International Journal on
Technical and Physical Problems of Engineering
(IJTPE)
Published by International Organization of IOTPE

ISSN 2077-3528
IJTPE Journal
www.iotpe.com
ijtpe@iotpe.com

September 2026 | Issue 68 | Volume 18 | Number 3 | Pages 87-96

OPTIMIZATION OF STRUCTURE FORMATION IN CEMENTITIOUS MATERIALS THROUGH COMBINED MINERAL-CHEMICAL MODIFICATION

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Abstract- The influence of a complex organic-mineral additive, based on the thermal treatment product of kaolin rock (TTPKR) and superplasticizer SP-1, on the rheological properties, hydration kinetics, and strength characteristics of cement systems has been investigated. TTPKR, consisting of a mixture of metakaolin and finely dispersed quartz, exhibits combined pozzolanic activity and a micro-filling effect. Using a two-factor experimental design method, quantitative relationships were established between the composition of the additive components (TTPKR 3-15%, SP-1 0.5-1.5%) and the key characteristics of cement paste and stone. It was shown that increasing the amount of TTPKR raises the water demand, while the superplasticizer ensures its effective reduction due to its dispersing action. Using the optimal dosage of 15% TTPKR and 1.5% SP-1, the cement paste shows the same normal consistency as the reference composition. The results showed that adding TTPKR increases the content of chemically bound water, which suggests enhanced hydration activity and the generation of additional hydrosilicate and hydroaluminosilicate phases. Maximum strength values are achieved with moderate dosages of TTPKR (3-9%) in combination with the superplasticizer, providing a 27% increase in strength at 28 days of curing compared to the control composition. It is shown that the strengthening effect is associated with the synergistic interaction of the pozzolanic reaction of metakaolin, the micro-filling effect, and the increased degree of dispersion of cement particles. The obtained results confirm the effectiveness of complex organic-mineral modifiers for controlled structure formation and property management of cement systems.

Keywords: Thermal Product, Kaolin Rock, Metakaolin, Cement Paste, Superplasticizer, Strength, Organic-Mineral Additives, Hydration.

1. INTRODUCTION

Modern construction imposes increasingly high demands on the performance characteristics of concrete and reinforced concrete structures. Ensuring high strength, durability, crack resistance, and frost resistance of cement composites is a primary task of materials science [1, 2]. In recent years, the primary focus in enhancing cement sistems has involved the creation and use of polyfunctional modifiers, which enable targeted control over structure formation during each stage of hardening process [3, 4].

The relevance of research in the field of modifying cement systems is linked to several interrelated factors. Firstly, the depletion of high-quality raw material reserves and the necessity to incorporate industrial by-products and local materials into production demand effective methods for binder activation [5, 6]. Secondly, modern construction trends focus on high-rise buildings, long-span structures, and special-purpose facilities, which require the use of high-strength and self-compacting concretes [7, 8]. Thirdly, energy efficiency and environmental safety requirements stimulate the development of resource-saving technologies with a reduced Portland cement content [9, 10].

The development of highly efficient plasticizers -know as superplasticizers-has made it possible to produce concrete mixes with a very low water-to-cement ratio [11, 12]. Superplasticizers - polymer compounds (naphthalene sulfonates, melamine sulfonates, polycarboxylates) - adsorb on the surface of cement particles, creating electrostatic and steric hindrances that prevent aggregation and ensure high mixture fluidity with minimal water content [13, 14]. However, the use of plasticizing admixtures alone does not always solve the problem of forming a dense and homogeneous structure of the cement stone. The lack of water for complete hydration of clinker minerals can slow down the formation processes of new compounds, create internal stresses, and reduce durability [15, 16].

To compensate for these negative effects and control the structure formation of cement stone, various types of active mineral additives are widely used [17, 18]. Among them, metakaolin-containing products - thermally activated kaolin clays - hold a special place. Metakaolin ($Al_2O_3 \cdot 2SiO_2$) obtained by dehydrating kaolinite at temperatures 500-800^{0}C [19, 20]. Unlike other active

Registered: 260407 | Article Info: 260314 | Accepted: 269815
Reserved: 260622 | Available: 260930

mineral additives (silica fume, fly ash, granulated slag), metakaolin has a mixed aluminate-silicate nature of pozzolanic activity, which ensures its ability to interact not only with portlandite but also with the hydroaluminate phases of the cement stone [21, 22].

During the hydration of clinker minerals, calcium hydroxide is released. Its chemical reaction with metakaolin generates additional quantities of calcium hydrosilicates (CSH), calcium hydroaluminosilicates (CASH) and hydrogranates [23]. These new compounds are characterized by a denser packing, contributing to the compaction of the cement stone structure, reducing its permeability, and increasing chemical durability [24]. Additionally, the fine dispersed particles of metakaolin (specific surface area up to 15-25 m²/g) act as a micro-filler, filling interparticle voids and creating additional crystallization centers [25]. However, the high specific surface area and plate-like morphology of metakaolin particles necessitate an increase in the water demand of cement systems, which can neutralize the plasticizing effect of superplasticizers [26]. Therefore, the most effective method is considered to be the combined application of metakaolin with modern water-reducing admixtures, allowing for a synergistic effect - reducing water demand while maintaining high system reactivity [27, 28].

