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Tailoring the performance of cementitious composites through zinc oxide – containing deep eutectic solvents

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Abstract. The reduction of clinker content in cementitious materials is considered one of the key strategies for lowering CO_2 emissions associated with cement production. However, low-clinker cements often exhibit reduced early-age performance and increased sensitivity to microstructural modification, creating a need for multifunctional admixtures capable of improving both technological and functional properties. This study investigates the effect of a choline chloride–urea deep eutectic solvent modified with ZnO (DES-ZnO) on low-clinker cement composites (CEM II/B-V, CEM II/A-LL, CEM V/A), including an assessment of their environmental performance. The evaluation encompassed workability, hydration kinetics, mechanical performance, microstructure, and antimicrobial activity. Incorporation of DES-ZnO improved workability in all analyzed systems, with the most pronounced effect observed for low-clinker cements. Flexural and compressive strength values increased throughout the curing period, reaching approximately 11–12 MPa and 55–65 MPa, respectively, after 56 days. SEM observations indicated a more homogeneous and continuous microstructure in the modified systems, while XRD analysis confirmed that the overall phase composition remained generally unchanged. Calorimetric measurements showed that the influence of DES-ZnO on hydration heat evolution was moderate and dependent on cement composition. Importantly, DES-ZnO imparted strong antimicrobial properties, substantially limiting microbial growth and, in some cases, achieving complete inhibition. From an environmental perspective, the addition of DES-ZnO resulted in only a minor increase in embodied carbon compared to the dominant contribution of cement. The results obtained demonstrate that DES-ZnO can act as a multifunctional admixture for low-clinker cement systems, improving mechanical performance, workability, and antimicrobial resistance without substantially altering the hydration mechanism.

Keywords: sustainable cement; eco-friendly additives; deep eutectic solvent; zinc oxide; antimicrobial performance.

1. INTRODUCTION

The construction sector faces critical challenges related to climate change, greenhouse gas emissions, and depletion of natural resources. It remains one of the most energy-intensive industries, responsible for over 30% of global CO_2 emissions, with cement production alone contributing approximately 5% [1]. These factors necessitate the development of low-carbon, resource-efficient materials and technologies.

Sustainable construction, rooted in the principles of Agenda 21 and operationalized through the Agenda 2030 framework, emphasizes emission reduction, responsible material use, and energy efficiency. In this context, reducing the clinker content in cement is recognized as a key strategy for lowering the environmental impact of construction materials.

One of the emerging approaches in sustainable construction chemistry involves the use of deep eutectic solvents (DES) as functional admixtures. DES are hydrogen-bonded systems with tunable physicochemical properties, low volatility, and relatively simple, cost-effective synthesis [2]. In cementitious systems, they can influence hydration kinetics, microstructure development, and phase formation, potentially enhancing both mechanical performance and durability [3].

Previous studies, including our earlier work, have shown that the use of DES admixtures significantly improves the mechanical properties and microstructure of cement composites based on Portland cement (CEM I) [4,5]. However, these studies were limited to high-clinker systems, which are associated with the highest environmental burden.

Despite the growing interest in DES, there is currently no systematic and comprehensive investigation of their effects in low-clinker, multi-component cements. This represents a significant and unresolved research gap in contemporary cement chemistry.

The present study addresses this gap by investigating the effects of a choline chloride–urea-based DES modified with zinc oxide on three low-clinker blended cements (CEM II/B-V, CEM II/A-LL, and CEM V/A). The analysis includes rheological be-

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havior, hydration heat evolution, mechanical performance, microstructural observations (SEM), and microbiological resistance.

The scientific novelty of this work lies not only in extending DES application to low-clinker cements but also in demonstrating that the response of DES-modified systems strongly depends on binder composition and clinker replacement strategy. Unlike previous studies focused mainly on CEM I systems [5], the present work evaluates DES performance in complex multicomponent binders containing supplementary cementitious materials.

The results provide new insight into the influence of DES on hydration behavior and microstructure development in reduced-clinker systems, revealing composition-dependent effects that cannot be directly extrapolated from conventional Portland cement. By combining rheological, calorimetric, microstructural, mechanical, and microbiological analyses within a single experimental framework, the study contributes to a broader understanding of DES applicability in advanced low-carbon cement technologies.

2. MATERIALS AND METHODS

2.1. Materials

A deep eutectic solvent was synthesized using choline chloride (≥ 98%), urea (99–100%), and zinc oxide (ZnO, particle size < 5 μm, 99%). All reagents were purchased from Merck KGaA (Darmstadt, Germany) and used as received without further purification.

