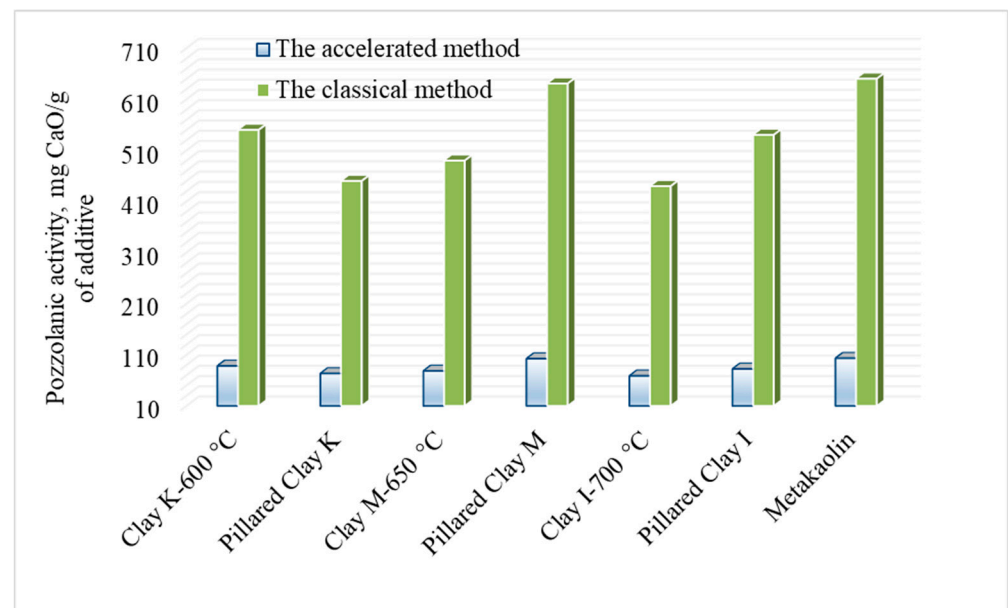


Figure 12. Pozzolanic activity (mg/g of additive) of pillared clays.

It should be noted that metakaolin absorbs a large amount of calcium hydroxide because of its highly developed specific surface area, which exceeds $16,000 \text{ cm}^2/\text{g}$, and its high amorphous phase content, which is at least 97%. Commercial metakaolin is produced from high-purity kaolinite, typically up to 99%, by conventional calcination without the use of a pillaring precursor agent. Nevertheless, this material was chosen for comparison because current regulatory documents specifically refer to this additive for the production of concrete mixtures and other construction mortars. By contrast, the clays used in this study are mixed-layered and have a more complex chemical composition.

These results confirm that kaolinitic clays are weakly susceptible to pillaring. The activity of pillared kaolinitic clay is almost 1.5 times lower than that of conventionally calcined kaolinite; i.e., metakaolin.

The authors suggest that the sharp increase in montmorillonite clay activity indicates that the process of pillar intercalation has disrupted the compact aggregates of scales, exposing the mineral's internal basal planes, as confirmed by previously obtained SEM images (Figure 8). It is this released surface that provides additional physical cohesion. Hydrate phases do not simply precipitate onto the clay, but rather grow through its defective structure. This is confirmed by the fact that, with similar overall porosity, samples with pillared clay exhibit higher activity and a developed specific surface area. This indicates the formation of closed pores or isolated rigid partitions (pillars) formed by nanoreinforcement.

3.3. Structure and Properties of Cement with Pillared Clays

Pillared montmorillonitic and illite–chlorite clays are expected to strengthen the cement structure and improve its density and durability. This assumption was confirmed by tests carried out over a period of 1 year. Furthermore, the authors previously studied the properties of limestone-containing cement, finding that limestone (10% by weight of cement) increases compressive strength by 4–5% after 28 days of curing due to the microfiller effect. The modified (pillared) clay is the primary contributor to the strengthening.

It is well known that cement can continue to gain strength throughout its service life, especially under favorable curing conditions; i.e., in a moist environment. However, the kinetics of strength development in blended cements remains insufficiently studied. Such cements are still treated with skepticism in the construction market because of their

higher water demand. Therefore, the strength development of cements containing calcined aluminosilicates was investigated.

In the first stage, the strength of cement with heat-treated clays was studied (Figure 13). All aluminosilicates were heat-treated at the optimal temperatures presented in Section 3.2.

