

Article

Decarbonizing Red Ceramics Through Sustainable Formulations of Complementary Raw Materials

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Abstract

Red ceramics remain essential in construction worldwide, but face challenges associated with high energy demand and CO₂ emissions. Sustainable alternatives require valorization of local georesources and adoption of circular economic approaches. This study evaluated two ceramic pastes formulations designed from locally available raw materials in southern Portugal: batch AD2, a 1:1 blend of residual clays from Corval, and batch XB1, a 1:1 blend of residual clay from Corval and a clay-schist from Barrancos. Raw materials were selected to balance contrasting properties, i.e., smectite-rich clays with high plasticity and shrinkage versus illitic (coarser) schists with lower plasticity and tempering effects. Batches were extruded, dried, fired at 1100 and 1150 °C, and tested for shaping moisture, shrinkage, water absorption, flexural strength, and mineralogical evolution. Results showed that the residual clays batch required high shaping moisture (20.04%) but achieved controlled drying shrinkage and high dry strength due to the smectite/temper balance. After firing, the material exhibited total shrinkage of 9.12 ± 0.28 and $9.78 \pm 0.11\%$, water absorption of 11.57 ± 0.30 and $9.85 \pm 0.27\%$, and flexural strength of 13.95 ± 2.30 and 14.85 ± 2.68 MPa, with mullite formation enhancing its performance. Clay and schist batch, after drying at 110 °C displayed low shaping moisture (6.22%), minimal drying shrinkage ($0.15 \pm 0.06\%$), and moderate fired (1100 and 1150 °C) shrinkage (1.59 ± 0.06 and $2.77 \pm 0.04\%$). Water absorption decreased from 12.10 ± 0.77 to $9.91 \pm 0.80\%$ as the temperature increased, while flexural strength rose significantly from 13.60 ± 0.74 to 19.69 ± 1.54 MPa. Both blends developed desirable red tones without efflorescence. These findings demonstrated that residual clays and clay-schist can be effectively blended to produce sustainable, high-quality red ceramics, meeting structural requirements while promoting resource efficiency, reducing transport, and supporting decarbonization strategies.

Keywords: red ceramics; residual clays; clay-schist; sustainable raw materials; firing properties



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1. Introduction

Ceramics have been necessary to human civilization for millennia. Archaeological evidence indicates that clay-based ceramics, including fired clay bricks and tiles, were utilized as structural building materials in ancient Mesopotamia, Egypt, and Rome [1]. Sun-dried and kiln-fired bricks have been used since at least the 4th millennium BC, providing durable construction units when stone was scarce [2]. This long legacy underpins the dominance of red ceramics (structural clay products) in construction worldwide, with masonry bricks remaining among the most prevalent building techniques today. Global

production of fired clay bricks, in 2020, was estimated at 2.18 Gt [3], translating to nearly a trillion bricks per year, illustrating that red ceramics remain a cornerstone of the global construction materials sector. Besides their historical importance, structural red ceramics also have contemporary relevance for infrastructure and housing applications. However, this demands a significant volume of raw material and has an environmental impact, driving current efforts to improve the sustainability of ceramic production. Traditional ceramic manufacturing is energy-intensive and has a substantial environmental footprint. Firing clay-based structural products require high temperatures (usually between 900 and 1150 °C), commonly achieved by burning fossil fuels (i.e., coal, oil, natural gas) in kilns. As a result, the ceramics industry contributes notably to anthropogenic CO₂ emissions globally, on the order of 19 Mt per year, arising from, e.g., fuel combustion for drying and firing, decomposition of mineral carbonates in the clay during firing, and indirect emissions from electricity use [4]. Only the breakdown of accessory carbonate minerals (e.g., CaCO₃ → CaO + CO₂) in red clays contributes to ≈17% of total ceramic CO₂ emissions. The reliance on carbon-intensive fuels, combined with process-related CO₂ release, makes decarbonization a pressing challenge for the ceramic sector. In recent years, there has been a strong motivation toward sustainable practices and decarbonization of the ceramic industry, exploring different strategies to reduce the CO₂ footprint, such as improving energy efficiency of kilns, transitioning to renewable or lower-carbon energy sources (e.g., biomass, hydrogen-fueled kilns, optimizing firing schedules to lower peak temperatures).

An important aspect of sustainable ceramic production is the use of locally available raw materials, which aligns with the principles of circular economy. Sourcing clays and other materials locally offers benefits. Economically, it decreases dependence on imported or distant raw materials and lowers transportation costs, while also supporting local economies, preserving traditional knowledge, and promoting employment, contributing to socio-economic sustainability. Also, environmentally, shorter transport distances reduce the carbon footprint of the supply chain [5]. A recent assessment highlighted that utilizing residual clay deposits from a nearby source can substantially reduce transport-related CO₂ emissions and energy consumption. The incorporation of locally sourced residual clays or low-value rocks, such as clay schists, into ceramic products encourages the efficient use of natural resources by valorizing them in ceramic formulations. By carefully characterizing clays and blending them appropriately, the raw material demand of a specific location can be reduced, and the need for materials from other locations can be minimized. Clay-rich schist, such as the ones from Barrancos considered a geotechnical byproduct of dimension stone quarrying, showed suitability to be a component for brick clays when properly processed [6]. The valorization of such local materials offers a low-impact alternative to traditional ceramic clays, promoting circular use of materials often considered as byproducts. In addition to environmental gains, this strategy diversifies the raw material base and can stimulate regional development, as local industries emerge to process and supply these materials.

Local georesources for red ceramics have been studied, reflecting a global interest in the sustainable use of indigenous materials. Correia et al. [7] reported that clayey soils used as raw material for red ceramics meet the strength and quality requirements for brick and tile production, and that, after proper processing, they can yield ceramic products compliant with construction standards, underscoring the viability of local clays. Sirbu-Radasanu et al. [8] characterized residual clays derived from weathered sericite schists in the Eastern Carpathians, finding an illite-rich composition with suitable mineralogical composition for ceramic applications. Kouonang et al. [9] reported that two local clayey raw materials (one more smectitic-plastic, and one more silty) studied for brick production, produced bricks with the characteristic red-orange color, undergoing the expected mineral

transformations on firing, and developed phases such as hematite (Fe_2O_3) and mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), showing proper vitrification and strength development. The linear shrinkage and water absorption of these bricks fell in acceptable ranges for structural use, confirming that those local alluvial and residual clays could be used to produce viable red ceramic products with standard firing procedures.

São Pedro do Corval (southern Portugal) is a region renowned for its pottery, which utilizes rich, residual clays formed by in situ chemical weathering of ancient metasedimentary rocks. The mineralogy of these clays reflects the parent lithologies, i.e., typically mixtures of illite and kaolinite, with variable amounts of smectite, especially in clays derived from more mafic or hydrothermally altered protoliths. Recent detailed studies on Corval clays [10] identified distinct clay samples with varying grain size distributions and clay mineral compositions. In Barrancos (southern Portugal), metamorphic clay schist raw materials were studied [6,10]. Unlike sedimentary clays, these raw materials are essentially a soft argillaceous rock, rich in Σ phyllosilicates (the total content of all phyllosilicate minerals, such as illite, smectite, kaolinite, and chlorite), due to retrograde metamorphism and weathering. Studies revealed that these schists can be used as an alternative clay source for red ceramics. Mineralogically, the Barrancos clay schist was dominated by illite with secondary kaolinite, and also presented a good amount of natural flux components (feldspars) and fillers (quartz, dolomite); however, the schist alone showed that it can be improved for extrusion. Simple technological adjustments, such as blending with more plastic clays or adjusting the particle size distribution, can overcome these limitations. The aim of this study is to evaluate the firing behavior and ceramic performance of two specific ceramic batches, using the studied residual clays from Corval and the Barrancos schist, after being subjected to industrial firing. Based on prior analyses, 1100 and 1150 °C were selected as the firing temperatures, as these fall within the typical range for structural red ceramics and are known to induce significant phase transformations (e.g., mullite crystallization) in illitic–smectitic clays. The study examined how each batch responded to firing in terms of key technological properties: linear shrinkage, bulk density, water absorption, and flexural (bending) strength of the fired bodies, as well as microstructural and phase developments. This study ultimately seeks to contribute to demonstrate that locally sourced formulations can produce high-quality ceramic products, while advancing the goals of resource efficiency and CO_2 reduction in the ceramics industry [11].