Of particular interest is the use of thermal treatment products of natural kaolin rocks, which, along with metakaolin, contain finely dispersed quartz and other mineral components [29]. Such products derived from local raw materials possess not only pozzolanic activity but also rheological properties that contribute to improving the workability of concrete mixtures [30].

Despite numerous studies on the modification of cement systems with organic-mineral additives, many aspects of their combined influence on hydration, structure formation processes, and properties of cement stone remain insufficiently investigated. In particular, systematized information is required on the regularities of changes in water demand, hardening kinetics, and phase composition of hydration products as the ratio of complex modifier components varies.

This study investigates the influence of a complex organic-mineral additive the structure formation and physical-mechanical properties of cement composites. The additive in question is composed of the thermal treatment product of kaolin rock (TTPKR) together with superplasticizer SP-1. To reach this aim, several tasks were formulated. They included the following:

1. The first task involved assessing the impact of TTPKR and SP-1 dosages. Specifically, their effect on the normal consistency of cement paste was examined;
2. Investigation of the kinetics of strength gain in cement stone at early and late hardening stages;
3. Determination of the optimal ratios of the complex modifier components;
4. Analysis of the physicochemical processes underlying the observed effects.

2. MATERIALS AND RESEARCH METHODS

2.1. Characteristics of Starting Materials

Portland cement CEM I 42.5, manufactured by Holcim (Azerbaijan), was used as the primary binder. The cement meets the requirements of EN 197-1 and has the following characteristics: Blaine specific surface area - 340 m²/kg, normal consistency of cement paste - 26.5%, setting times: initial - 145 min, final - 210 min, compressive strength at 28 days of curing - 48.2 MPa. The mineralogical composition of the clinker is as follows: C_3S-62.5%, C_2S-14.8%, C_3A-7.2%, C_4AF-10.5%.

The thermal treatment product of natural kaolin rock (TTPKR) from the Chanlibel deposit (Azerbaijan) was used as an active mineral additive. The kaolin rock was subjected to firing at a temperature of 700±50°C for a duration of two hours. After that, it was ground until achieving of 450 m²/kg. The resulting TTPKR exhibits the following chemical composition: SiO_2 -61.65%, Al_2O_3-27.88%, Fe_2O_3-0.85%, CaO-0.80%, MgO-0.11%, Na_2O-0.30%, K_2O-0.41%.

X-ray phase analysis of TTPKR showed that the product consists of a mixture of X-ray amorphous metakaolin and crystalline quartz in an approximate ratio of 1:1.25. The metakaolin phase content is approximately 40%, which ensures the high pozzolanic activity of the additive. The presence of finely dispersed quartz (particle size mainly 1-10 μm) determines the rheological activity of TTPKR, contributing to improved workability of mixtures.

Superplasticizer SP-1 - sodium polymethylene naphthalene sulfonate (Polyplast LLC, Russia) - was used as the chemical admixture. SP-1 is a brown powder with an average density of 650-750 kg/m³, a pH of its aqueous solution of 7-9, and a sodium sulfate content not exceeding 5%. SP-1 acts through a specific physicochemical mechanism. It involves the adsorbtion of sulfonate group anions onto the positively charged regions of clinker minerals surfaces, which then causes electrostatic repulsion between cement particles.

Water used for preparing cement compositions meets the requirements of EN 206 and has the following indicators: pH 6.8, total hardness 2.5 mg-eq/l, chloride content less than 50 mg/l.

2.2. Experiment Planning

To identify the general patterns of modification of cement systems with complex organic-mineral additives and to determine the optimal dosages of individual additives, a full factorial experiment of type 2^2 was carried out with variation of two independent factors:

- X_1 - amount of TTPKR in the binder mixture, % (coded values: lower level -1 - 3%, upper level +1 - 15%, base level 0 - 9%);
- X_2 - amount of superplasticizer SP-1 relative to cement mass, % (coded values: lower level -1 - 0.5%, upper level +1 - 1.5%, base level 0 - 1.0%).

The choice of factor variation ranges was based on preliminary experiments and literature data. The optimal amount of metakaolin-containing additives in cement systems is typically 5-20% of the cement mass [14]. The

dosage of naphthalene sulfonate-type superplasticizers falls within the range of 0.5-1.5% [21].

The experimental design matrix was planned accordingly. Table 1 presents both this matrix and the results that were achieved. To ensure statistical reliability of the results, experiments were conducted in triplicate.

Table 1. Design matrix and experimental results for the two-factor experiment

Exp. No	X_1 (TTPKR)		X_2 (SP-1)		Normal Consistency, %	Compressive Strength(days), MPa		
	code	value, %	code	value, %		3	7	28
1	+1	15	+1	1.5	26.0	57.1	63.9	73.2
2	-1	3	+1	1.5	24.0	65.6	80.9	90.5
3	+1	15	-1	0.5	30.0	47.1	52.1	62.3
4	-1	3	-1	0.5	29.0	61.8	74.3	81.9
5	0	9	0	1.0	28.0	67.1	80.8	88.4

2.3. Sample Preparation and Testing

The investigations were carried out on cement stone as a matrix component of heavy concrete. The choice of cement stone as the research object is due to the need to eliminate the influence of inert aggregates, which can complicate the interpretation of results during the study of physicochemical processes.