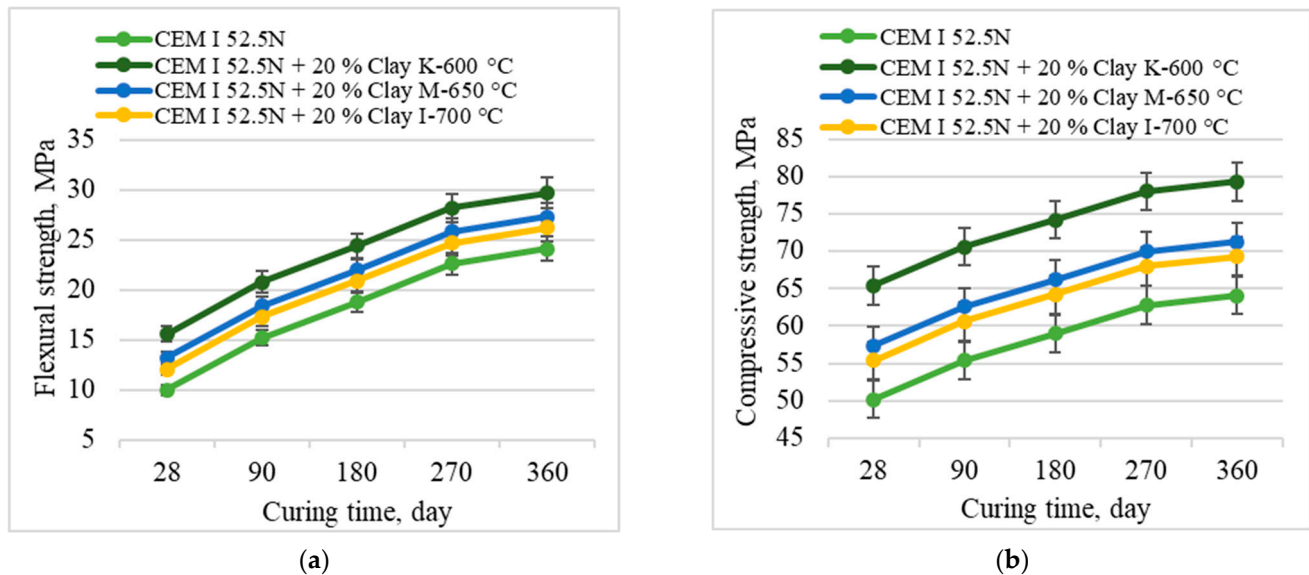


Figure 13. Strength of cement with heat-treated clays: (a) flexural strength, MPa; (b) compressive strength, MPa.

The strength of standard specimens (Figure 13) was monitored for 1 year (360 days), and all samples were stored in water. Analysis of the flexural and compressive strength data showed that the additive-free cement, CEM I 52.5 N (Figure 13), gained strength between 28 and 360 days. The flexural strength increased from 10 MPa to 24.1 MPa (Figure 13a), while the compressive strength increased from 50.2 MPa to 64.1 MPa (Figure 13b).

The composition containing 20% heat-treated kaolinite clay exhibited the highest strength gain: compressive strength after 360 days of curing reached 79.3 MPa, 1.2 times greater than that of the untreated sample. Moreover, compositions containing heat-treated montmorillonite and illite–chlorite clay demonstrated similar strength gain dynamics and, taking measurement error into account, were virtually identical. Thus, the flexural strength of cement containing heat-treated montmorillonite clay changed as follows: from 13.2 MPa to 27.3 MPa and from 55.4 MPa to 71.3 MPa in compression (from 28 days to 360 days, respectively).

The obtained data confirm the mechanism of clay action: heat-treated kaolinite clay contains a metastable phase (metakaolin), which actively binds with calcium hydroxide. Classic heat treatment of montmorillonite and illite–chlorite clays does not fully realize their potential. Unlike kaolinite, mixed-layer smectite aluminosilicates undergo dehydroxylation with a reduction in interlayer space, which limits the binding of portlandite during cement hydration.

The high flexural strength to compressive strength ratio (~ 0.38 – 0.40), which exceeds the typical values for ordinary Portland cement after 28 days of curing (~ 0.15 – 0.20), is explained by the long curing period (360 days) and the specific nature of the resulting composite. Over the course of a year, the calcium silicate hydrous structure significantly compacts, and the addition of pillared clay further enhances this process through pozzolanic reactions and crack inhibition.

In the second stage, the strength gain kinetics of cement with pillared clays was studied (Figure 14). Pillared clays, like heat-treated clays, were incorporated into CEM

I 52.5 N cement at a rate of 20% of the cement mass. Strength gain differed from that of samples with heat-treated clays. Cement with pillared Clay K did not reach its maximum strength, confirming the theory of a weak intercalation process. Meanwhile, cement with pillared Clay M and Clay I developed maximum strength, exceeding the strength of samples without a pillaring agent by 1.2–1.4 times, respectively.

