

EFFECT OF HIGH-ENERGY-MILLED KAOLIN ON THE PERFORMANCE OF CERAMIC GLAZES

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ABSTRACT

The present study evaluated the influence of high-energy-milled kaolin (K_{HEM}) on the development of high-temperature ceramic glazes in comparison with raw kaolin (K_R). High-energy milling reduced the kaolin particle size to $D_{90} < 1 \mu m$ and significantly increased the specific surface area from 8 to $145 m^2 \cdot g^{-1}$. From a mineralogical perspective, a reduction in kaolinite crystallinity was observed, evidenced by the increase in the amorphous fraction after milling (from 29.3% to 52.8%). Minor chemical changes were identified, with the most significant being a reduction in Al_2O_3 content (-1.7%), associated with increased structural disorder induced by mechanical activation. The thermal behavior of K_{HEM} indicated greater surface water adsorption and a shift of the dehydroxylation process to lower temperatures, suggesting enhanced material reactivity. Two glazes were developed: a standard glaze (STD) containing raw kaolin (K_R) and a test glaze (F1) with a 50% reduction in kaolin content using K_{HEM} . The F1 glaze exhibited suitable rheological behavior, with viscosity and density values close to those of the standard glaze. Dilatometric analyses revealed significant changes in the thermal behavior of the glaze, including a reduction in glass transition temperature and an increase in softening temperature. From a technological perspective, the F1 glaze exhibited a lower surface porosity area (0.37%) compared to the standard glaze (0.91%), while maintaining similar colorimetric properties and gloss. The results demonstrate the potential of K_{HEM} to optimize ceramic glazes by reducing kaolin consumption without compromising technological performance.

Kaolin is one of the most important raw materials used in ceramic glazes, especially in high-temperature systems, due to its multifunctional role during processing and firing. In ceramic suspensions, kaolin acts primarily as a suspending agent, improving the stability of glaze slurries by preventing the sedimentation of denser particles, such as frits and fluxes, during storage and application. This behavior is mainly associated with the fine particle size, lamellar morphology, and surface charge of kaolinite particles, factors that contribute to rheological control and suspension stability. In addition, kaolin improves the adhesion of the glaze to the ceramic substrate prior to firing, reducing defects associated with irregular deposition and poor coating homogeneity. The rheological behavior of kaolinitic suspensions has been widely associated with particle interactions and surface activity, directly influencing viscosity and dispersion stability [1–4].

In addition to its role during glaze preparation, kaolin plays an essential part in the firing stage of ceramic glazes. In high-temperature glaze systems, kaolin acts as a stabilizing component, supplying alumina and silica to the system, increasing the viscosity of the molten glaze, and helping to control excessive fluidity during firing. This characteristic is particularly important for preventing defects such as blistering, bubble formation, pinholes, and excessive gas evolution, which are often associated with gas release during sintering and inadequate melt viscosity. The alumina provided by kaolin contributes to the formation of a more stable glassy network, improving the balance between melt fluidity and gas release during firing, which is a key factor in obtaining dense and defect-free glaze surfaces [5–9].

Kaolin is predominantly composed of kaolinite, a layered aluminosilicate naturally characterized by low plasticity and moderate specific surface area [10,11]. However, its physicochemical behavior can be substantially modified through high-energy milling (HEM), a mechanical activation process capable of promoting intense particle size reduction, increased specific surface area, reduced crystallinity, and the induction of structural disorder or partial amorphization. Previous studies have demonstrated that HEM increases the reactivity of kaolin, modifies its thermal behavior, and significantly intensifies particle interactions due to the increase in surface energy. Furthermore, the reduction of particle size to submicrometric ranges promotes greater interaction with water molecules, potentially improving the rheological behavior and stability of ceramic suspensions [12–15].

In porcelain tile systems, previous studies involving high-energy milling (HEM) have mainly focused on its influence on properties such as plasticity, densification, firing shrinkage, sintering behavior, dimensional stability, and microstructural evolution of ceramic bodies. Mechanical activation has been reported as an efficient strategy to improve the processability of ceramic materials [14,16,17]. However, despite the advances related to high-energy milling in porcelain tile production, investigations remain predominantly focused on the ceramic body, with limited exploration in glaze systems.