2. Methodology

2.1. Geological Contexts and Sampling

For this study, three residual clays and one schist sample were used, characterized previously by Candeias et al. [6,10]. Residual clays were collected near the village of São Pedro do Corval, Portugal (Figure 1), located within the Ossa-Morena Zone (OMZ) of the Iberian Massif, a geotectonic unit composed of Precambrian to Paleozoic metamorphic and igneous rocks affected by multiple tectonothermal events [10,12]. The regional bedrock consists mainly of phyllites, schists, quartzites, and minor carbonates, deformed during the Variscan Orogeny [13]. Intense chemical weathering of these metasedimentary rocks produced residual clay deposits, rich in smectite and kaolinite, depending on parent lithology and hydrothermal influences [14]. For this study, three representative clay samples were selected: A2, located near the contact with the Barrancos Formation schists; B1, collected at metabasite outcrops; and D2, obtained close to the Reguengos Eruptive Massif granites [10]. Sampling was conducted at a depth of 40–50 cm to minimize surface alteration and ensure characterization of the residual deposits [15]. The clay schist was sampled at a quarry in Barrancos, Portugal (Figure 1), where schist blocks are traditionally extracted for construction purposes [6]. Geologically, the site is located within the OMZ of the Iberian Massif and

corresponds to the Barrancos Formation (Lower Ordovician), which attains a thickness of ≈ 800 m in this area [16]. The upper part of the formation is dominated by greenish-gray micaceous schists with millimetric lamination, while the lower sections include purple-violet and gray micaceous schists interbedded with fine-grained varieties [17,18]. The sampled clay schist, oriented NW–SE, was collected from the upper part of the formation, on the NE flank of an anticline structure bounded by Silurian formations [6].



Figure 1. Sampled raw materials pits (left Corval; right Barrancos) and location in Portugal (in blue Corval; in red Barrancos). Scales, in the left image, a house, and in the right image, persons. Adapted from [6,10,19].

2.2. Formulation of Ceramic Batches

Clayey raw materials are a fundamental component in the formulation of ceramic batches, not always having, by itself, the most suitable composition for this purpose, mainly due to certain properties such as high plasticity, high shrinkage during drying and firing, or high-water absorption (WA) content. It is necessary to blend other materials that suitably modify these parameters. Previously, raw materials were collected in two nearby pits (Figure 1), one in Corval with residual clays and another in Barrancos with clay-schist [6,10]. Raw materials analysis results showed that blending would improve shrinkage, WA, and flexural strength (FS). For the present study, two distinct mixtures were formulated by using a 1:1 mass proportion of: (a) batch XB1—composed by a schist from Barrancos and a residual clay B1 from Corval; and (b) batch AD2—composed by clays A2 and D2 from Corval (Tables S1–S4) [6,10]. These formulations were selected taking in consideration raw materials characteristics, aiming to balance their contrasting behaviors, i.e., the brown clay A2 a smectite-rich (83% in fraction <0.002 mm), with very high plastic index (PI 48.6%), high extrusion moisture (26.14%) and shrinkage ($9.63 \pm 0.15\%$), with the risk of over-firing/efflorescence; the dark-orange B1 clay, with 30%–50% kaolinite–illite content (<0.002 mm fraction), balanced granulometry ($\approx 58\% < 0.002$ mm), good FS (25.59 ± 2.98 MPa/ 261.05 ± 30.39 kgf/cm²) and low porosity (WA = $6.49 \pm 0.42\%$) after firing at 1100 °C; the brown clay D2 with a coarser texture (58% > 0.063 mm), smectite-rich (83% in fraction < 0.002 mm), low extrusion moisture (18.26%), green-to-dry shrinkage ($5.32 \pm 0.43\%$), and FS (6.84 ± 0.51 MPa/ 69.76 ± 5.24 kgf/cm²); and the beige clay-schist illite-dominant ($>80\%$ in fraction < 0.002 mm), with very low shrinkage green-to-dry ($0.25 \pm 0.04\%$), and reduced total shrinkage ($0.34 \pm 0.03\%$) after firing 1100 °C. Taking these properties into consideration, samples A2 and B1 were used to improve strength/PI results, while D2 and the schist were selected as stability/temper phases.

2.3. Formulations Analysis

The raw materials used in the formulations were previously analyzed, and the results (Tables S1–S4) were presented in Candeias et al. [6,10]. Formulated ceramic batches AD2 and XB1 were shaped according to the desired geometry. After, two batches of each, were dried at 110 °C and fired at 1100 °C and 1150 °C (in total, six specimens of each batch), and studied. A portion of the fired batches was removed and pulverized in an agata mill to identify the mineral phases formed. An X-ray diffraction (XRD) analysis was conducted using a Philips/Panalytical powder diffractometer, model X'Pert Pro MPD (Malvern Panalytical, Malvern, Worcestershire, UK). The equipment uses a Cu X-ray tube operated at 50 kV and 30 mA, with data collected from 2 to 70° 2 θ with a step size of 0.01° and a counting interval of 0.02 s. Diffractograms were interpreted using a combination of procedures proposed by Brown and Brindley [20] and Heigh Score Plus v4.9[®] with the International Centre for Diffraction Data (ICDD) database.

For the determination of shaping moisture (SM), each dried batch (AD2 and XB1) was oven-dried at 110 $\pm$ 5 °C to a constant mass and then cooled in a desiccator to prevent rehydration. Incremental water additions were performed in a tared mixer, followed by aging for 12–24 h in sealed polyethylene bags to ensure uniform moisture distribution. Workability was assessed using a Netzsch 250/05 laboratory extruder (Netzsch Group, Selb, Germany) equipped with a vacuum system capable of 0.85 Pa, operated at a constant extrusion speed. The minimum workable moisture was defined as the lowest water content at which the extrudate produced a continuous, smooth bar free of edge fissures, tearing, or lamination, and with stable die swell. The optimum SM corresponded to the first reproducible condition ($n \geq 3$) fulfilling these criteria. After extrusion, representative extrudate samples were again oven-dried at 110 °C to constant mass, and SM was calculated according to $SM (\%) = 100 \times (M_{wet} - M_{dry})/M_{wet}$. This procedure followed the ASTM C326-09 [21], consistent with the ISO 10545-1:2021 [22], recommending standardized drying conditions and mass-loss determination for ceramic bodies.