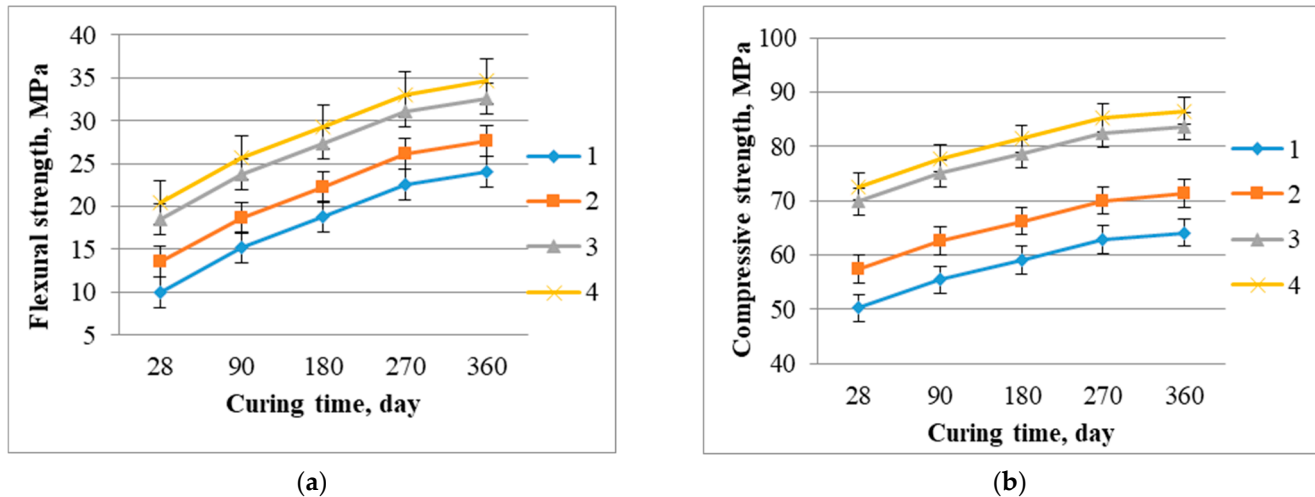


Figure 14. Strength of cement containing pillared clays: (a) flexural strength, MPa; (b) compressive strength, MPa. Mix compositions: 1, CEM I 52.5 N without additives; 2, CEM I 52.5 N + 20% pillared Clay K; 3, CEM I 52.5 N + 20% pillared Clay I; 4, CEM I 52.5 N + 20% pillared Clay M.

Pillared clays were added to CEM I 52.5 N cement at 20% by mass of cement. The greatest strength gain was observed for Portland cement containing pillared montmorillonitic clay (composition 4, Figure 14a,b). At 360 days of curing, the flexural strength reached 34.6 MPa (Figure 14a), while the compressive strength reached 86.5 MPa (Figure 14b). This is consistent with the previously obtained pozzolanic activity data.

The obtained data confirm fundamental differences in the permeability of aluminosilicates. Pillared montmorillonite clay has a 2:1 swelling structure. After heat treatment with the $\text{Al}_2(\text{SO}_4)_3$ precursor, rigid oxide pillars form within the interlayer space. These pillars act not only as crystallization centers for the C–S–H phase but also as a physical reinforcing framework that physically blocks phase mobility, causing microcrack growth. This is why compositions containing this clay exhibit the highest strength gains.

Samples containing pillared kaolinitic clay (composition 2, Figure 14) also showed higher strength than the additive-free reference sample, but their strength remained lower than that of the samples with pillared montmorillonitic and illite–chlorite clays (composition 3, Figure 14).

The continuous strength gain of compositions 3 and 4 for up to 360 days eliminates the effect of simply filling voids with clay. This demonstrates the slow chemical reaction of $\text{Ca}(\text{OH})_2$ binding under humid conditions, which is physically impossible without a transformation of the internal structure of the hydrated paste.

3.3.1. Sulfate Resistance

To assess the durability of cement containing pillared clays, its ability to retain strength under aggressive conditions was examined. Hardened cement mortar is often damaged by groundwater, which commonly contains a wide range of chemical species, including salts, acids, and alkalis, and sodium sulfate solutions are widely used to simulate sulfate attack on cement-based materials.

For this reason, a 5% sodium sulfate solution (Na_2SO_4) was used as the aggressive medium. After the standard specimens had reached their nominal strength following 28 days of curing, some of them were immersed in the sulfate solution, while the rest were left to continue curing in water. After 6 months (180 days) and 12 months (360 days), the specimens were tested for strength (Table 8). The experimental data were subjected to standard statistical processing, with the determination of a confidence interval at a significance level of $\alpha = 0.05$. The standard deviation for the compressive strength was on average ± 1.6 MPa.

Table 8. The strength of hardened cement pate with pillared clays in an aggressive environment.

№	Type of Cement	Compressive Strength, MPa, During Hardening Conditions					K _S After 12 Months
		In the Water			In a 5% Solution Na ₂ SO ₄		
		28 Days	6 Months	12 Months	6 Months	12 Months	
1	CEM I 52.5 N	50.2	59.0	64.1	63.2	56.3	0.88
2	CEM I 52.5 N + 20-% pillared Clay K	57.4	66.2	71.3	68.4	63.2	0.89
3	CEM I 52.5 N + 20-% pillared Clay I	69.8	78.6	83.7	80.1	79.5	0.95
4	CEM I 52.5 N + 20-% pillared Clay M	72.6	81.4	86.5	83.2	85.4	0.98

The strength of ordinary Portland cement began to decline after 6 months of exposure to the aggressive medium (composition 1, Table 8). After 12 months, the resistance coefficient was 0.88, while the compressive strength decreased from 63.2 MPa at 6 months to 56.3 MPa at 12 months, approaching its nominal 28-day strength.

By contrast, the strength of cement containing pillared clays remained almost unchanged, and for composition 4 with 20% pillared montmorillonitic clay, it even increased to 85.4 MPa after 1 year of exposure to the aggressive medium. As a result, the sulfate resistance coefficient K_s reached 0.98 (composition 4, Table 8). Sulfate resistance is commonly assessed by a corrosion or resistance coefficient comparing strength after sulfate exposure with that of water-cured specimens at the same age.

The strength of cement containing pillared kaolinitic clay (composition 2, Table 9) started to decrease after 12 months of curing in the aggressive medium, reaching 63.2 MPa. Accordingly, the sulfate resistance coefficient decreased to 0.89, following a trend similar to that of the additive-free cement. This behavior may be associated with the higher porosity of these specimens, which facilitates the penetration of sulfate ions and promotes further deterioration. Sulfate ions are well known to contribute to the long-term degradation of cement-based materials exposed to aggressive environments.

Table 9. Density and porosity of composite cements.