Although the effects of high-energy milling on kaolin have been investigated in porcelain tile bodies, there is still an important scientific gap regarding its application in ceramic glazes. In particular, little attention has been paid to understanding how the increased specific surface area, structural disorder, and enhanced rheological behavior of mechanically activated kaolin may enable a reduction in kaolin content without compromising suspension stability, thermal behavior, and the final performance of the glaze.

Therefore, the present study aimed to evaluate the influence of high-energy-milled kaolin on the technological performance of high-temperature ceramic glazes through the partial replacement of conventional kaolin in the composition. The hypothesis of this work is that

mechanical activation promotes the development of a more viscous and efficient suspending system, allowing a reduction in kaolin content in ceramic glazes without compromising rheological, thermal, and surface properties. To verify this hypothesis, the physicochemical modifications induced by milling and their effects on rheology, dilatometric behavior, porosity, colorimetric properties, and gloss of the glazes were systematically evaluated.

1. KAOLIN

For this study, a high-purity kaolin (K_R) was used as starting raw material. The high-energy milling (HEM) process was carried out under controlled conditions to obtain a nanometric-scale kaolin, targeting a particle size of $D_{90} \leq 1 \mu\text{m}$. Milling was performed using a MasterMix agitator coupled to a Netzsch Discus 30 horizontal mill, with a milling chamber capacity of 26 L, internally lined with silicon carbide (SiC). Cerium-stabilized zirconia beads (Netzsch CeraBeads), with a diameter of 0.4 mm and density of $3.8 \text{ kg}\cdot\text{dm}^{-3}$, were used as the grinding media, totaling 65.5 kg of beads and occupying approximately 65% of the milling chamber volume. To minimize process variability and avoid interference from chemical agents, milling was conducted exclusively in deionized water, without the addition of dispersants or auxiliary additives.

The chemical composition of the kaolin samples was determined by wavelength-dispersive X-ray fluorescence (WDXRF) using a PANalytical AxiosMax spectrometer. Loss on ignition (L.O.I.) was determined at 1000 °C to assist in the identification of impurities, accessory minerals, and possible contaminants present in the kaolin.

The qualitative and quantitative mineralogical characterization was performed by combining X-ray diffraction (XRD) with Rietveld refinement [18]. XRD analyses were carried out using a Siemens D-5000 diffractometer (Erlangen, Germany) equipped with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$), operating at 40 kV and 30 mA, over a 2θ range from 3° to 75°, with a step size of 0.05° and counting time of 1 s per step. Quantitative phase analysis was performed using TOPAS software (version 5, Bruker AXS, Karlsruhe, Germany), employing crystallographic models available in the ICDD database. The amorphous phase content was quantified using the internal standard method [19,20], with the addition of 15 wt.% ZnO (zinc oxide, 99.0% purity, Panreac) as the internal reference material.

The thermal behavior of the samples was investigated through simultaneous differential thermal analysis (DTA) and thermogravimetric analysis (TGA) using a Netzsch STA 409 Jupiter F3 analyzer (Germany). Analyses were performed from room temperature to 1100 °C, at a heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, under a synthetic air atmosphere, aiming to identify endothermic and exothermic events, mass loss behavior, and possible phase transformations.

Particle size distribution (PSD) was determined using the gravitational sedimentation method monitored by X-rays, with a SediGraph III Plus V1.00 analyzer. Calculations were based on Stokes' law [21] and the Beer–Lambert law [22]. Analyses were performed for both raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}) to evaluate changes in cumulative and class particle size distributions after mechanical activation.

The specific surface area (SSA) of the K_R and K_{HEM} samples was determined using the Brunauer–Emmett–Teller (BET) method, employing a Quantachrome Nova 1200e analyzer with liquid nitrogen as the adsorbate. The results obtained complemented the particle size analysis and

provided evidence of the effectiveness of mechanical activation, reflected in the expected increase in the specific surface area of K_{HEM} compared to the untreated K_R .