Firing tests were conducted on the four extruded and dried batches at 1100 °C and 1150 °C using a Termolab electric chamber furnace (Nabertherm GmbH, Lilienthal, Germany) with a heating rate of 5 °C/min and a soaking time of 60 min at the target temperature. In all six batches shrinkage was measured on dried batches using a caliper [23], and the FS of the shaped 3 $\times$ 4 $\times$ 45 mm blocks was determined according to standard [24] on the green bodies, using a Lloyd Instruments testing machine (Lloyd Instruments Ltd., Bognor Regis, West Sussex, UK), with a loading rate of 1 N/s at 20 $\pm$ 2 °C, under ambient conditions. Each batch was placed on two support rollers 40 mm apart and loaded at the mid-point using a third roller (three-point bending configuration), with a minimum of three replicates per sample tested to ensure reproducibility. The FS values were calculated from the maximum load recorded at failure using the standard formula provided in the ASTM method.

The WA capacity of the fired batches was determined according to the procedures defined in ASTM C373-88 [25]. Test specimens were immersed in distilled water, boiled for 2 h, and subsequently cooled for 4 h at room temperature (20 $\pm$ 2 °C). Excess surface water was gently removed using a damp, lint-free cloth, and the saturated mass (M_1) was immediately recorded. Samples were then oven-dried at 110 $\pm$ 5 °C for 24 h, cooled in a desiccator to constant weight, and the dry mass (M_0) was recorded. The WA was calculated according to $WA (\%) = 100 \times (M_1 - M_0)/M_0$. All measurements were conducted in triplicate to ensure reproducibility, with the mean values reported as representative of the batch results. The batches were placed in a tray filled with deionized water that reached halfway up their height, left to rest for 24 h, and then dried in an oven at 110 °C for 24 h. The presence of efflorescence was assessed semi-quantitatively. The color of the dried and fired bodies at different temperatures was visually assessed. All assays adhered to

internationally defined standards and good laboratory practice protocols for structural ceramic materials, ensuring inter-laboratory comparability of results.

3. Results and Discussion

After blending and drying (110 °C), batch AD2 (1:1 residual clays A2 and D2) [10] showed a relatively high SM (SM; 20.04%) requirement (water content for workable extrusion), reflecting the fine particle size (51% <0.002 mm) of raw A2 clay and smectite content of A2 (71%) and D2 (83%) clays. Nevertheless, its green-to-dry shrinkage (GDS) upon drying at 110 °C ($7.82 \pm 0.18\%$) was lower than that of raw A2 clay ($9.63 \pm 0.15\%$), as the inclusion of raw D2 (58% >0.063 mm size) and lower PI acted as a temper, improving dimensional stability. The AD2 dried green FS (9.33 ± 0.82 MPa/ 95.17 ± 8.39 kgf/cm²) (Figure 2; Table S5) was high, benefitting from the interparticle cohesion of the smectite-rich raw clays, although FS was slightly reduced when compared to A2 (FS 13.13 ± 0.48 MPa/ 133.93 ± 4.93 kgf/cm²) due to D2 (FS 6.84 ± 0.51 MPa/ 69.76 ± 5.24 kgf/cm²) dilutive effect. The abundant smectite content disclosed high PI and water retention, leading to greater SM demand. However, the D2 coarser fraction and lower specific surface area (SSA; 14.1 m²/g vs. A2, 22.2 m²/g) limited water uptake and shrinkage. Thus, dried AD2 batch achieved a balance between workability and drying behavior, requiring significant water for shaping due to smectitic clay bonding, but showed controlled drying shrinkage and maintained strong dry strength, from the tempering effect of D2 non-clay components and the cohesive matrix provided by A2. Results highlighted that blending a highly plastic, smectite-rich clay with a less plastic, coarser clay (rich in fillers) can improve drying behavior (lowering GDS) without compromising green strength, as evidenced in AD2 (Figure 2). Nandi et al. [26] on a study about fast-drying materials, proposed a mixture design strategy that optimize plasticity, drying stability, and strength, supporting the rationale to combine smectitic and illitic fractions and to engineer the silt/coarser window for robust extrusion and rapid drying. Such strategies include: (i) partial substitution with an illitic coarser phase (e.g., 10%–30% schist or feldspathic sand); (ii) lower peak temperature with longer oxidation holds (≤ 1050 – 1100 °C), what will avoid over-firing; and (iii) efflorescence control (raw-mix washing or Ba-carbonate at low levels, when possible). These actions were consistent with A2 over-firing susceptibility and D2 limited densification.

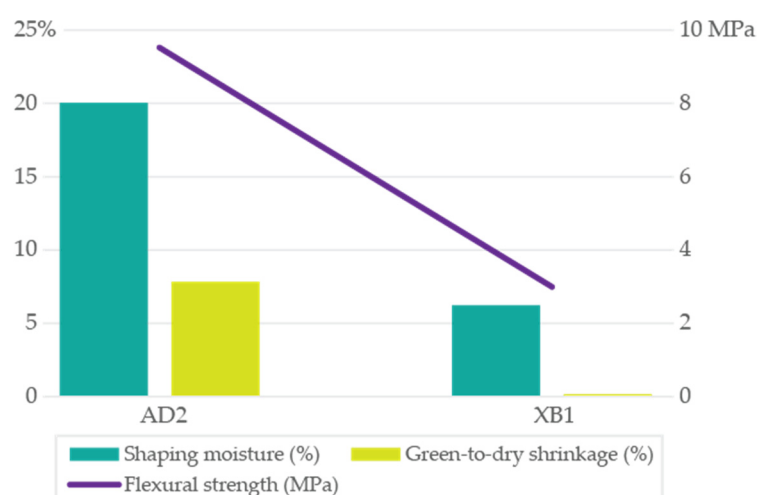


Figure 2. The SM (%), GDS (%), and FS (MPa) of the green bodies of batches AD2 and XB1 after drying at 110 °C. Specimens sizes: AD2 green $\approx 45.0 \times 10.0 \times 5.0$ mm, and after dried at 110 °C $\approx 41.5 \times 9.2 \times 4.6$ mm; XB1 green $\approx 50.0 \times 50.0 \times 5.0$ mm, and after dried at 110 °C $\approx 49.9 \times 49.9 \times 5.0$ mm.

Batch XB1 (residual clay B1 and clay schist 1:1 blend) [6,10], after drying at 110 °C, showed lower required SM (6.22%) than raw clay B1 (23.6%). The illite-dominated schist (85%) contributed to lower plasticity and lower water demand, thereby reducing the SM of XB1 (Figure 2; Table S5). Consistently, the GDS was minimal ($0.15 \pm 0.06\%$), indicating good dimensional stability during drying. This behavior was attributed to the prevalence of non-expanding clay minerals in the blend (85% illite in the schist, and 55% kaolinite from B1), reflecting the low expandability (Exp) and cation exchange capacity (CEC) of the raw materials. Batch XB1 exhibited limited shrink–swell upon drying, thereby mitigating the risk of cracking. The FS after drying was lower in XB1 (2.93 ± 0.49 MPa/ 29.91 ± 5.03 kgf/cm²) than in B1 (8.11 ± 0.31 MPa/ 82.76 ± 3.15 kgf/cm²), reflecting the reduced smectite content (B1 15%) and the lower green cohesion in the XB1 batch. Raw B1 clay green FS was diluted by the schist component, which yielded only low green strength, with illite providing structural stability but not a high bond strength, as with smectite. Even so, XB1 dried FS remained adequate for handling, benefiting from the B1 clay minerals content that enhanced dry strength and ensured a low moisture requirement and shrinkage during drying, due to the illite dimensional stability, while maintaining sufficient mechanical strength for safe handling. Results showed the effectiveness of incorporating a low-CEC, illite-rich schist as a temper to improve drying behavior in ceramic batches without introducing efflorescence or warping issues. Assunção et al. [27] reported that higher illite content can enhance FS in red-ceramic bodies, through better packing and earlier viscous sintering, suggesting that the addition of illitic or feldspathic phases to the blend can compensate for the strength deficit without raising shrinkage excessively. Boukili et al. [28,29] demonstrated that clay raw materials, which exhibit low PI or poor firing response, can be optimized through blending and/or minor additions, such as bentonite or feldspar, thereby achieving adequate strength while controlling shrinkage and efflorescence. Gu and Ling [30] proposed that quartz–kaolinite–illite assemblages, characterized by moderate Fe₂O₃, minor alkalis, and limited carbonates, tend to exhibit predictable vitrification and firing strength gain with increasing temperature, consistent with the B1 and schist trends.