№	Type of Cement	Density (ρ), g/cm ³	Porosity (P), %
1	CEM I 52.5 N	2.309	13.2
2	CEM I 52.5 N + 20-% pillared Clay K + 10% limestone	2.350	12.8
3	CEM I 52.5 N + 20-% pillared Clay I + 10% limestone	2.395	11.1
4	CEM I 52.5 N + 20-% pillared Clay M + 10% limestone	2.410	10.8

In contrast, the hardened cement paste containing pillared montmorillonitic and illite–chlorite clays had a denser structure with minimal pore content due to the pozzolanic reaction, which improved both resistance to deterioration and continued strength

development. Pozzolan reactions are widely associated with pore refinement, denser microstructure, and enhanced durability of cementitious materials.

In addition to the strength of the cement in an aggressive environment and the calculation of K_s , the samples were periodically removed from the solution, and their length was measured using a comparator with an accuracy of up to 0.001 mm. Throughout the entire exposure period, the cement samples with pillared clay demonstrated stable dimensions with minimal expansion ($<0.02\%$), which is significantly below the destruction threshold (0.1%). At the same time, the control sample of CEM I showed an expansion of 0.08% by the 9th month of testing.

The change in the mass of the cement was recorded gravimetrically after the removal of surface moisture. For the modified samples, an initial mass gain was observed (up to 1.5% over the first 90 days), which was associated with the filling of open capillaries with reaction products, followed by stabilization. The absence of a sharp increase in mass in the second half of the year indicates the absence of intensive leaching or accumulation of hygroscopic salts within the structure.

Macro photography and visual inspection of the samples were carried out regularly. Local efflorescence and the beginning of microcrack formation were recorded on the control samples at the age of 10–11 months. The surface of the low-carbon samples remained visually intact, without chips or signs of impaired adhesion of the cement stone to the sand.

3.3.2. Freeze–Thaw Resistance

Since cement in many regions of the world is exposed to repeated temperature fluctuations between subzero and positive values, freeze–thaw action is another important cause of material degradation. Supplementary cementitious systems are often regarded as relatively resistant to frost damage, and the freeze–thaw resistance of Portland cement containing calcined aluminosilicates was therefore examined (Figure 13). Before the start of the experiment, all samples gained grade strength within 28 days of hardening in water. After that, the samples were tested in accordance with GOST 10060-2012. Repeated freeze–thaw cycling is known to cause cracking, surface damage, and strength loss in cement-based materials.

It was found that the strength of the additive-free cement (composition 1, Figure 15) decreased by 11.0% after 200 freeze–thaw cycles, whereas the cement containing pillared kaolinitic clay (composition 2, Figure 15) lost 9.7% of its strength. The other compositions showed only minor strength losses: 6.1% for the cement with pillared illite–chlorite clay (composition 3, Figure 15) and 5.5% for the cement with pillared montmorillonitic clay (composition 4, Figure 15). These results indicate their better resistance to alternating freezing and thawing, which can be attributed to their lower porosity and higher pozzolanic activity. The improved freeze–thaw performance of denser cementitious systems is consistent with the role of refined pore structure in limiting damage development.

Moreover, the mass loss for all tested samples did not exceed 2% , which meets standard requirements and confirms the integrity of the samples' structures. The standard deviation for compressive strength averaged ± 2.3 MPa.

The use of a sodium chloride solution simulates the actual conditions of concrete service in northern regions. The combined effects of salt osmotic pressure and alternating freezing and thawing cause extreme stress on capillary pores. The fact that composites with dynamically piled clay retain less than 6% of their strength demonstrates their exceptional resistance to this aggressive global compound.

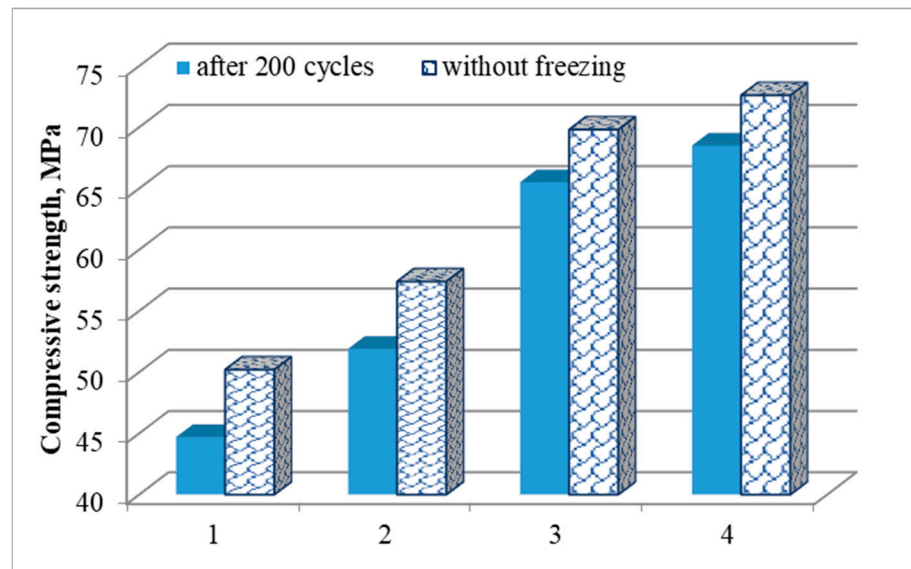


Figure 15. Frost resistance of hardened cement mortar with pillared clays (compositions are given in Table 8).