2. GLAZES

For the development of the glazes (Table 1), a commercial frit widely used in the ceramic industry was employed, together with auxiliary reagents, including carboxymethyl cellulose (CMC) as a binder and a commercial deflocculant. The reference glaze consisted of a high-temperature transparent glaze containing 17.5 wt.% kaolin, in which 50 wt.% of the conventional kaolin (K_R) was replaced by high-energy-milled kaolin (K_{HEM}) to evaluate the influence of mechanical activation on the technological performance of the glaze.

Glazes	frit	K_R	K_{HEM}	CMC	deflocculant	water
STD	330.0	70.0	-	0.8	0.8	140.0
F1	363.0	-	35.0	0.8	1.6	140.0

Table 1. Composition of glazes containing raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}) (g).

For each milling batch, 400 g of solid raw materials, comprising frit and kaolin, were used. The CMC content was kept constant in both glazes (0.2 wt.% based on the solid content) to avoid interference with the rheological behavior of the suspensions. In contrast, the deflocculant content required adjustment, as preliminary studies demonstrated that the same dosage used in the standard glaze did not promote adequate dispersion of the suspension containing K_{HEM} . This behavior was mainly attributed to the increased specific surface area of the high-energy-milled material. Therefore, the deflocculant content varied between 0.2 wt.% and 0.4 wt.%, based on the solid mass.

The glaze suspensions were prepared in a 1 L jar mill (Servitech) using a volumetric composition of 40 vol.% solids and 40 vol.% grinding media, while the amount of added water corresponded to 35 wt.% of the solid mass. A milling time of 30 min was adopted to ensure adequate homogenization and dispersion of the ceramic suspension constituents.

After glaze preparation, the rheological properties were evaluated by determining the suspension density and viscosity using a Ford Cup No. 4, aiming to verify the suitability of the glazes for industrial application conditions. Subsequently, a fraction of each glaze was dried in an oven at 100 °C and later used for the evaluation of the thermal behavior of the glazes by contact dilatometry (Netzsch DIL 402 EP). The tests were performed at a heating rate of 10 °C·min⁻¹ up to 900 °C, enabling the assessment of possible changes in the melting behavior and thermal shrinkage of the glazes.

The glazes, prepared as ceramic suspensions, were applied onto a compacted ceramic substrate obtained from the industrial production line, which had previously received an engobe layer. Glaze application was carried out using a metallic container with two independent compartments, allowing simultaneous deposition of the test glazes under the same conditions. Subsequently, the specimens were fired in an industrial roller kiln, following the thermal parameters commonly used in the production of glazed porcelain tiles. The total firing cycle lasted 41 min, with a residence time of 5 min at the maximum temperature of 1225 °C. After

sintering, the specimens underwent industrial polishing, maintaining the conventional abrasive material, polishing speed, and operational conditions adopted for glazed porcelain tiles.

The glazes were evaluated regarding surface porosity, stain resistance (impregnation), and gloss, aiming to identify the most suitable glaze for subsequent industrial-scale validation. The relative porosity area was determined by optical microscopy using a BEL Photonics STM Pro stereomicroscope at 50× magnification. The resulting images were processed using ImageJ software (NIH, Bethesda, USA) through digital binarization, allowing the quantification of the surface pore area of the glaze.

The impregnation test was performed to evaluate the surface open porosity of the glazes by applying a petroleum jelly-based mixture containing black dye onto the sample surface. Glaze resistance to impregnation was determined by spectrophotometry (CM-26d, Konica Minolta) using the ΔE^* parameter, corresponding to the color difference between impregnated and non-impregnated regions. Lower ΔE^* values indicate lower impregnation levels and, consequently, better surface performance of the glaze.

Surface gloss, a property directly related to the visual quality and surface roughness of the glaze, was measured using a Horiba IG-320 gloss meter, allowing comparison between the test glazes (STD and F1).

3. EFFECTS OF HIGH-ENERGY MILLING ON KAOLIN CHARACTERISTICS

The chemical analysis of the studied high-purity kaolin (Table 2) showed a composition close to that theoretically expected for a predominantly kaolinitic kaolin, indicating a high degree of mineralogical purity (theoretical composition: $\text{SiO}_2 = 46.3 \text{ wt.}\%$, $\text{Al}_2\text{O}_3 = 39.8 \text{ wt.}\%$, L.O.I. = $13.9 \text{ wt.}\%$ [23]). The remaining oxides were present at concentrations below $1 \text{ wt.}\%$, with only minor variations ($<0.5 \text{ wt.}\%$), which may be associated with the analytical uncertainty of the applied method.