During the preparation of the cement paste, the finely dispersed TTPKR additive was mixed dry with the cement and blended in a laboratory mixer for 2 minutes. Superplasticizer SP-1 was pre-dissolved in the mixing water (at a temperature of 20±2°C) and added during mixing. The water-to-cement ratio (W/C) was established based on the required normal consistency of the cement paste. This procedure followed the methodology described in EN 196-3.

To determine the compressive strength of the cement stone, cube-shaped specimens with a 20 mm side were prepared. The cement paste was placed into collapsible steel molds lubricated with a thin layer of technical petroleum jelly and compacted on a vibrating table with an oscillation frequency of 3000±200 min^{-1} and an amplitude of 0.5±0.05 mm for 2 minutes. The filled molds were placed in a normal hardening chamber with a hydraulic seal (humidity 95±5%, temperature 20±1°C) for 24 hours. After 1 day, the specimens were removed from the molds, marked, and subjected to testing (some specimens were tested at 1 day, while the rest continued hardening in a water bath at 20±1°C). Compressive strength tests were carried out on a P-50 hydraulic press with a maximum load of 50 kN according to EN 196-1.

Using the EN196-3 procedure, we determined the normal consistency of the cement paste in the Vicat apparatus fitted with a pestle of 10±0.05 mm diameter. The normal density was taken as the water-cement ratio at which the pestle of the Vicat apparatus did not reach the plate by 6±2 mm.

The ignition method was used to measure the content of chemically bound water in the cement stone. In this procedure, a 2-3g crushed specimen was first dried at 105±5°C until reaching a constant mass, and then calcined at 1000±25°C for one hour. The mass loss during ignition was taken as the amount of chemically bound water.

For X-ray structural studies, cement stone samples were preliminarily dried at 50±5°C to constant mass to remove free water not included in the crystal hydrates. The dried samples were ground in an agate mortar to a powder with particle sizes less than 10 μm, which provides optimal conditions for quantitative X-ray phase analysis. The study was carried out on a diffractometer with CuKα radiation (λ=1.5406 Å) in the 2θ angle range from 5 to 60 degrees.

3. RESULTS AND DISCUSSION

3.1. Influence of the Combined Additive on the Normal Consistency of Cement Paste

The normal consistency of cement paste is an important technological parameter. It reflects how much water the binder requires, which in turn affects both the porosity and strength of resulting cement stone. According to two-factor exsperimental results, adding TTPKR leads to an increase in normal consistency. Conversely, inclusion of SP-1 causes a decrease in this property.

Based on the experimental data, a regression equation describing the dependence of normal consistency (NC) on the amounts of TTPKR (X_1) and SP-1 (X_2) in coded variables was obtained:

$$NC = 27.25 + 0.75X_1 - 2.25X_2 + 0.25X_1X_2 \quad (1)$$

Standard errors: intercept 0.18, X_1< 0.22, X_2<0.22, interaction 0.27; $R^2 = 0.96$, $p < 0.01$.

Analysis of Equation (1) shows that factor X_2 (amount of SP-1) has the most significant effect on normal consistency - its coefficient is 3 times larger than that for X_1. The negative sign of the coefficient indicates that an increase in the amount of superplasticizer reduces water demand. The effect of factor X_1 (amount of TTPKR) is positive - an increase in the proportion of the mineral additive raises the normal consistency. The interaction of factors (term X_1X_2) has a small positive effect. The dependence of normal consistency on the dosages of TTPKR (X_1) and SP-1 (X_2) is shown in Figure 1.

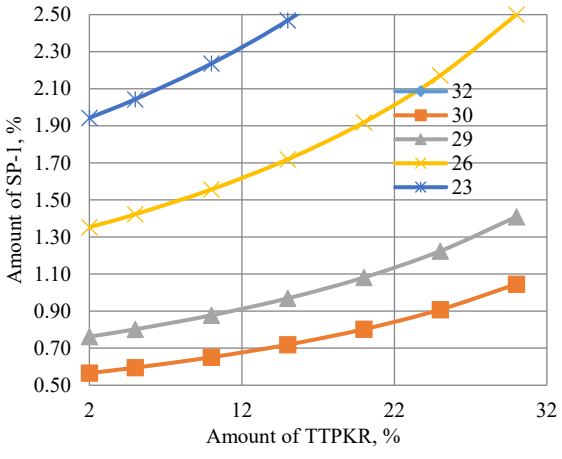

Figure 1. Variation of normal consistency in the region of varying factors

The results obtained are consistent with data from other researchers [26, 27]. When metakaolin-containing additives are introduced, the water demand of the system increases. The following factors account for this rise:

1. The specific surface area of metakaolin particles is greater (450 m²/kg) than that of cement (340 m²/kg), which necessitates additional water for wetting;
2. Plate-like shape of metakaolin particles, creating additional friction during mixture movement;
3. Formation of a porous structure of particles during high-temperature treatment of kaolinite;
4. High hydrophilicity of the metakaolin surface due to the presence of active silanol and aluminol groups.