The samples are currently undergoing laboratory testing. Preliminary non-destructive testing data from 540-day-old samples confirms the preservation of their visual density and integrity. This study lays the foundation for understanding durability, and a full-scale five-year observation will be the subject of a separate publication.

3.4. Structure of Low-Carbon Blended Cement

At the final stage of the study, the strength and structure of a low-carbon blended cement containing a complex additive composed of pillared clay (20% by mass of cement) and limestone (10% by mass of cement) were investigated. Low-carbon cements based on limestone and calcined clay are widely associated with reduced clinker content and improved performance through synergistic reactions between the alumina-bearing clay component and limestone.

The incorporation of the complex additive increases the structural density (Table 9) due to the formation of additional hydrate phases, including calcium silicate hydrates, calcium aluminate hydrates, and calcium carboaluminates, including stratlingite ($\text{Ca}_4\text{Al}_2(\text{OH})_{12}[\text{AlSi}(\text{OH})_8]_2 \cdot 2\text{H}_2\text{O}$).

Given that the specific surface area of montmorillonite clay nearly doubled (Table 6), the reduction in macropores coupled with sustained high pozzolanic reactivity indicates their occlusion by fine reaction products directly within the intergranular space. Furthermore, the observed decrease in total porosity correlates with strength enhancement and is corroborated by microscopic imaging data.

The additive-free mixture exhibits the lowest density of 2.309 g/cm^3 among all tested samples (Table 9), as specified in Section 2.2.9. The incorporation of 30% of the complex additive increased the density of the cement system, with the maximum value of 2.410 g/cm^3 obtained for the composition containing pillared montmorillonitic clay (composition 4, Table 9).

The density data correlate well with the porosity values: the higher the density of the hardened cement paste, the lower the porosity. An inverse relationship between density and porosity is widely recognized in porous materials and cement-based systems.

Accordingly, the lowest porosity, 10.8%, was observed for the cement containing 20% pillared montmorillonitic clay and 10% limestone. By contrast, pillared kaolinitic clay appears not to undergo effective intercalation, so its structure changes only slightly

compared with that produced by conventional thermal treatment. Intercalation in kaolinite is typically associated with measurable interlayer expansion and structural modification; if this does not occur, the effect of treatment on reactivity and structure may remain limited.

For this reason, pillared kaolinitic clay can be regarded as not fully functioning as an active mineral additive, and the density and porosity of composition 2 (Table 8) differ only slightly from those of the additive-free cement.

To confirm these findings, the microstructure of the obtained samples was examined by SEM (Figure 16).