After firing at 1100 and 1150 °C, batch AD2 exhibited clear variations in physical, mechanical, and mineralogical properties, reflecting the balance between densification, porosity control, and phase transformations. At 1100 °C, it presented a total shrinkage of $9.12 \pm 0.28\%$, FS of 13.95 ± 2.30 MPa (142.25 ± 23.49 kgf/cm²), and WA of $11.57 \pm 0.30\%$ (Figure 3; Table S6). At 1150 °C, total shrinkage was $9.78 \pm 0.11\%$, FS 14.85 ± 2.68 MPa (151.43 ± 27.36 kgf/cm²), and WA $9.85 \pm 0.27\%$. Results showed that increasing the firing temperature by 50 °C promoted additional densification, reflected by the reduction in WA and increase in mechanical strength. The FS increase (13.6 to 19.7 MPa) from 1100 to 1150 °C correlates with the densification indicators of dry-fired shrinkage (DFS) 1.82 ± 0.04 to $2.98 \pm 0.06\%$; WA: 12.10 ± 0.77 to $9.91 \pm 0.80\%$). At 1150 °C, the formation of a larger, lower-viscosity alkali–silicate liquid derived from feldspars and illite, facilitated viscous-flow sintering, particle rearrangement, and the rounding and closure of pores. Simultaneously, the mullite content and crystallinity increase, providing an interlocking crystalline skeleton within the glassy matrix. Partial quartz dissolution reduces interfacial flaws and improves glassy bonding. Together, these processes progressively reduced the proportion of open, interconnected pores, which dominate WA, and promoted the development of isolated closed pores, explaining the decrease in WA at 1150 °C. This transition in pore morphology was consistent with classical porosity–strength relations, therefore the $\approx 45\%$ rise in MOR (modulus of rupture). The variation in FS between the optimized batches (AD2 vs. XB1) and between firing temperatures was primarily explained by differences in liquid-phase formation, mineralogical reactivity, and resulting bulk density. The AD2 formulation, richer

in smectite and alkali-bearing phases, generated a larger amount of low-viscosity liquid at 1150 °C, promoting stronger vitrification and earlier pore closure, but with slightly lower final strength than XB1 due to its higher open-porosity retention. In contrast, XB1 contained a greater proportion of illite and feldspathic components, which produced a more effective high-temperature melt and greater mullite crystallinity, yielding a denser and mechanically stronger microstructure at 1150 °C. These mineralogical and densification differences collectively account for the observed strength range. The microstructural evolution can be interpreted from the XRD-derived phase assemblages and the technological behavior of the bodies. Batch AD2, richer in smectite and alkali-bearing minerals, generated an earlier but more diluted and less viscous liquid phase, which limited pore closure and preserved a higher proportion of open porosity after firing. In contrast, the illite–feldspar–rich XB1 blend produced a more effective high-temperature silicate melt and stronger mullite development, resulting in a denser glassy matrix with fewer interconnected pores and, consequently, higher flexural strength. The moderate WA values ($\approx 10\%$ – 12%) indicated that open porosity still dominated the ceramic body at both 1100 and 1150 °C, as expected for red ceramics not yet fully vitrified. However, the reduction in WA at 1150 °C suggested the onset of partial conversion from open to closed porosity as glassy-phase formation becomes more pronounced.

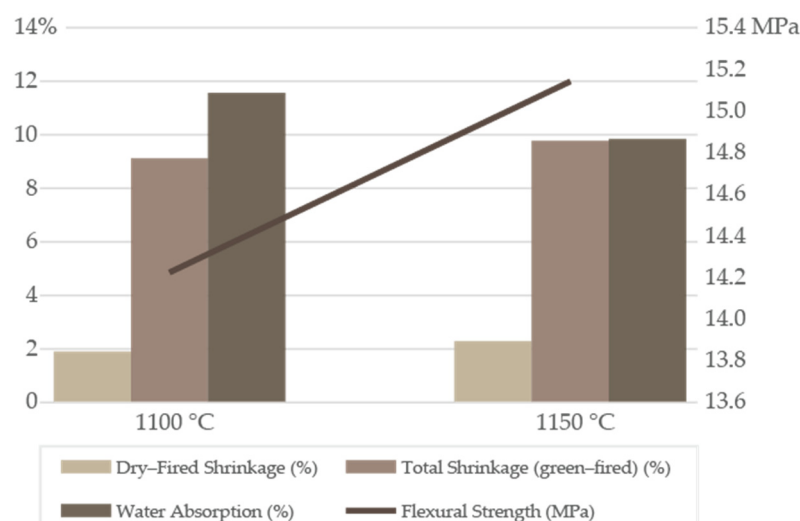


Figure 3. Technological properties of batch AD2 after firing at 1100 and 1150 °C: dry-fired shrinkage (%), total shrinkage (green-fired, %), WA (%), and FS (MPa).

Results fell within the expected ranges for red ceramic products, where shrinkage is typically controlled $<12\%$ and WA ideally remains $<15\%$ for structural bricks and tiles [31,32]. The improvement in FS from 1100 to 1150 °C can be attributed to enhanced vitrification and the progressive development of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), a key phase that confers mechanical stability at high temperatures [33]. The identified mineral phases (Figure 4) showed that both firing temperatures led to the persistence of quartz (SiO_2) and K-feldspars (KAlSi_3O_8), while muscovite ($\text{K}_2\text{Al}_4(\text{Si}_6\text{Al}_2)\text{O}_{20}(\text{OH})_4$) peaks diminished due to dehydroxylation. At 1150 °C, mullite reflections intensified in agreement with increased mechanical resistance. Hematite (Fe_2O_3), which influences the reddish coloration, remained stable at both temperatures, with the color changing from orange at 1100 °C to a darker red at 1150 °C (Figure 5), corresponding to an enhanced Fe^{3+} concentration in the ceramic matrix [34]. At both 1100 °C and 1150 °C firing temperatures, no efflorescence was observed on AD2-fired batches. The formation of a limited spinel phase (MgAl_2O_4) at intermediate positions suggested transitional reactions of aluminosilicates. Such mineralogical evolution was coherent with the firing behavior of Fe-rich illitic-smectitic clays [35]. The comparison

with the raw samples of the AD2 batch showed that the A2 exhibited higher shrinkage and densification due to its smectite-rich composition, whereas D2 tended to buffer shrinkage due to its higher quartz content and medium plasticity. The 1:1 mixture of raw clays A2 and D2 balanced the behavior, i.e., shrinkage remained moderate, avoiding excessive warping, while sufficient vitrification ensured good mechanical strength, indicating the advantage of blending different raw materials to optimize processing properties, a practice reported in different ceramic studies (e.g., [36–38]).