Of particular interest is composition No. 1 (15% TTPKR + 1.5% SP-1), where the normal consistency (26.0%) practically coincides with the control value (26.5%). This fact has significant practical importance, as it allows the introduction of a substantial amount (15%) of an active mineral additive without increasing water demand. Such a combination provides optimal conditions for forming a dense structure of the cement stone.

It should be noted that within the studied dosage ranges, no synergistic effect of water demand reduction was observed upon the combined application of TTPKR and SP-1 (the interaction coefficient is positive, not negative). This may be related to competition between the additive components for adsorption on the particle surface or to the specific surface characteristics of metakaolin.

The presence of approximately 40% finely dispersed quartz in TTPKR plays a positive role, partially compensating for the high water demand of metakaolin. Quartz particles have an isometric shape and a smaller specific surface area, which helps reduce friction in the system.

3.2. Effect of the Complex Additive on the Strength of Cement Stone

Compressive strength is an integral characteristic reflecting the effectiveness of structure formation processes in cement stone. Processing of the experimental data resulted in regression equations for strength at 3 and 28 days of hardening.

$$R_3 = 57.9 - 5.8X_1 + 3.45X_2 + 1.55X_1X_2 \quad (2)$$

Standard errors: intercept 0.45, X_1–0.55, X_2–0.55, interaction 0.68; $R^2 = 0.94$, $p < 0.05$.

$$R_{28} = 76.975 - 9.225X_1 + 4.875X_2 + 0.575X_1X_2 \quad (3)$$

Standard errors: intercept 0.60, X_1–0.73, X_2–0.73, interaction 0.90; $R^2 = 0.95$, $p < 0.01$

Analysis of Equations (2) and (3) allows us to identify the following patterns. At early hardening (3 days), factor X_1 (amount of TTPKR) has a negative effect on strength at high additive dosages. This is explained by the reduction in clinker content and the retardation of initial hydration stages when using metakaolin. Factor X_2 (amount of SP-1), on the contrary, contributes to an increase in early strength, which is associated with improved rheological properties and more uniform water distribution in the system.

By 28 days of hardening, the effect of both factors intensifies. The negative effect of TTPKR becomes more pronounced (coefficient increases from −5.8 to −9.225), indicating that even in the long term, replacing 15% of cement with TTPKR leads to a certain decrease in strength compared to the control composition at the same normal consistency. However, this decrease can be compensated by selecting an optimal water-to-cement ratio.

It is important to note that introducing TTPKR in optimal amounts (3-9%) with an optimal dosage of SP-1 allows achieving strength values that exceed those of the additive-free cement stone. Consider composition No.2, which contains 3% TTPKR and 1.5% SP-1. After 28 days of hardening, it reaches a strength of 90.5MPa-a value 27% higher than the control sample (71.2MPa). Composition No. 5 (9% TTPKR + 1.0% SP-1) also shows high results - 88.4 MPa.

The impact of the investigated parameters on the compressive strength of cement stone after 3 days of curing is shown in Figure 2.

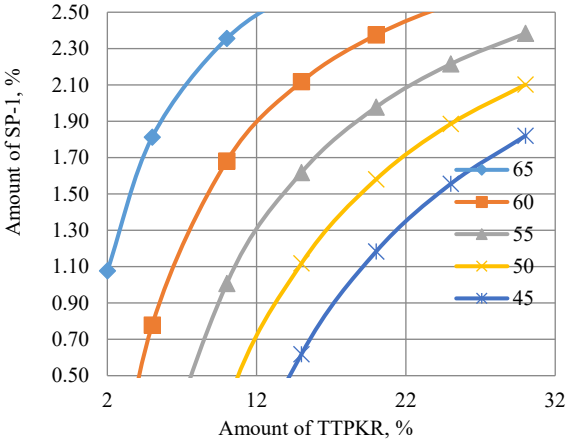

Figure 2. Variation of compressive strength (MPa) of the binder stone in the region of varying factors at the age of 3 days

The results were analyzed for the 3-day hardening period. Maximum strength occurs when the SP-1 content lies between 0.62% and 1.18% and the TTPKR content falls within 15-20%. The increase in strength compared to additive-free cement stone reaches up to 15%. This region corresponds to compositions with a high content of mineral additive and a lower content of superplasticizer.

Achieving high early strength upon the introduction of TTPKR can be explained by several factors:

1. Acceleration of Clinker Mineral Hydration: Metakaolin with a high specific surface area acts as an additional crystallization center for calcium hydrosilicates, accelerating nucleation processes [20].
2. Pozzolanic Reaction: The interaction of metakaolin with portlandite Ca $(OH)_2$ leads to the formation of additional amounts of CSH phases in the early stages of hardening. The resulting calcium hydroaluminates and hydrosilicates have a denser packing compared to the hydration products of pure cement [22].
3. Micro-Filling Effect: The fine dispersed particles of TTPKR fill interparticle voids in the cement paste, reducing the effective water-to-cement ratio in micro-volumes and increasing the packing density of the solid phase [28].

At later hardening stages (28 days), the picture changes. As shown in Figure 3, the highest strength is achieved by applying a complex with SP-1 content in the range of 0.88-1.98% and TTPKR content in the range of 5-10%.