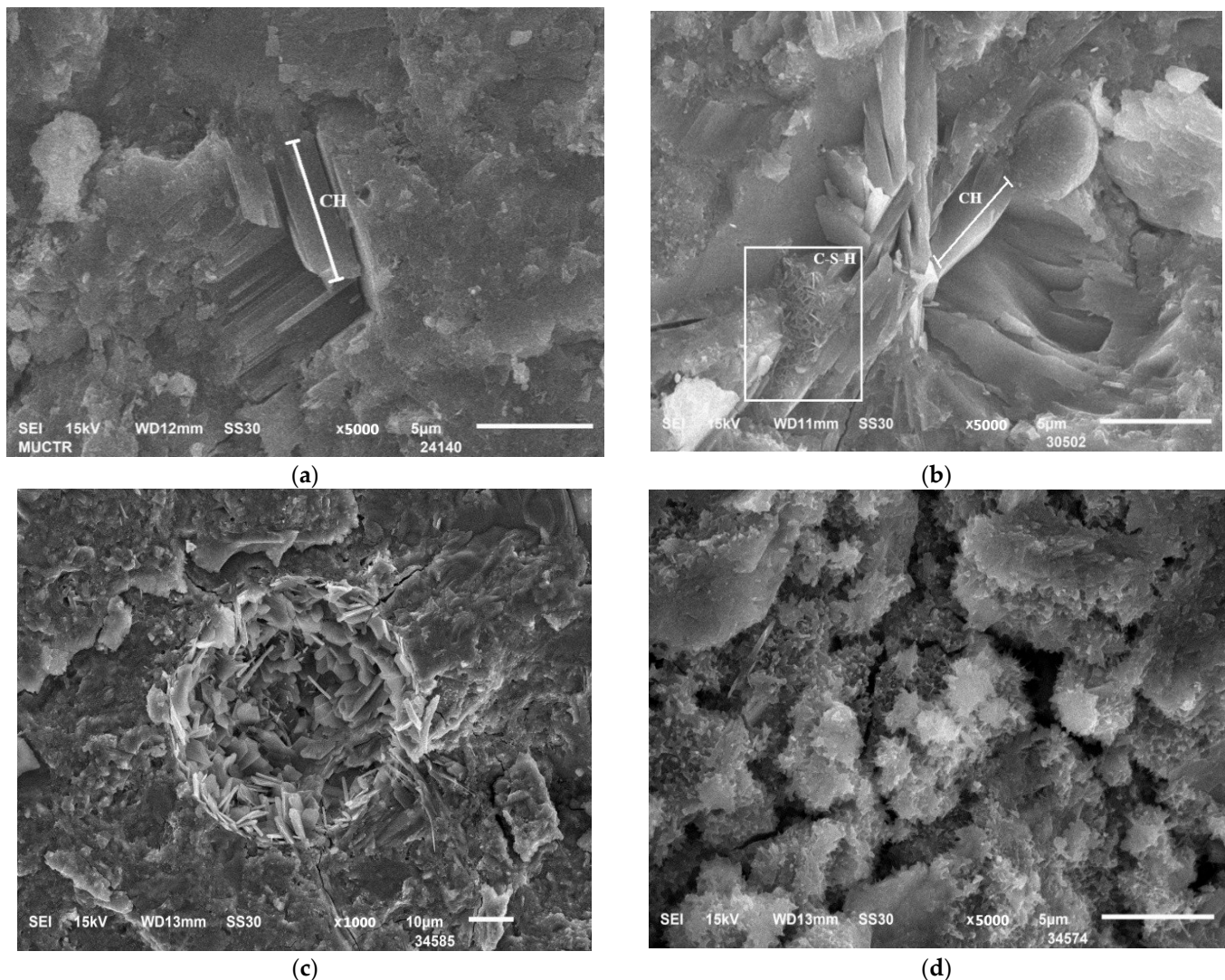


Figure 16. SEM micrographs of cement microstructure after 28 days of curing (compositions are given in Table 7): (a) CEM I 52.5 N, 5000 $\times$; (b) CEM I 52.5 N with 20% pillared Clay K and 10% limestone, 5000 $\times$; (c) CEM I 52.5 N with 20% pillared Clay I and 10% limestone, 1000 $\times$; (d) CEM I 52.5 N with 20% pillared Clay M and 10% limestone, 5000 $\times$.

The additive-free cement paste exhibited a porous microstructure and contained large portlandite crystals with an edge length of about 5 μm (Figure 16a). In contrast, the composition containing pillared kaolinitic clay also showed a small amount of coarse portlandite crystals (CH, Figure 16b), together with the formation of fine needle-like calcium silicate hydrates (C-S-H). The appearance of C-S-H supports the occurrence of a pozzolanic reaction, since pozzolanic materials consume portlandite and form additional

C–S–H, although in this case the reaction was evidently less intense than would be expected for metakaolin.

The samples containing pillared illite–chlorite clay and limestone (Figure 16c) showed clusters of intergrown hexagonal plates of calcium hydrocarbonaluminate phases. The surrounding matrix was dense and well defined, which further supports the synergistic effect of the two-component additive system. Limestone-calcined clay systems are known to promote carboaluminate formation and microstructural densification through interactions between reactive alumina and limestone.

The most distinctive microstructure was observed for the cement containing pillared montmorillonitic clay and limestone (Figure 16d). Numerous twisted leaf-like formations developed on the particle surfaces and appear to correspond to calcium silicate hydrate phases. According to the authors, their intergrowth resembled a “zip-lock” arrangement, which may explain the strength increase even at a high level of clinker replacement, as additional C–S–H is associated with pore filling, microstructural refinement, and improved mechanical performance.

4. Discussion

Cement production is one of the largest industrial sources of anthropogenic CO₂ emissions [1–5], accounting for about 8% of global CO₂ emissions according to widely cited estimates. A large share of these emissions arises from limestone calcination and clinker production [3,19].

The present results showed that replacing 30% of clinker with pillared aluminosilicates and limestone can reduce the carbon footprint of cement by about 25–30%, which is consistent with published estimates [10,81,82]. This reduction is associated with two main factors:

- Lower fuel demand, because aluminosilicates are calcined at about 650 ± 50 °C, which is far below the clinker burning temperature of about 1450 °C.
- Lower limestone consumption, because clinker production relies heavily on limestone and releases CO₂ during calcination ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), so partial clinker replacement directly decreases process emissions.

A conventional route for low-carbon cement development is LC3 technology, which combines calcined clay and limestone and is commonly based on kaolinite-rich clays. At the same time, the LC3 literature also emphasizes the importance of kaolinite content for performance, which makes the use of alternative aluminosilicate resources an important research direction.

As an alternative to such systems, the authors propose the pillaring of mixed-layer clays (e.g., montmorillonite and illite–chlorite). To date, pillared clays have been extensively studied primarily in petrochemistry and environmental catalysis [68–71]. However, their application as supplementary cementitious materials (SCMs) or pozzolanic additives remains in its infancy.

While contemporary research on clay activation predominantly focuses on conventional thermal treatment (calcination) [40,43–45], studies investigating pillared aluminosilicates in cementitious matrices are scarce and do not address their function as active mineral admixtures.

This study is among the first to systematically transfer the concept of inorganic “oxide pillars” from catalytic chemistry into construction materials science. It demonstrates that pillared mixed-layer clays serve not merely as fillers but likely provide a dual reinforcement mechanism within the cement system: chemical (high pozzolanic activity comparable to metakaolin) and physical (nano-reinforcement of microcracks by the rigid oxide pillar framework). This approach enables the development of cost-effective “green” cements based

on locally available non-kaolinitic raw materials. Nevertheless, further investigation is required to directly validate the hypothesis of physical reinforcement through crack propagation analysis, hydration kinetics monitoring, and quantitative pore structure characterization.

Quantitative assessment reveals that pillared montmorillonite exhibits a pozzolanic activity of 640.8 mg CaO/g, which is nearly identical to that of industrial metakaolin (650.2 mg CaO/g) (Figure 12). The key advantage, however, lies in energy efficiency: upon proper thermal activation, aluminosilicates of this composition achieve comparable pozzolanic reactivity while consuming approximately half the electricity.