After the high-energy milling process, a slight increase in SiO_2 ($+0.6 \text{ wt.}\%$) and loss on ignition ($+0.7 \text{ wt.}\%$) was observed, accompanied by a reduction in Al_2O_3 content ($-1.7 \text{ wt.}\%$). These variations may be related to the structural modifications induced by mechanical activation, particularly the greater exposure of aluminol hydroxyl groups (Al-OH) present in the kaolinite structure, as well as the possible crystalline disorder induced by milling.

Materials	Oxides (%)			
	SiO_2	Al_2O_3	L.O.I.	others
K_R	46.0	39.4	13.7	0.9
K_{HEM}	46.6	37.7	14.4	1.3

L.O.I. Loss on Ignition

Table 2. Chemical analysis of raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}) determined by X-ray fluorescence (XRF).

The mineralogical composition obtained by X-ray diffraction (XRD) for the raw kaolin (K_R) and the high-energy-milled kaolin (K_{HEM}) is presented in Figure 1. The results revealed the predominance of the clay mineral kaolinite ($Si_2Al_2O_5(OH)_4$, ICDD No. 14-0164), accompanied by traces of illite ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$, ICDD No. 29-0370).

The reduction in mineral crystallinity induced by the milling process was clearly observed in the K_{HEM} sample, mainly through the formation of an amorphous halo between 20° and 30° (2θ), indicating an increased degree of structural disorder in kaolinite, as also reported by Derouiche and Baklouti (2021)[24]. This modification was further corroborated by the Hinckley Index (HI) [25], which classified K_R as a high-crystallinity material (HI = 1.32) and K_{HEM} as a low-crystallinity material (HI = 0.30).

The mineralogical quantification obtained by Rietveld refinement (Table 3) revealed a pronounced increase in the amorphous fraction (+23.44%) after milling, accompanied by a reduction in kaolinite content (-29.11%). This behavior indicates the partial disruption of the original crystalline framework of kaolinite, favoring the formation of a structurally disordered phase, frequently associated with a mechanically induced proto-metakaolin state. In addition, a relative increase in the illite phase (+5.67%) was observed, possibly associated with the relative enrichment of this phase due to the reduced crystallinity of kaolinite and the inherent limitations of quantitative refinement in partially amorphized systems. This amorphization phenomenon after milling was also reported by Bombazaro and Bernardin (2022) [14].

Figure 1. Mineralogical analysis obtained by X-ray diffraction (XRD) of raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}) samples.

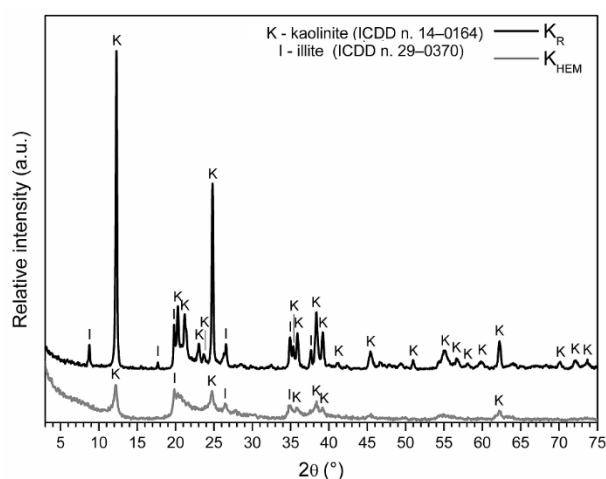


Table 3. Mineralogical composition of raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}) determined by Rietveld refinement.

Phases (%) / Materials	K_R	K_{HEM}
Kaolinite	64.5	35.3
Illite	6.2	11.9
Amorphous phase	29.3	52.8

The thermal analyses (Figure 2) revealed, for the K_R sample, a behavior characteristic of kaolinitic clay minerals [26–28]. Up to 300°C , a mass loss of approximately 0.92 wt.% was observed, accompanied by an endothermic peak at 96°C , associated with the removal of physically adsorbed surface water [29,30]. Between 300°C and 800°C , a 16.5 wt.% mass loss occurred, with an endothermic peak near 600°C , attributed to the dehydroxylation of kaolinite, resulting in the formation of metakaolinite [31,32].