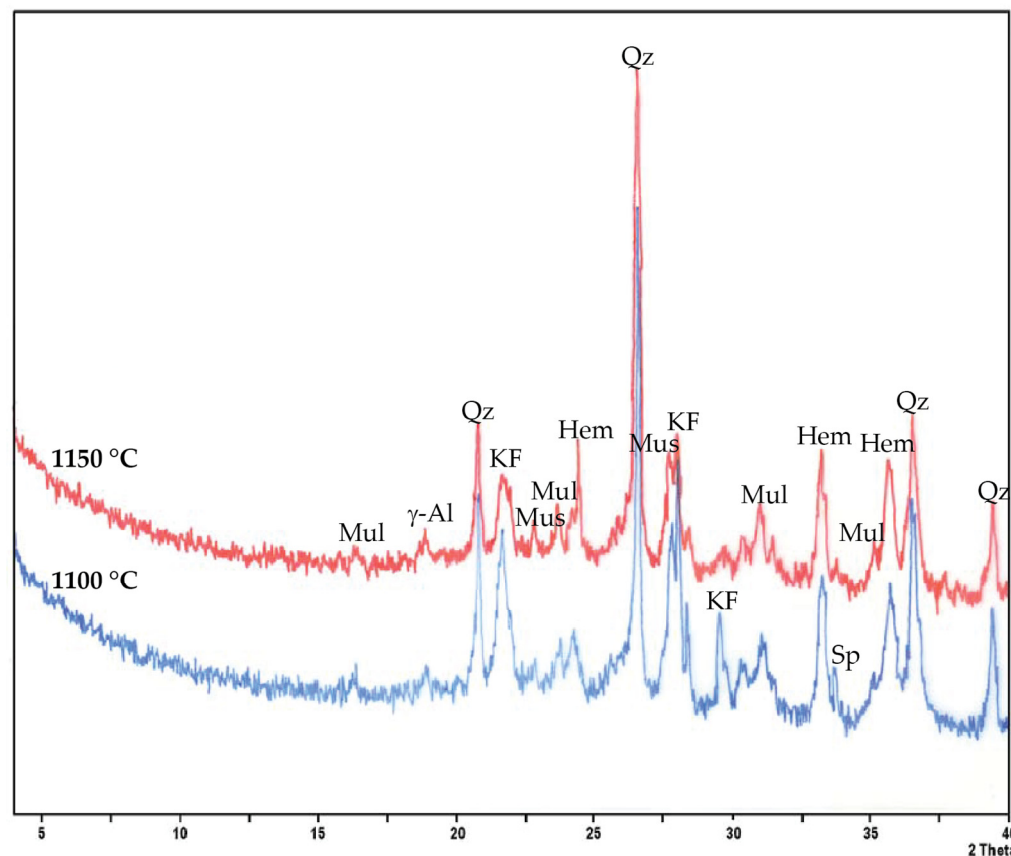


Figure 4. Diffraction patterns of clay AD2, fired at 1100 °C (blue line), and 1150 °C (red line). Minerals: Mul—mullite, Qz—quartz; Sp—spinel-type phase; Hem—hematite; Mus—muscovite; KF—K-feldspar; γ -Al— γ -alumina.

The firing temperatures (1100 and 1150 °C) yielded products with acceptable ceramic properties. For structural red ceramics, European standards [39] specified WA values < 20% for load-bearing clay units and equivalent FS > 5 MPa (10 MPa for compressive strength). The results obtained for batch XB1 after firing at 1100 °C, preferred from an energy-saving perspective, were WA $\approx$ 12.1%, FS $\approx$ 13.7 $\pm$ 0.74 MPa, both within the regulatory limits, confirming its suitability for structural applications. However, at 1150 °C, it conferred slightly higher mechanical resistance and lower porosity, which is beneficial for durable ceramic applications, such as roof tiles subjected to environmental stress. Similar behavior, where increasing the firing temperature improved mechanical strength and densification, was reported by Karaman et al. [40], demonstrating that higher firing temperatures resulted in increased compressive and bending strength, greater density, and reduced porosity and absorption.

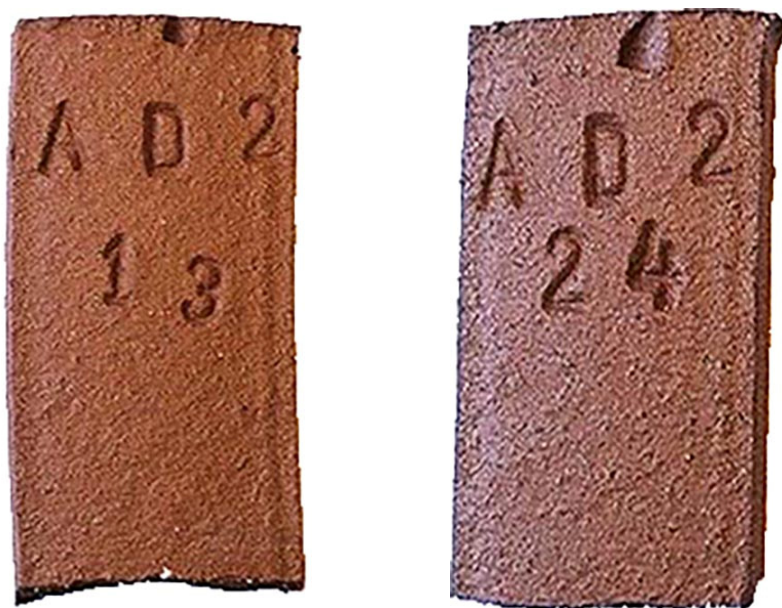


Figure 5. Sample AD2 batch specimens after firing at 1100 °C (left; orange) and 1150 °C (right; dark red). Specimen sizes after firing at 1100 °C were $\approx 40.9 \times 9.1 \times 4.5$ mm, and after firing at 1150 °C were $\approx 40.6 \times 9.0 \times 4.5$ mm.

Batch XB1, after the 1100 to 1150 °C step increased FS from 12.10 ± 0.77 to 9.91 ± 0.80 MPa, while lowering WA from 12.10 ± 0.77 to $9.91 \pm 0.80\%$, with concurrent increase in dry-fired and green-fired shrinkage. The coupled decrease in WA and increase in shrinkage indicated net densification (reduced open porosity/neck growth), which quantitatively agrees with classic porosity–strength relations for ceramics [41], where MOR increased as porosity fell. The stronger glassy bonding and higher mullite content/crystallinity at 1150 °C further supported the interpretation of a microstructure increasingly dominated by smaller, more isolated pores and a reduced interconnected pore network.

Batch XB1 (1:1 blend of residual clay B1 and Barrancos schist) [6,10] upon firing at 1100 °C, undergo dehydroxylation and breakdown of clay minerals, coupled with the formation of new high-temperature phases (Figure 6). Clay minerals decompose between ≈ 500 – 700 °C, losing hydroxyl groups and long-range order. Carbonate impurities, when decomposed (≈ 600 – 800 °C), release CO_2 and yield Fe oxide, resulting in the formation of hematite. Hematite was identified at both 1100 °C and 1150 °C, suggesting the persistence of Fe_2O_3 as a distinct phase, confirmed by the coloration of the fired batches. The dried XB1 batch showed a light orange color, related to dispersed Fe-oxides. After firing at 1100 °C, the color changed to orange ceramic, and at 1150 °C, it gained a darker orange color (Figure 7). The darkening tone evolution with temperature could be attributed to Fe-oxidation state and concentration effects, once at higher temperature, Fe is in the Fe^{3+} form, promoting slight glass phase development that intensified color saturation. Nevertheless, no undesirable color effects, such as black coring or spotting, were observed, indicating that the firing cycle allowed for the complete burn-out of any organic matter present in the dried batch and the full oxidation of Fe throughout the body. Mullite, a strengthening phase, occurred at 1100 °C and intensified at 1150 °C, reflecting its increasing crystallinity and abundance. The K-feldspar peak was present at 1100 °C and was significantly reduced at 1150 °C, due to melting into the glassy phase. Quartz persistence after firing promoted dimensional stability, with the absence of cracking after firing, suggesting that its content and grain size were not high enough to cause thermal stress or that the cooling was sufficiently controlled.