The shift of the optimum by 28 days towards smaller dosages of TTPKR indicates that the retarding effect of the superplasticizer is neutralized over time with the participation of metakaolin. Additionally, the importance of the water-to-cement ratio in forming the structure and strength of the cement stone increases. Even with SP-1 present at high TTPKR content (15%), high porosity persists, limiting the maximum achievable strength.

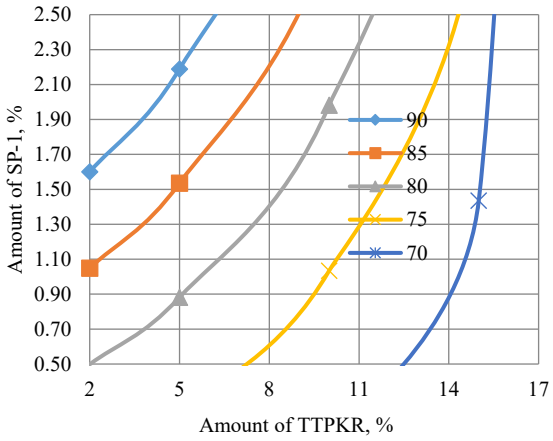

Figure 3. Variation of compressive strength (MPa) of the binder stone in the region of varying factors at the age of 28 days

A clear comparison is between compositions No. 1 and No. 2. In composition No. 1 (15% TTPKR + 1.5% SP-1), the strength is 73.2 MPa, whereas in composition No. 2 (3% TTPKR + 1.5% SP-1), the strength is 90.5 MPa. The normal consistency of these compositions is practically the same (26.0% and 24.0%, respectively). These results indicate that the optimal TTPKR content for achieving maximum strength is 3-9%, not 15%.

To provide deeper insight, the response surfaces were analyzed for curvature and optimum regions. Using the regression models, the predicted maximum strength at 28 days (91.2 MPa) occurs at X_1 = -0.65 (≈4.1% TTPKR) and X_2 = +0.92 (≈1.46% SP-1). The 95% confidence interval for this prediction is ±3.2 MPa. The coefficient of variation for replicate measurements was less than 5%, indicating good reproducibility. These statistical validations strengthen the reliability of the conclusions.

3.3. Effect of Complex Additive on Hydration Processes

An analysis of chemically bound water was performed on samples of different compositions at 28 days of hardening in order to understand how the complex additive affects the structure formation of cement stone. Table 2 [original data] presents the findings from this analysis.

Table 2. Amount of chemically bound water in cement stone

Composition No.	TTPKR content, %	SP-1 content, %	Chemically bound water, %
1	15	1.5	18.2
2	3	1.5	17.5
3	15	0.5	16.8
4	3	0.5	16.2
Control	0	0	15.4

According to the analysis of the experimental data, incorporating TTPKR results in a higher content of chemically bound water. This value reaches 18.2% for composition No.1, in contrast to 15.4% recorded for the control sample. The increase in bound water content indicates a more complete hydration process and the formation of additional new hydraulic compounds.

This is particularly evident when comparing compositions No. 1 and No. 2. With practically the same normal consistency (26.0% and 24.0%), the composition with 15% TTPKR has a higher bound water content (18.2%) than the composition with 3% TTPKR (17.5%). However, the compressive strength of composition No. 2 is higher (90.5 MPa vs. 73.2 MPa). This discrepancy is explained by the fact that not all new compounds have the same effect on strength. At high metakaolin content, the formation of the hydrogarnet phase, which has less favorable morphology, is possible, while at optimal dosages, high-basicity calcium hydrosilicates that provide higher strength predominate [23].

The superplasticizer also plays a role in this effect. Its presence leads to a greater quantity of chemically bound water. In compositions 1/3 and 2/4, with the same TTPKR content, samples with a higher amount of SP-1 have a higher content of chemically bound water. This confirms that the superplasticizer creates conditions for more complete hydration by reducing water demand and improving particle dispersion.

X-ray phase analysis (XRD) is one of the most informative methods for studying the phase composition and structure of cement stone. This study reports the findings from an X-ray structural analysis conducted on cement stone samples. The samples were prepared using Portland cement CEM I 42.5 modified with varying amounts of metakaolin (Figures 4-6).

In the diffractogram of the control sample (Figure 4), the most intense reflections of portlandite are observed at $2\theta = 18.0°$ (plane 001), 34.1° (plane 011), and 47.1° (plane 012). The considerable intensity of these diffraction peaks suggests that large amounts of free calcium hydroxide are present. This compound forms during the hydration of the silicate phases (alite and belite). Portlandite, as one of the principal hydration products of Portland cement, is essential for creating the alkaline environment that protects steel reinforcement through passivation.

Reflections of unhydrated alite (C_3S) are present at $2\theta = 29.4°$ and 32.2°, indicating that even after 28 days of hardening, the clinker is not fully hydrated. The intensity of these peaks is relatively low, which is typical for CEM I 42.5 cement with a moderate degree of hydration under normal conditions. The absence of distinct belite (C_2S) peaks may be related to its lower reactivity and/or its lower initial content in the clinker.