The high-energy milling process significantly altered the thermal behavior of the material. For the K_{HEM} sample, a more pronounced removal of surface water was observed, with a 4 wt.%

mass loss up to 200 °C, associated with an endothermic peak at 97 °C. This behavior suggests an increase in the specific surface area and greater water adsorption capacity after mechanical activation.

Between 200 °C and 800 °C, the K_{HEM} sample exhibited a 17 wt.% mass loss, accompanied by an endothermic peak at 567 °C, associated with the dehydroxylation of kaolinite and the formation of metakaolinite [30,33–35]. The shift of this event toward slightly lower temperatures suggests a reduction in the structural stability of kaolinite after milling, attributed to increased crystalline disorder and greater exposure of aluminol hydroxyl groups, corroborating the observations reported by Leonel et al. (2014) [12].

The correlation between the XRD results and thermal analyses suggests that the mass loss observed at intermediate temperatures may be associated with the presence of structurally disordered regions of partially amorphized kaolinite, exhibiting thermal behavior distinct from that of the untreated material.

Finally, both samples exhibited an exothermic peak near 980 °C, associated with the crystallization of metakaolinite into mullite precursor phases (mullite I) [36,37]. However, the lower intensity of this peak for K_{HEM} suggests a greater degree of structural disorder in the formed metakaolinite, reducing the initial crystallization degree of mullite.

The particle size distributions (Figure 3) and average particle diameters (Table 4) demonstrate the effectiveness of the high-energy milling process in reducing the particle size of the studied kaolin (K_R). The material exhibited a significant reduction in particle size, reaching $D_{90} < 1 \mu\text{m}$, corresponding to an approximately 11.5-fold decrease relative to the original material.

A pronounced refinement of the particle size distribution was also observed, with the fraction of particles smaller than $1 \mu\text{m}$ increasing from less than 9% to over 90%, accompanied by an approximately 83% reduction in average particle diameter. This behavior demonstrates the effectiveness of mechanical activation, which, in addition to promoting particle refinement, favors the amorphization process of kaolinite, as evidenced by the XRD results and reported by Őze and Makó (2023) [38].

Figure 2. Thermogravimetric (mass loss) and differential thermal analyses of raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}).

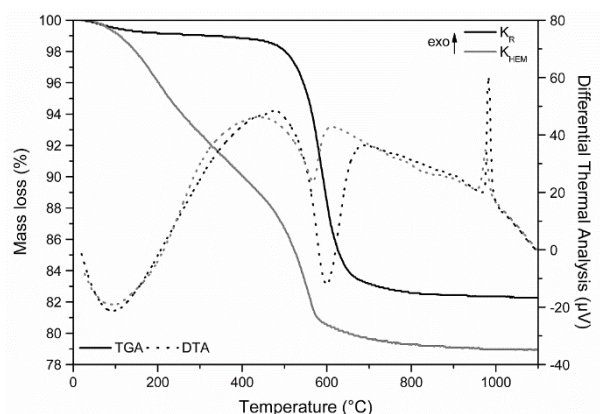
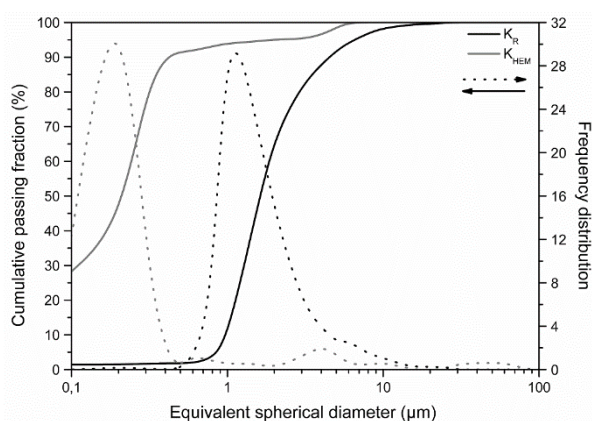


Figure 3. Particle size distribution of raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}) samples.