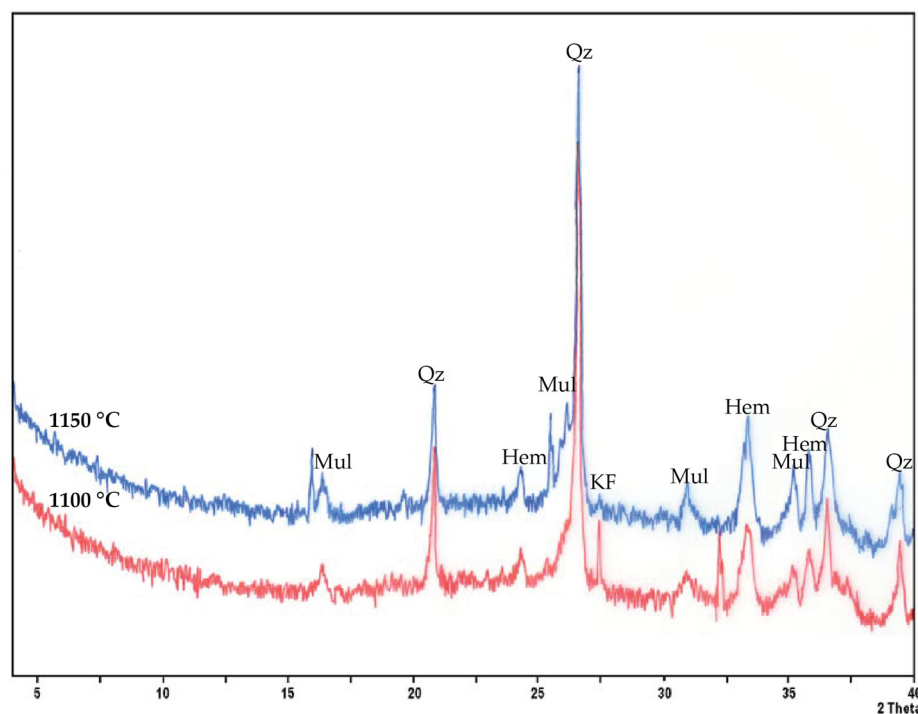


Figure 6. Diffraction patterns of clay XB1, fired at 1150 °C (blue line), and 1100 °C (red line). Minerals: Mul—mullite, Qz—quartz; Hem—hematite; KF—K-feldspar.

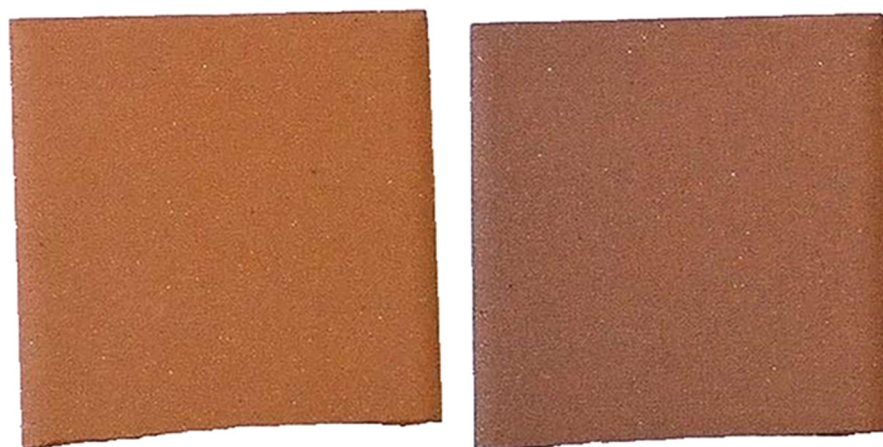


Figure 7. Sample XB1 batch specimens after firing at 1100 °C (left) and 1150 °C (right). Specimen sizes after firing at 1100 °C were $\approx 49.2 \times 49.2 \times 4.9$ mm, and after firing at 1150 °C were $\approx 48.6 \times 48.6 \times 4.9$ mm.

Batch XB1 ceramic properties exhibited minimal shrinkage during drying at 110 °C (Figure 2) and only moderate shrinkage upon firing (Figure 8; Table S7), due to the balanced residual clay/schist formulation. Raw B1 clay, being very fine and plastic, was prone to higher drying shrinkage and cracking; however, blending with the schist, which contributed coarser particles, reduced the risk. After firing at 1100 °C, the total linear shrinkage was $1.59 \pm 0.06\%$, a low value for a clay-based ceramic. At 1150 °C, it slightly increased to $2.77 \pm 0.04\%$, and the shrinkage from the dry state to the fired state was $2.98 \pm 0.06\%$. These findings were below the $\approx 8\%$ upper limit cited for good structural clays [42]. A slightly higher shrinkage at 1150 °C was expected, as the increased liquid phase formation promoted closer particle packing and pore consolidation. The low firing shrinkage will produce products that will retain the molded dimensions closely, with minimal warpage, which can be considered an advantage in manufacturing. These results aligned with obser-

variations of similar illitic–kaolinitic (XB1) blends, which reported moderate total shrinkage at 1100–1150 °C [43]. Consistent with the shrinkage, batch XB1 retained a portion of open porosity after firing (Figure 8). At 1100 °C, the material showed a porosity typical of structural brick bodies (WA $12.10 \pm 0.77\%$), which decreased by 2% when the temperature was increased by 50 °C (WA $9.91 \pm 0.80\%$). This represented a significant pore closure, a direct consequence of liquid-phase sintering and glass formation, resulting in denser and less permeable ceramic bodies. This improvement is crucial for the durability of ceramic products, as a WA $\leq 15\%$ is considered to have robust performance, particularly in terms of moisture resistance and structural durability [44]. Overall, XB1 batch porosity at both temperatures showed reasonable results for red structural ceramics, reflecting sufficient vitrification without over-firing.

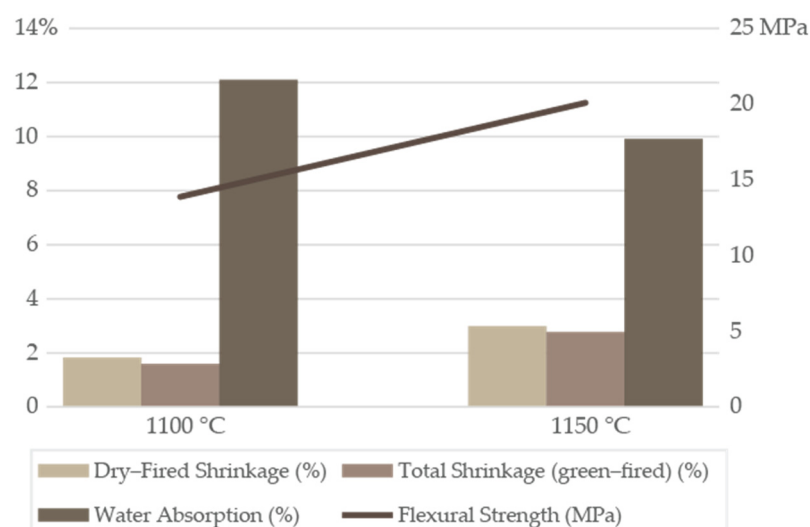


Figure 8. Technological properties of batch XB1 after firing at 1100 and 1150 °C: dry-fired shrinkage (%), total shrinkage (green-fired, %), WA (%), and FS (MPa).