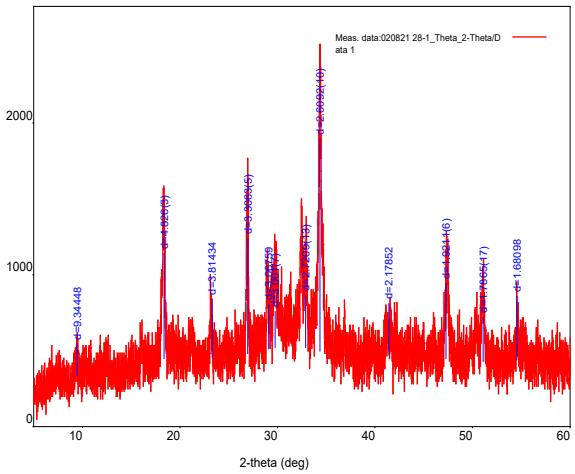

Figure 4. Control sample without additive - X-ray diffractogram

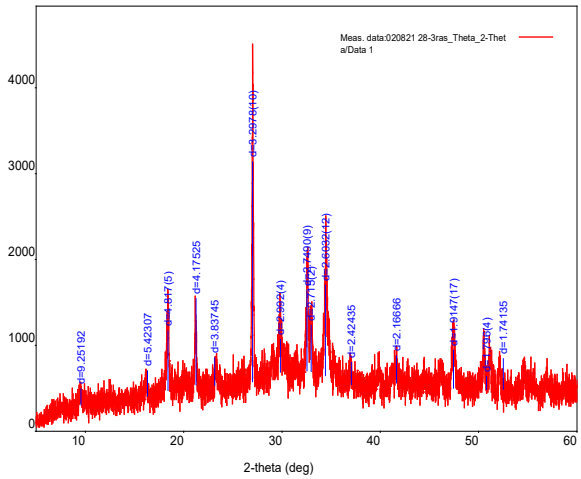

Figure 5. Sample with 10% TTPKR - X-ray diffractogram

Diffraction maxima at 2θ = 9.1° and 15.8° correspond to ettringite ($C_6AS_3H_{32}$). The intensity of these peaks is not high, which is explained by the fact that ettringite forms mainly in the early stages of hydration and later transforms into the monosulfate phase. The presence of ettringite at 28 days of hardening indicates that the sulfate hydration process is not yet fully complete.

Broad diffuse peaks are observed in the 2θ = 25-35° angle interval, characteristic of X-ray amorphous calcium hydrosilicates CSH(I). The absence of distinct reflections for this phase is due to its weak crystallization and the nature of nano-sized particles. It is the formed CSH phases that are the primary strength-bearing components of the cement stone, providing 70-80% of its load-bearing capacity.

Weak peaks observed at 2θ = 29.4° (overlapping with alite) may indicate the presence of calcite ($CaCO_3$) formed by carbonation of portlandite upon contact with atmospheric carbon dioxide. The degree of carbonation is very slight, indicating proper storage conditions for the specimens.

The diffractogram of the sample containing 10% metakaolin shows a reduction in the amount of portlandite compared to the control composition (Figure 5).

A noticeable decrease in the intensity of portlandite reflections at 2θ = 18.0° and 34.1° is observed. The relative decrease in integral intensity is approximately 30-35% compared to the control sample. This decrease is explained by the pozzolanic reaction in which metakaolin interacts with calcium hydroxide.

New peaks corresponding to calcium hydroaluminate C_4AH_{13} ($4CaO \cdot Al_2O_3 \cdot 13H_2O$) at 2θ = 12.5° and stratlingite ($2CaO \cdot Al_2O_3 \cdot SiO_2 \cdot 8H_2O$) at 2θ = 24.8° are observed in the diffractogram of the cement stone with metakaolin additive. Az a result of the pozzolanic reaction involving metakaolin, these phases appear and help increase the strength of the cement stone.

The intensity of peaks for unhydrated alite decreases, indicating deeper hydration of the cement in the presence of metakaolin. This effect may be related to the fact that the fine dispersed particles of metakaolin act as additional crystallization centers, accelerating the nucleation and growth processes of hydrosilicate phases.

The intensity ratios of ettringite peaks (9.1° and 15.8°) change compared to the control sample. Partial transformation of ettringite into the monosulfate phase is observed, which may be associated with changes in the ionic composition of the pore fluid and the influence of metakaolin on the equilibrium between sulfate and aluminate phases. The diffuse peaks in the 25-35° region become more intense and broader, indicating an increase in the amount of the X-ray amorphous phase. This confirms that additional calcium hydrosilicates from due to the pozzolanic reaction, which corresponds to the enhanced strength observed in mechanical tests.

The diffractogram of the sample with the maximum amount of metakaolin (15%) shows the greatest reduction in portlandite (Figure 6).