The determination of the specific surface area (Table 4) revealed a substantial increase after the milling process, rising from approximately 8 to 145 $\text{m}^2\cdot\text{g}^{-1}$, corresponding to an increase of nearly 18-fold. This result confirms the effectiveness of the mechanical activation process and reinforces the material's potential for applications that depend on surface reactivity and enhanced interfacial interactions. It is noteworthy that the typical specific surface area values for kaolinites generally range between approximately 10 and 50 $\text{m}^2\cdot\text{g}^{-1}$ [39,40], highlighting the intensity of the modifications induced by high-energy milling.

Materials	D ₉₀	D ₅₀	D ₂₀	D ₁₀	D _{average}	<10	<1	SSA
	μm					%		m^2/g
K _R	4.49	1.60	1.18	1.02	1.10	98	9	8
K _{HEM}	0.39	0.22	0.18	0.18	0.18	100	94	145

Table 4. Results of particle size distribution, average particle diameter, and specific surface area (SSA) of raw kaolin (K_R) and high-energy-milled kaolin (K_{HEM}).

4. GLAZES

The rheological properties presented in Table 5 demonstrate that the glaze containing high-energy-milled kaolin (F1) maintained an adequate rheological behavior, even with a 50% reduction in kaolin content. A slight reduction in viscosity, from 52 s to 48 s, and a small decrease in suspension density, from 1.81 to 1.79 $\text{g}\cdot\text{cm}^{-3}$, were observed. However, to achieve adequate stability and dispersion of the suspension containing K_{HEM}, it was necessary to use twice the amount of deflocculant compared to the standard glaze. This behavior is directly related to the increase in specific surface area promoted by high-energy milling, which enhances particle interactions and increases the demand for dispersing additives. Despite this additional requirement for deflocculant, the results demonstrate that the mechanically activated kaolin was effective as a suspending agent, maintaining rheological characteristics compatible with the requirements for industrial application of ceramic glazes.

The dilatometric curves (Figure 4) of the standard glaze (STD) and F1 were analyzed, allowing the determination of the coefficients of thermal expansion (α) as well as the characteristic processing temperatures, corresponding to the softening temperature (T_m), glass transition temperature (T_g), and coupling temperature (T_a). The glaze containing K_{HEM} and a 50% reduction in kaolin content exhibited noticeable changes in thermal behavior compared to the standard glaze.

A reduction in the glass transition temperature (T_g), from 705 °C to 680 °C, was observed, along with a decrease in the coupling temperature (T_a), indicating higher reactivity and lower viscosity during the initial stages of melting. This behavior is associated with the reduction in structural alumina supplied by kaolin (due to the lower kaolin content), resulting in a less structured glassy network with greater ease of thermal mobility.

In contrast, an increase in the softening temperature (T_m) was observed, rising from 790 °C to 815 °C, suggesting greater resistance to viscous flow at elevated temperatures. This effect may be related to the enhanced reactivity of kaolin after high-energy milling, favoring structural

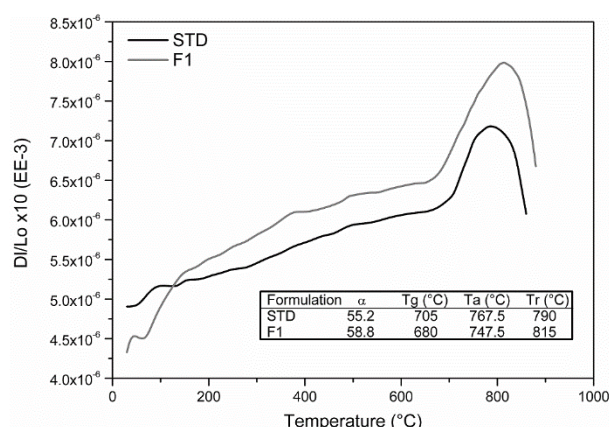
reorganization mechanisms and a possible intensification of secondary crystallization phenomena.