Batch XB1 FS (Figure 8; Table S7) increased significantly from the dried body (2.93 ± 0.49 MPa/ 29.91 ± 5.03 kgf/cm²) to 1100 °C (13.60 ± 0.74 MPa/ 138.69 ± 7.52 kgf/cm²), and further at 1150 °C (19.69 ± 1.54 MPa/ 200.88 ± 15.69 kgf/cm²), reflecting the microstructural bonding changes. After drying, XB1 microstructure was of a typical clay body, with clay particles packed with silt-sized quartz and feldspar particles from the schist, acting as a skeletal framework. Pores between particles were relatively large, which on drying become air-filled voids yielding the initial porosity. At 1100 °C, the microstructure evolved through sintering, with the appearance of an initial liquid phase due to the melting of feldspathic and illitic components (≈ 1000 – 1050 °C), forming a silicate melt that bonded the remaining solid particles. Although the mullite content at 1100 °C was not abundant, it provided a crystalline framework within the glass. The presence of hematite dispersed in the matrix could influence the microstructure, but do not contribute to bonding except by occupying space. The partially sintered microstructure explained the relatively high, yet not maximal, strength at 1100 °C, with a structure mechanically capable for load-bearing masonry applications, such as structural bricks and roof tiles, where FS values >5 MPa are typically required to ensure safe performance under wall or roof self-weight and service loads. At 1100 °C, batch XB1 FS exceeded the lower limit defined for structural red ceramics and consistent with studies on optimized illitic–kaolinitic clays [45]. Therefore, at this firing temperature, XB1 presented a densified, vitrified matrix capable of resisting bending and compression stress typical of structural brickwork.

The strength gained from 1100 to 1150 °C was attributed to sintering, characterized by increased glassy-phase bonding and growth in mullite content and crystallinity, which

strengthened the ceramic matrix, enabling it to resist higher stress before fracture and reducing the risk of cracking. Mullite, a refractory phase, contributed to the long-term stability of the ceramic body by enhancing its thermal shock and fire resistance. Similarly, quartz partially dissolved, promoting bonding with the matrix, which resulted in a strong, vitrified microstructure with lower porosity and higher FS. Firing at 1150 °C enhanced the sintering processes and mechanical performance of the XB1 batch, resulting in more robust products, such as bricks with higher load-bearing capacity or tiles with lower water permeability. However, a higher firing temperature implies higher energy consumption and costs, as well as a larger carbon footprint for the firing process. The darker color at 1150 °C might be considered a limitation when a lighter shade is desired. Firing at 1100 °C, the lower end of the typical firing range for structural ceramics, will reduce energy needs and emissions. The slightly higher porosity, while strong, may not meet the most stringent standards for low WA or strength for some applications such as high-performance bricks, but for, e.g., interior masonry units or traditional roof tiles, can be considered sufficient. Additionally, no efflorescence was observed on XB1 fired batches at either 1100 or 1150 °C. Raw clay B1 and schist were primarily composed of silicate minerals with low soluble sulfate or chloride content. Most alkalis (K, Na) were derived from feldspars/illite, and upon firing, they ended up in the glassy phase, rather than remaining as free salts. The absence of efflorescence suggested that XB1 bricks/tiles would not develop unsightly white deposits or suffer associated degradation.

Studies have consistently highlighted the environmental advantages of partially substituting clays with nearby materials or waste-derived materials, as this approach reduces pressure on raw material extraction and lowers the embodied carbon of ceramic products. Bonet-Martínez et al. [46] demonstrated that replacing up to 25% of natural clay with Al-recycling residues produced fired bricks exhibiting equal or higher mechanical strength and lower thermal conductivity, thereby achieving the dual benefits of waste valorization and improved product performance. Similarly, studies incorporating up to 25% of construction and demolition waste into clay matrices have maintained mechanical behavior comparable to that of conventional clay bricks, reinforcing the sustainability potential of circular raw materials in the ceramic sector [47]. Compared with a conventional single-clay formulation, the blended clay–schist bodies can reduce CO₂ emissions primarily by enabling earlier vitrification and thus lowering the required firing temperature by 50 °C. For typical structural-ceramic compositions, an equivalent non-flux-optimized clay would generally require ≥ 1150 °C to achieve similar densification and strength, meaning that the 1100 °C firing adopted for the optimized blends directly avoids the additional 60–170 MJ/t and corresponding 3–10 kg CO₂/t associated with higher-temperature processing. This showed that the strength of the blend lay not only in the use of residual resources but in tangible, quantifiable decarbonization through reduced thermal demand.

From a sustainability perspective, the use of a 1:1 clay–schist blend is significant. In the present work, this mixture not only combined complementary mineral compositions but also allowed for a reduction in firing temperature from 1150 to 1100 °C, a 50 °C decrease that directly contributes to energy and CO₂ savings. Such a reduction represents a meaningful optimization step in red-ceramic production, especially when similar physical and mechanical properties can be achieved at lower thermal input. Because fuel demand in tunnel kilns increases approximately linearly with peak temperature, even moderate reductions yield quantifiable energy benefits. For industrial brick and roof-tile production in Europe, validated energy benchmarks indicate that the specific thermal energy consumption (SEC) of modern tunnel kilns typically ranges from 2.0 to 3.6 GJ/t, depending on kiln configuration, heat recovery efficiency, and product characteristics [48]. More detailed national datasets report average SEC values of ≈ 2.31 GJ/t for EU plants and, for example, ≈ 2.07 GJ/t for

Belgian brick and roof-tile facilities, values consistent with the Intergovernmental Panel on Climate Change (IPCC) benchmarks for efficient tunnel-kiln operations [49]. Although Belgium is cited in the IPCC datasets due to the availability of comprehensive industrial statistics, Portugal also presents relevant case studies. For instance, Almeida et al. [50] and Carvalheira et al. [51] reported energy audits and life-cycle assessments of Portuguese ceramic plants, confirming comparable SEC magnitudes, although nationally aggregated data remain limited.