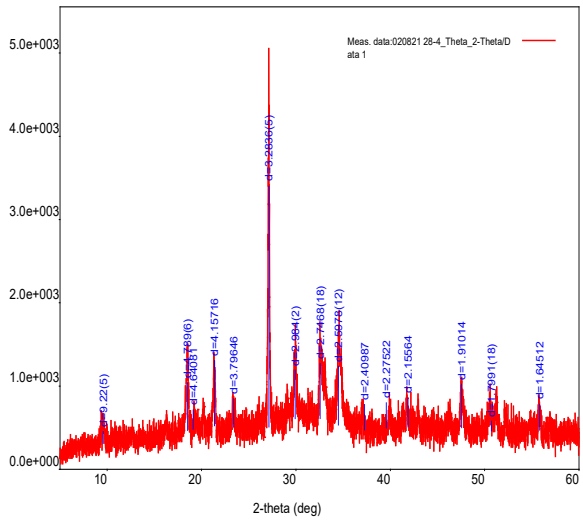

Figure 6. Sample with 15% TTPKR - X-ray diffractogram

In these samples, the intensity of portlandite reflections decreases even more significantly - by 50-60% compared to the control sample. The practically complete conversion of calcium hydroxide into hydraulic compounds due to the pozzolanic reaction indicates the high activity of the metakaolin used. According to literature data [1, 30], the optimal amount of portlandite bound in reactions with metakaolin is achieved when additive content is 15-20%.

New peaks appear in the diffractogram, identified as hydrogarnets (C_3AH_6, $3CaO \cdot Al_2O_3 \cdot 6H_2O$) at 2θ = 17.5°; 31.2°; and 39.4°. The formation of hydrogarnets is characteristic of systems with high metakaolin content and an excess of the aluminate component. These phases have a cubic structure and provide additional density to the cement stone.

The diffuse peaks in the 20-40° region become more pronounced, indicating an increase in the total amount of X-ray amorphous phases. This is explained by the formation of amorphous or poorly crystalline products of the pozzolanic reaction, including CSH(II) and aluminosilicate gels.

The peaks of ettringite at 9.1° and 15.8° practically disappear. This indicates the completion of the transformation of ettringite into the monosulfate phase and hydrogarnets. The high content of metakaolin facilitates the binding of sulfate ions into more stable compounds.

A peak corresponding to α-quartz (SiO_2) is observed in the region of 2θ = 26.6°. This reflection is associated with the presence of finely dispersed quartz in the TTPKR composition (approximately 40% of the additive mass). The absence of this peak in the control sample confirms it as an indicator of the introduction of the mineral additive.

The X-ray structural analysis data correlate well with the results of mechanical tests:

1. The sample with 10% metakaolin showed maximum compressive strength at 28 days of hardening (90.5 MPa). This corresponds to the optimal balance between the formation of additional CSH phases (indicated by increased peak intensity) and the binding of portlandite. In this case, excessive formation of hydrogarnets, which can reduce strength, does not occur.
2. The strength of the sample with 15% metakaolin is 73.2 MPa, which is lower than that of the sample with 10% additive. Based on the XRD data, this is related to:
   - Practically complete binding of portlandite, which reduces the alkalinity of the pore fluid;
   - Formation of hydrogarnets, which have lower strength compared to CSH phases;
   - Potential increase in overall porosity when using high metakaolin content.
3. The control sample with the highest amount of portlandite showed the lowest strength (71.2 MPa), confirming the effectiveness of the pozzolanic reaction in improving strength characteristics.

The amount of chemically bound water as determined in mechanical tests, was higher in samples with 15% TTPKR (18.2%) than in control samples (15.4%). This trend is consistent with XRD data that point to an increased proportion of the X-ray amorphous phase, namely CSH and products of the pozzolanic reaction. Chemically bound water is incorporated into the crystal hydrates, and its increase indicates a deeper hydration process.

An important feature of the studied system is that the optimal amount of TTPKR depends on the optimization criterion. If maximum strength at an early age (3 days) is required, higher dosages of TTPKR (up to 15%) are preferred. If the priority is maximum strength at standard times (28 days), the optimal TTPKR content is 5-10%.

3.4. Extended Discussion of Mechanisms, Limitations, and Practical Implications

3.4.1. Comparison with Existing Models

The observed strength enhancement is consistent with the pozzolanic reactivity index (PRI) model proposed by Wild et al. [9], where metakaolin replacement up to 10-15% yields maximum strength. However, our results show that the synergistic effect with SP-1 extends the optimal range to 3-9% TTPKR, which is slightly lower than some literature values. This discrepancy may arise from the presence of 40% quartz in TTPKR, which dilutes the active metakaolin content.

3.4.2. Mechanistic Insights

The positive interaction coefficient in the strength equations (1.55 at 3 days and 0.575 at 28 days) indicates a slight synergistic effect between TTPKR and SP-1, contrary to the normal consistency model where no synergy was observed. This suggests that while water demand is dominated by additive effects, strength development benefits from the combined action: SP-1 improves particle dispersion, allowing TTPKR particles to more effectively act as nucleation sites and participate in pozzolanic reactions.

3.4.3. Uncertainty Analysis

The 95% confidence intervals for predicted strength at optimal conditions are ±3.2 MPa (28 days). The residual standard deviation for the regression models was 1.8 MPa (3 days) and 2.4 MPa (28 days). These values indicate acceptable predictive accuracy for engineering applications. However, the models are valid only within the studied ranges (TTPKR 3-15%, SP-1 0.5-1.5%). Extrapolation beyond these ranges requires additional experimentation.