Beyond direct performance comparison, a fundamental distinction exists regarding the feedstock. Conventional LC3 technology critically depends on deposits of pure kaolin. In contrast, our methodology allows for the utilization of widely abundant secondary mixed-layer clays, whose reserves are significantly larger and requirements for raw material purity are substantially lower.

Under controlled conditions, the intercalation of mixed-layer clays leads to the formation of PHC, such as $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$. Subsequent thermal treatment in the presence of a precursor induces dehydroxylation and the formation of rigid oxide clusters (pillars) within the clay's interlayer space. This calcination step is critical: the inherent tendency of aluminosilicate layers to undergo collapse upon heating severely limits the direct application of raw mixed-layer clays as supplementary cementitious materials (SCMs).

The expanded interlayer space ensures maximum occurrence of the pozzolanic reaction (due to a greater number of active sites). This ensures the formation of an additional amount of calcium hydrosilicates and hydroaluminates. Additionally, unlike metakaolin, pillars create isolated cavities with a size of 1–3 nm inside the clay structure. C–S–H nucleation occurs directly on the surface of these internal pillars (Figure 17). Collectively, these factors account for the observed strength development even at high levels of clinker substitution.

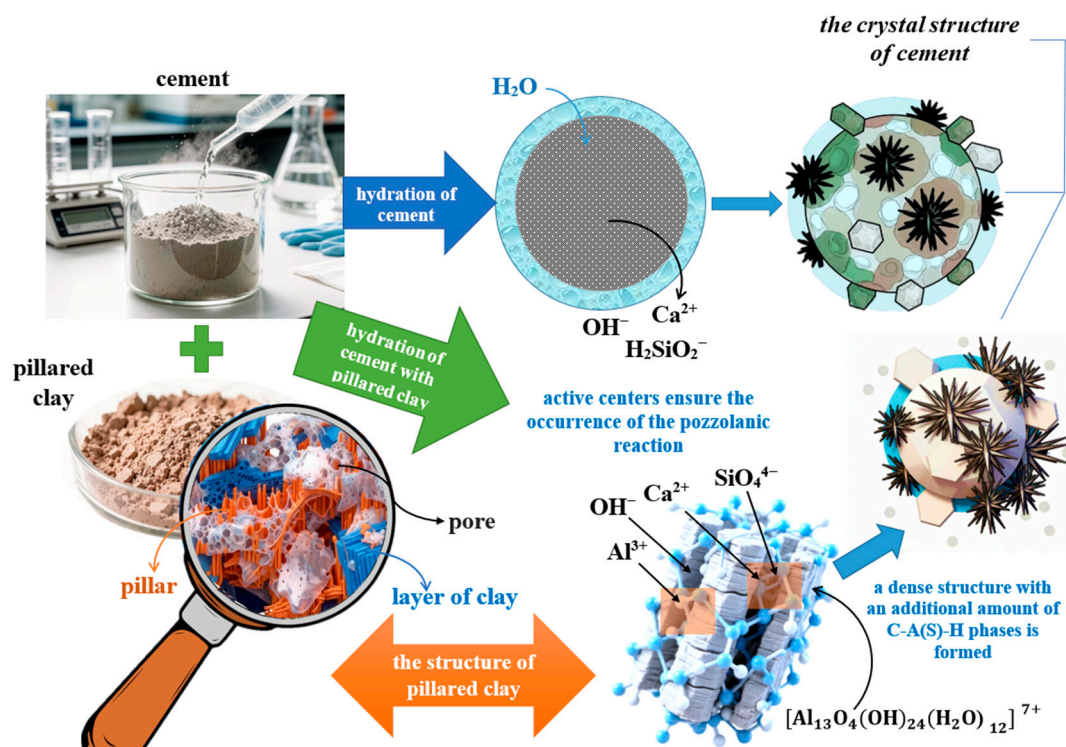


Figure 17. The mechanism of interaction between cement and pillared clay (proposed by the authors; some parts of the image were created using the GigaChat artificial intelligence model. Sber AI model).

Pillaring represents a cost-effective and scalable method for producing supplementary cementitious materials. The precursor, aluminum sulfate, costs 3–5 times less than kaolinite feedstock (Table 10). This significant economic advantage renders the technology viable for regions lacking access to traditional pozzolanic additives.

Table 10. Techno-economic comparison of cements containing different supplementary cementitious materials (SCMs).

Parameter	Beneficiated Kaolin Clay	Pillared Montmorillonite Clay
Calcination temperature, °C	(600–800) ± 50	650 ± 50
Specific energy consumption for clay calcination (MJ/t)	~900 (at T = 800 °C)	~740 (at T = 650 °C)
Raw material cost (ruble/t)	4000–5000	500–800
Cost of chemical activation, rub	Not required	900–1100
Compressive strength at 28 days (MPa)	50.2	72.6
Production cost of 1 tonne of cement (ruble)	6500	5900

Furthermore, the pillaring technology does not require the construction of new production facilities. A spraying unit for the salt solution can be seamlessly integrated into the existing SCM feeding line upstream of the cement mill. This eliminates the need for capital-intensive investments in dedicated calcination kilns.

Nevertheless, scaling up from laboratory conditions to industrial-scale production entails two primary engineering challenges: ensuring uniform mass transfer and controlling the exothermic effect during dehydroxylation. In a laboratory setting, mixing is performed with magnetic stirrers or manually (for small batches), guaranteeing complete wetting of each clay flake by the pillaring solution. For industrial processing, high-shear continuous mixers or spray dryers are recommended. These systems enable instantaneous dispersion of the aluminum sulfate solution, limiting contact time to less than one second and preventing premature particle aggregation prior to drying.