Additionally, the increase in the thermal expansion coefficient (α), from $55.2 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ to $58.8 \times 10^{-7} \text{ }^{\circ}\text{C}^{-1}$, confirms the formation of a less rigid glassy structure with greater ionic mobility. Overall, the results demonstrate that the reduction in kaolin content, combined with the use of an ultrafine mechanically activated raw material, significantly alters the melting kinetics and rheological behavior of the glaze.

Table 5. Rheological properties of viscosity and density of the studied glazes.

Property	STD	F1
Viscosity (s)	52	48
Density ($\text{g}\cdot\text{cm}^{-3}$)	1.81	1.79

Figure 4. Dilatometric curves of the studied glazes.



The surface analysis of the glazes (Figure 5) revealed differences in surface porosity between the studied glazes. The standard glaze (STD) exhibited a relative porosity area of 0.91%, whereas the glaze containing high-energy-milled kaolin (F1) showed a reduction to 0.37%, corresponding to an approximate 59% decrease in surface porous area. The images obtained by optical microscopy and processed using ImageJ visually confirmed the lower amount and distribution of surface defects in the F1 glaze.

This behavior may be associated with the smaller particle size and higher specific surface area of K_{HEM} , factors that favor improved particle packing, greater glaze homogeneity, and enhanced accommodation during melting. In addition, the higher reactivity of mechanically activated kaolin may have contributed to optimizing the sintering dynamics and pore closure during firing, resulting in a denser and more uniform surface.

These results demonstrate that the use of K_{HEM} promotes improvements in the surface quality of the glaze, reducing defects associated with open porosity.

The colorimetric and gloss properties presented in Table 6 indicate that the partial replacement of conventional kaolin with high-energy-milled kaolin (K_{HEM}) did not promote perceptible changes in the visual appearance of the glazes. The lightness (L^*) remained virtually unchanged between the STD (91.24) and F1 (91.31) glazes, indicating the preservation of the whiteness of the glaze. Similarly, the chromatic parameters a^* and b^* exhibited only minor variations, demonstrating that the incorporation of K_{HEM} did not significantly alter the glaze hue.

A high gloss level was also observed for both glazes, with only slight variation between them (88.3 for STD and 87.7 for F1), indicating that the reduction in surface porosity observed for the

F1 glaze did not compromise the specular reflectance of the glaze. These results demonstrate that the use of mechanically activated kaolin enables a reduction in the content of conventional kaolin while maintaining the aesthetic and visual characteristics of the ceramic glaze.