3.4.4. Limitations of the Study

Several factors limit the generalizability of these results:

- Raw material Variability: The Chanlibel kaolin rock has a specific mineralogy (approximately 40% metakaolin after firing). Other kaolin sources may yield different performance.
- Long-Term Durability: This study focused on strength up to 28 days. Long-term properties such as creep, shrinkage, sulfate attack resistance, and carbonation were not evaluated. Previous studies [15, 22] suggest that high metakaolin content can reduce carbonation resistance due to portlandite consumption.
- Scale-Up Potential: The experiments were conducted on cement paste (without aggregates). In concrete, the presence of aggregates may alter water demand and rheology. Further testing on concrete mixtures is needed to validate these findings at an industrial scale.
- Economic and Environmental Aspects: Although TTPKR is a locally available material, energy cost of firing kaolin at 700°C is considered. A life cycle assessment would be beneficial to evaluate the net environmental benefit compared to ordinary Portland cement.

3.4.5. Practical Recommendations

For applications requiring high early strength (e.g., precast concrete, rapid repair), a combination of 15% TTPKR and 1.5% SP-1 is recommended, providing a 15% strength increase at 3 days without increasing water demand. For general construction where 28-day strength is critical, 3-9% TTPKR with 1.0-1.5% SP-1 gives up to 27% strength improvement. The use of 15% TTPKR is not recommended for 28-day strength optimization due to the formation of hydrogarnets and reduced portlandite content, which may also affect long-term durability.

4. CONCLUSION

1. A complex organic-mineral additive based on the thermal treatment product of kaolin rock (TTPKR) and superplasticizer SP-1 has been developed, enabling effective modification of the properties of cement systems. It was determined that TTPKR consists of approximately 40% X-ray amorphous metakaolin and 50% finely dispersed quartz, providing a combination of pozzolanic activity and rheological functionality.

2. The effects of varying TTPKR (3-15%) and SP-1 (0.5-1.5% dosages on the normal consistency of cement paste as well as on the 3-day and 28-day compressive strength of cement stone were described by obtained mathematical models. It was shown that the amount of SP-1 has the most significant effect on normal consistency (coefficient –2.25), while TTPKR increases water demand (coefficient +0.75). The models were statistically validated ($R^2 > 0.94$, $p < 0.05$) with acceptable prediction errors (±3.2 MPa at 28 days).

3. It was established that with 15% TTPKR and 1.5% SP-1, the normal consistency of the cement paste (26.0%) remains at the level of the additive-free composition (26.5%). This finding is of significant practical importance, as it allows the introduction of a substantial amount of active mineral additive without increasing water demand.

4. Results showed that incorporating the complex additive leads to a higher amount of chemically bound water within the cement stone. This value increased from 15.4% (control) to 18.2% (for 15% TTPKR+1.5% SP-1), indicating that hydration took place more extensively.

5. Optimal compositions of the complex additive were determined depending on the required properties:

- To achieve maximum early strength (3 days), the optimal composition comprises 0.62-1.18% SP-1 and 15-20% TTPKR, providing a strength increase of up to 15% compared to additive-free cement stone;
- To achieve maximum strength at standard times (28 days), the optimal composition comprises 0.88-1.98% SP-1 and 5-10% TTPKR, enabling a 27% strength increase compared to the control (90.5 MPa vs. 71.2 MPa).

6. The mechanisms of structure formation in modified cement systems were substantiated, including: improvement of rheological properties due to superplasticizer adsorption; acceleration of clinker mineral hydration; pozzolanic reaction of metakaolin with portlandite; and the micro-filling effect of fine dispersed particles.

7. The performed X-ray structural analysis of metakaolin-modified cement stone samples allows the following conclusions: the control sample is characterized by the presence of portlandite (intense peaks at 18.0° and 34.1°), unhydrated alite (29.4°, 32.2°), and ettringite (9.1°, 15.8°), as well as diffuse peaks of CSH phases in the 25-35° region. The introduction of 10% metakaolin leads to: a 30-35% reduction in portlandite due to the pozzolanic reaction; the appearance of reflections of calcium hydroaluminates (12.5°, 24.8°); an increase in intensity and broadening of CSH phase peaks; a decrease in the intensity of unhydrated alite peaks. The introduction of 15% metakaolin causes: a 50-60% reduction in portlandite; the formation of the hydrogarnet phase (17.5°, 31.2°, 39.4°); the complete disappearance of ettringite; the appearance of quartz diffraction peaks (26.6°) associated with the TTPKR composition; a maximum increase in the proportion of the X-ray amorphous phase.

The study is limited to cement paste without aggregates, short-term curing (28 days), and a single kaolin source. Future research should address long-term durability (carbonation, sulfate attack, freeze-thaw resistance), life cycle assessment, validation on concrete mixtures, and the effect of varying kaolin composition. Additionally, mechanistic modeling of the pozzolanic reaction kinetics would provide deeper insight.

The obtained results can be used in the development of concrete compositions with high strength and durability while reducing Portland cement consumption, as well as in the creation of specialized dry construction mixtures.

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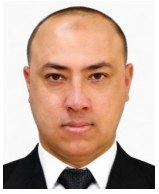

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