Thermal management is a critical scale-up factor. The dehydroxylation of montmorillonite is highly exothermic. When transitioning to large-capacity fluidized bed tunnel kilns or rotary kilns, there is a significant risk of local material overheating above 750 °C due to the heat released by the reaction. This may lead to aggregate sintering and subsequent loss of microporosity. To facilitate industrial implementation, it is necessary to implement furnace zoning with an excess supply of recirculated cooled gas directly into the intensive reaction zone (550–650 °C). Additionally, waste heat recovery systems should be installed to preheat incoming raw materials.

It is worth noting that the capital expenditures (CAPEX) for implementing this technology are minimal. The intercalation unit represents a standard solution preparation and nozzle system, which integrates easily into the existing mineral additive feed line before the cement mill without requiring new calcination plants.

Thus, pillared clays represent more than just an alternative to metakaolin; they embody a new philosophy of cement design. Firstly, they allow for a broad range of feedstocks, where any locally available clay can serve as an active filler. Secondly, they reduce CO₂ emissions by up to 30% through partial clinker substitution. Thirdly, the process offers superior economic accessibility compared to conventional activation methods.

Additional environmental benefits of producing green cement with pillared clays should also be noted. Beyond the direct reduction of CO₂ emissions by 30% via lower clinker factors, the proposed technology demonstrates significant advantages across other impact categories. Preliminary life cycle inventory (LCI) analysis indicates an 18% reduction

in cumulative non-renewable energy demand (CED) compared to the production of an equivalent volume of CEM I.

This gain is achieved not only by lowering the calcination temperature of aluminosilicates but also by eliminating deep kaolin beneficiation. Mining ordinary local clays via open-pit operations requires significantly less energy and obviates chemical bleaching—a step necessary for producing high-quality metakaolin—thereby reducing eutrophication and wastewater toxicity at the extraction stage.

The carbon footprint is further reduced by minimizing transportation distances: while kaolin mining is often tied to remote deposits, common mixed-layer clays are ubiquitous and typically located within the immediate vicinity of cement plant quarries. Furthermore, future prospects include the utilization of industrial wastes containing aluminosilicates (e.g., rice husk ash or sewage sludge ash). Such investigations are currently underway by the authors. Ultimately, this approach enables the development of future infrastructure without compromising climate objectives.

5. Conclusions

This study proposes a novel concept for activating layered aluminosilicates by forming interlayer oxide complexes (pillars) via the pillaring method. The key findings are as follows:

1. The intercalation of PHC effectively activates 2:1- and 2:1:1-type clays (montmorillonite and illite–chlorite), which are traditionally considered less reactive than kaolinite. For the first time, it is demonstrated that this approach nearly doubles the specific surface area of such clays compared to conventional thermal treatment, reaching values comparable to industrial metakaolin.
2. A dual reinforcement mechanism—combining chemical pozzolanic activity with physical “lock-and-key” nano-armoring—has been validated. SEM micrographs reveal dense agglomerations of calcium silicate hydrate (C–S–H) phases enveloping the clay particles. This unique microstructural arrangement accounts for the material’s exceptional resistance to aggressive environments.
3. Substituting up to 30% of clinker with a composite additive (pillared clay + limestone) reduces the cement carbon footprint by 25–30%. This formulation increases the density of the hardened paste to 2.4 g/cm³ while delivering superior durability metrics: the sulfate resistance coefficient exceeds 0.97, and strength loss after 200 freeze–thaw cycles remains below 5%.

By enabling the activation of non-kaolinitic aluminosilicates, this methodology facilitates the utilization of widely available local raw materials, eliminating the dependency on expensive high-purity kaolin deposits. Consequently, this pathway enables the production of cost-effective, low-carbon cements suitable for sustainable construction.

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Abbreviations

The following abbreviations are used in this manuscript:

$\text{Al}_2(\text{SO}_4)_3$	0.25 M aluminum sulfate solution
BET, S_{BET}	Specific surface area determined by the BET method
C_2S	Dicalcium Silicate (belite)
C_3A	Tricalcium Aluminate
C_3S	Tricalcium Silicate (alite)
C_4AF	Tetracalcium aluminoferrite
$\text{Ca}_4\text{Al}_2(\text{OH})_{12}[\text{AlSi}(\text{OH})_8]_2 \cdot 2\text{H}_2\text{O}$	Stratlingite
CaCO_3	Calcite
C–A–H	Calcium hydroaluminates
CH	Calcium Hydroxide (Portlandite)
Clay I	Clay in which the mineral illite predominates
Clay K	Clay in which the mineral kaolinite predominates
Clay M	Clay in which the mineral montmorillonite predominates
C–S–H	Calcium hydrosilicates
FTIR	Fourier transform infrared spectroscopy
GOST, GOST R	Russian State Standard
IR	Infrared Spectroscopy
K_S	Sulfate resistance coefficient, which is the ratio of the strength of a sample stored in a Na_2S_4 solution to the strength of a similar sample stored in distilled water.
NaCl	Sodium chloride solution
PHC	Polynuclear hydrocomplexes
SEM	Scanning Electron Microscopy/Microscope
XRD	X-Ray Diffraction
XRFA	X-Ray Fluorescence Analysis
σ	Strength

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