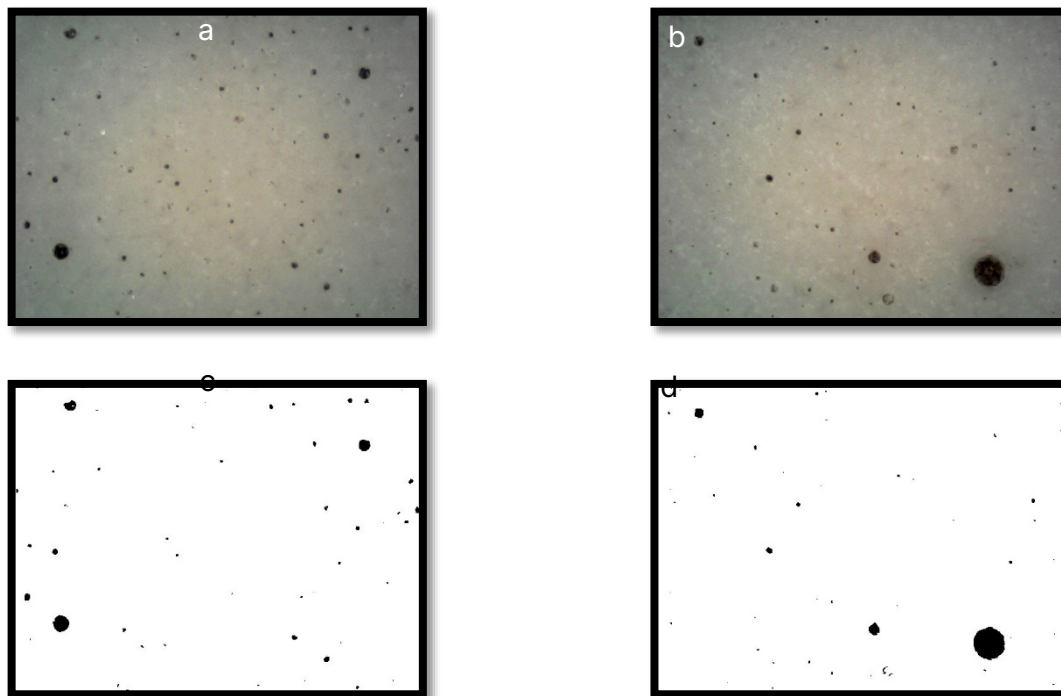


Figure 5. Optical microscopy images (50 $\times$) and processed with ImageJ of the glazes: (a) and (c) STD; (b) and (d) F1.

Glazes	L*	a*	b*	Gloss
STD	91.2	-0.68	0.99	88.3
F1	91.3	-0.58	0.53	87.7

Table 6. Colorimetric and gloss properties of the studied glazes.

The present study demonstrated that high-energy milling (HEM) modifies the physicochemical, mineralogical, thermal, and technological behavior of kaolin, enabling its more efficient use in high-temperature ceramic glazes. The HEM process promoted particle size refinement, achieving $D_{90} < 1 \mu\text{m}$, which corresponds to an approximately 11.5-fold reduction compared to raw kaolin (K_R). Simultaneously, a substantial increase in specific surface area was observed, rising from 8 to $145 \text{ m}^2\cdot\text{g}^{-1}$ (approximately 18-fold higher), confirming the effectiveness of mechanical activation and its ability to enhance the surface reactivity of the material. From a mineralogical perspective, milling induced a reduction in crystallinity, evidenced by the formation of an amorphous halo between 20° and 30° (2θ) and an increase in the amorphous

phase content, indicating partial structural disorder of kaolinite. From a chemical perspective, only minor compositional changes were observed after milling, the most relevant being the reduction in Al_2O_3 content (-1.7%), probably associated with structural rearrangements and the greater exposure of aluminol hydroxyl groups (Al-OH) resulting from mechanical activation. Thermal analyses further confirmed that milling altered the thermal stability of kaolin, promoting greater surface water adsorption and shifting the dehydroxylation event to slightly lower temperatures, suggesting lower structural stability and higher reactivity of the mechanically activated material. In glaze development, the results confirmed the fundamental role of kaolin as a suspending and stabilizing agent in high-temperature ceramic glazes. The glaze containing 50% high-energy-milled kaolin (K_{HEM}) (F1) exhibited adequate rheological behavior, with viscosity (48 s) and density ($1.79 \text{ g}\cdot\text{cm}^{-3}$) values close to those of the standard glaze (52 s and $1.81 \text{ g}\cdot\text{cm}^{-3}$, respectively). These results indicate that mechanically activated kaolin can compensate for the reduction in conventional kaolin content due to its higher surface area and greater interaction with the aqueous medium. Dilatometric analyses revealed modifications in the thermal behavior of the glaze containing K_{HEM} , including reductions in the glass transition temperature (T_g) and coupling temperature (T_a), indicating higher reactivity and lower viscosity during the initial melting stages. In contrast, the increase in softening temperature (T_m) suggests greater resistance to viscous flow at elevated temperatures, possibly associated with structural reorganization promoted by ultrafine kaolin. Additionally, the increase in the thermal expansion coefficient (α) indicates the formation of a less rigid glassy structure with greater ionic mobility. From a technological perspective, the glaze containing K_{HEM} showed superior performance, with a reduction in surface porosity area (from 0.91 to 0.37%) while maintaining colorimetric properties and gloss values comparable to those of the standard glaze. These results indicate that replacing conventional kaolin with mechanically activated ultrafine kaolin does not compromise the aesthetic characteristics of the glaze and contributes to improved glaze surface quality. Overall, the results demonstrate that high-energy-milled kaolin represents a promising strategy for the optimization of high-temperature ceramic glazes, allowing a reduction in kaolin content without impairing rheological stability while enhancing surface performance. This approach holds technological potential for industrial applications, contributing to greater process efficiency and optimized raw material utilization.

5. ACKNOWLEDGEMENTS

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