An EU Climate Action study [52] found that frost-resistant pavers, fired at higher peak temperatures (typically $>1100\text{ }^{\circ}\text{C}$), consume approximately $+30\text{ Nm}^3$ of natural gas per 1000 wire-cut bricks, equivalent to $\approx 130\text{ kWh/t}$ ($\approx 468\text{ MJ/t}$) of additional energy relative to standard bricks. Similarly, the CER BREF [53] indicated that higher firing temperatures, used to obtain lighter color tones or denser microstructures, can increase energy consumption by $\approx 47\text{--}120\text{ kWh/t}$ ($\approx 170\text{--}430\text{ MJ/t}$). Considering kiln-to-kiln variability (heat recovery, firing profile, and body fluxing), the temperature reduction from 1150 to $1100\text{ }^{\circ}\text{C}$ can conservatively yield $\Delta E \approx 60\text{--}170\text{ MJ/t}$ of thermal energy savings, with a central estimate of 100 MJ/t . Applying EU-consistent CO_2 emission factors, natural gas $56.1\text{--}56.4\text{ kg CO}_2\text{ GJ}^{-1}$ [54], fuel oil $\approx 77.4\text{ kg CO}_2\text{ GJ}^{-1}$, and coal $\approx 94.6\text{ kg CO}_2\text{ GJ}^{-1}$ [53], produces per-ton CO_2 savings of approximately, natural gas: $3.4\text{--}9.6\text{ kg CO}_2\text{/t}$ (central $\approx 5.6\text{ kg/t}$); fuel oil: $4.6\text{--}12.8\text{ kg CO}_2\text{/t}$ (central $\approx 7.7\text{ kg/t}$); coal: $5.7\text{--}16.3\text{ kg CO}_2\text{/t}$ (central $\approx 9.6\text{ kg/t}$). Although modest per ton, these reductions become operationally significant at an industrial scale. For a 100 kt/y facility, the $50\text{ }^{\circ}\text{C}$ reduction could prevent $\approx 0.3\text{--}1.6\text{ kt CO}_2\text{/y}$ for natural-gas-fired kilns, with even greater avoidance for oil- or coal-fired systems. Beyond direct emission mitigation, lowering the peak temperature by $50\text{ }^{\circ}\text{C}$ also extends kiln lifetime, reduces refractory wear, and lowers production costs, representing essential advantages along the European ceramic sector's decarbonization pathway.

The 1:1 illitic-feldspathic-schist blend used in this work facilitated vitrification at lower temperatures owing to its natural alkali-flux content, in line with previous European research, where optimized clay formulations achieved $10\%\text{--}20\%$ reductions in firing energy without compromising mechanical integrity or durability [50]. This evidence highlighted the dual role of material design and firing control as complementary strategies to enhance energy efficiency and reduce emissions in sustainable red-ceramic production. Overall, the $50\text{ }^{\circ}\text{C}$ temperature decrease corresponds to energy savings of $\approx 60\text{--}170\text{ MJ/t}$ and CO_2 emission reductions of $\approx 3\text{--}10\text{ kg/t}$, depending on the fuel type. When extrapolated to industrial volumes, such optimization can result in the avoidance of hundreds of tons of CO_2 annually, supporting flux-optimized formulations that lower vitrification thresholds and advance the decarbonization of the European ceramic industry.

Beyond its technical significance, this work directly contributed to global sustainability targets defined by the United Nations Sustainable Development Goals (SDGs). By enabling lower-temperature, energy-efficient ceramic processing, it supports SDG 7 (Affordable and Clean Energy) through reduced thermal energy demand and enhanced energy efficiency. The development of innovative, locally sourced clay-schist formulations aligned with SDG 9 (Industry, Innovation and Infrastructure) by fostering resilient, low-carbon industrial processes based on regional raw materials. Moreover, the valorization of residual clays and schists exemplifies SDG 12 (Responsible Consumption and Production), minimizing extraction pressures and promoting circular use of georesources. Finally, the demonstrated CO_2 reduction potential of lower-temperature firing contributes directly to SDG 13 (Climate Action), reinforcing the role of sustainable materials engineering in achieving decarbonization pathways for Europe's ceramic sector.

4. Conclusions

Two ceramic batches were formulated based on a 1:1 blend of residual clays from Corval and a 1:1 blend of a residual clay from Corval and a Barrancos schist (Portugal), to evaluate their technological performance after firing at 1100 and 1150 °C. Both formulations achieved properties compatible with structural ceramics, with the clay + schist batch exhibiting higher dimensional stability and mechanical strength, while the residual clay batch presented higher plasticity with controlled shrinkage and porosity. Increasing the firing temperature from 1100 to 1150 °C resulted in a moderate improvement in strength and a decrease in WA, albeit at the expense of higher energy consumption. Results demonstrated that local residual clays and schist materials can be successfully blended to produce sustainable red ceramics with strong technological performance, supporting the principles of circular economy, resource efficiency, and decarbonization. The evolution from an open to a more refined pore network, between 1100 and 1150 °C, marked by partial conversion of interconnected pores into smaller closed cavities, further contributed to the strength gains and reduced water absorption observed. This microstructural densification confirmed that both formulations undergo effective early-stage vitrification despite their distinct mineralogical compositions.

The 50 °C reduction in firing temperature, from 1150 to 1100 °C, represents a meaningful optimization step in red-ceramic manufacturing, particularly when adequate mechanical performance is retained at lower thermal input. Based on validated European benchmarks, this reduction corresponds to an energy saving of approximately 60–170 MJ/t and a CO₂ reduction of ≈3–10 kg/t, depending on the kiln fuel used. When scaled to an industrial production of 100 kt/y, this adjustment can prevent ≈0.3–1.6 kt CO₂/y for natural-gas-fired kilns, and proportionally more for oil- or coal-fired systems. Beyond direct CO₂ mitigation, lowering the firing peak also extends kiln lifetime, reduces refractory wear, and lowers production costs, representing a practical contribution to the decarbonization pathway of the ceramic sector. To further enhance the performance and sustainability of these formulations, future work should explore, (i) different blending ratios beyond 1:1, which may optimize SM and green strength; (ii) intermediate firing temperatures to identify the best compromise between energy savings and mechanical resistance; and (iii) minor additions of fluxing agents such as feldspar or recycled glass, to promote early vitrification and reduce firing demand. Overall, the valorization of Corval residual clays and Barrancos schist confirmed the technical feasibility of producing locally sourced, low-carbon red ceramics while reducing transport impacts, enhancing regional economic resilience, and contributing to European climate goals for sustainable construction materials.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/min15121258/s1>, Table S1. Mineral phases identified in the raw materials <0.063 mm fraction (obtained by wet sieving of non-grounded samples; in %; tr—trace) [6,10]. When the sum of minerals is not 100%, it is related to rounding errors in laboratory procedures (Σ phyllosilicates represents the total content of all phyllosilicate minerals, such as illite, smectite, kaolinite, and chlorite); Table S2. Mineral phases identified in the raw materials <0.002 mm fraction (obtained by sedimentation of non-grounded samples; in %) [6,10]. When the sum of minerals is not 100%, it is related to rounding related to laboratorial procedures; Table S3. Chemical composition of the raw materials <0.063 mm fraction (obtained by wet sieving of non-grounded samples; in %). When the sum of minerals is not 100%, it is related to rounding related to laboratorial procedures; Table S4. Plastic index (PI) and flexural strength (FS; in kgf/cm² and MPa) of the raw materials <0.063 mm fraction [6,10]; Table S5. Shaping moisture (SM; in %), green-to-dry shrinkage (GDS; in %), flexural strength (FS; in kgf/cm² and MPa), and color of the studied batches, after drying at 110 °C; Table S6. Temperature (T; in °C), dry-fired shrinkage (DFS; in %), total shrinkage (green-fired) (TS; in %), flexural strength (FS; in kgf/cm² and MPa), water absorption (WA; in %),

and color of the AD2 batch specimens fired at 1100 and 1150 °C; Table S7. Temperature (T; in °C), dry-fired shrinkage (DFS; in %), total shrinkage (green-fired) (TS; in %), flexural strength (FS; in kgf/cm² and MPa), water absorption (WA; in %), and color of the XB1 batch specimens fired at 1100 and 1150 °C.

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