Cement composites were prepared using three types of commercially available cements supplied by Holcim Polska S.A. (Małogoszcz, Poland): (*i*) CEM II/A-LL 42.5R – Portland-limestone cement (LL), classified as a multi-component Portland cement. The main oxide composition is $CaO–SiO_2–Al_2O_3–Fe_2O_3$ ($+SO_3$) with an additional $CaCO_3$ component. Specific surface area (Blaine) is 4670 cm^2/g and density 3110 kg/m^3; (*ii*) CEM II/B-V 42.5R – Portland-fly ash cement containing a significant fraction of siliceous fly ash (V). The oxide composition is $CaO–SiO_2–Al_2O_3–Fe_2O_3$ ($+SO_3$), with the fly ash providing a silico-aluminate component. Specific surface area (Blaine) is 4300 cm^2/g and density 2820 kg/m^3; (*iii*) CEM V/A (S-V) 42.5N – LH/HSR/NA – multi-component cement, in which part of the clinker was replaced with mineral additives, including blast furnace slag (S) and siliceous fly ash (V). The oxide composition is $CaO–SiO_2–Al_2O_3–Fe_2O_3$ ($+MgO$, $+SO_3$). Specific surface area (Blaine) is 4830 cm^2/g and density 2880 kg/m^3.

Standard quartz sand with particle size 0–2 mm and density 2650 kg/m^3 (Kwarcmix, Tomaszów Mazowiecki, Poland) was used as aggregate. Distilled water was used for all mixtures.

2.2. Synthesis of DES-ZnO

For the synthesis of the deep eutectic solvent, choline chloride (69.81 g, 0.5 mol) and urea (60.06 g, 1 mol) were placed in a 250 mL round-bottom flask. The mixture was stirred at 60°C for 24 h until a clear, homogeneous liquid was obtained. Subsequently, zinc oxide (1.05 g, 0.8 wt.%) was added, and the stirring continued at 90°C for 24 h to ensure uniform dispersion of the oxide particles. After cooling to room temperature, a colorless, viscous DES containing ZnO was obtained, suitable for use as an admixture in cement composites. The characterization of the resulting DES-ZnO was reported in our previous study [5].

2.3. Preparation of cement composites

Cement mortars were prepared using 450 g of cement, 1350 g of quartz sand, and 225 mL of water. For modified mixes, DES-ZnO was added at a dosage of 0.25 wt.% relative to the cement mass. The present study, therefore, investigates whether the optimal dosage established for CEM I [5] systems can also be effectively applied to low-clinker blended cements characterized by different hydration mechanisms and phase compositions.

Reference mortars were prepared by combining cement and water in an automatic mortar mixer. The mixture was stirred at low speed for 30 s, followed by the addition of sand and stirring at high speed for 30 s. After a 90 s pause to collect material from the mixer walls, stirring was resumed at high speed for 60 s.

For mortars containing DES-ZnO, the admixture was first dissolved in water and stirred to obtain a homogeneous solution. The mortar was then prepared following the same mixing procedure as the reference samples, replacing the water with the DES-ZnO solution.

The fresh mortars were cast into molds in two layers, each layer being compacted using a tamping rod with 60 strokes per layer. After leveling the top surface, the specimens were left in the molds for 24 h, then demolded and cured in water at 20 ± 2°C.

For each cement type, six prism specimens were prepared for mechanical testing at each curing age (3, 7, 28, and 56 days).

All procedures were conducted in accordance with PN-EN 196-1 [6].

2.4. Characterization of cement composites

The flow of cement mortars was determined using a flow table in accordance with PN-EN 1015-3 [7]. The moistened mold was filled in two layers, each compacted with 10 strokes of the tamping rod. After removing the mold, the mortar was subjected to 15 drops of the flow table at a rate of 1 rotation per second. The flow diameter was reported as the average of two perpendicular measurements.

The heat of hydration was measured using a semi-adiabatic calorimetric method in accordance with PN-EN 196-9 [8]. Freshly prepared mortar was placed into a calorimeter manufactured by TESTING Bluhm & Feuerherdt GmbH (Berlin, Germany), and the temperature evolution due to hydrate formation was continuously recorded. The cumulative hydration heat was calculated by summing the energy retained within the calorimeter and accounting for heat dissipation to the surroundings. Temperature data for the test specimens were evaluated relative to a reference calorimeter under the same conditions.

Mechanical strength tests were conducted in accordance with PN-EN 196-1 [6]. Flexural strength was measured on mortar prisms of $40 \times 40 \times 160$ mm placed on the support rollers of a

Servo-Plus Evolution testing machine (Matest S.p.A., Treviolo BG, Italy). Load was applied continuously at a rate of 50 ± 10 N/s until specimen failure. Compressive strength was subsequently determined on the halves of the prisms obtained from the flexural test. The halves were positioned between two square loading plates, and load was applied at a rate of 2.4 ± 0.2 kN/s until failure.

The microstructure of the cement composites was examined using scanning electron microscopy (SEM) with a Tescan VEGA3 microscope (Tescan Orsay Holding a.s., Brno, Czech Republic). Specimens were taken from 28-day-cured cement mortar prisms and sectioned into fragments approximately 5 × 5 × 10 mm in size. Prior to SEM observation, the samples were dried in a laboratory oven at ~ 50°C.

Phase analysis of base and modified cements was performed by X-ray diffraction (XRD, SmartLab SE, Rigaku, Akishima, Tokyo, Japan) using Cu Kα radiation (λ = 0.154184 nm) and a HyPix-400 2D detector. The diffraction patterns were recorded over a 2θ range of 5–80° (scan speed: 4°/min, step size: 0.04°), and phase identification was conducted by Rigaku SmartLab Studio II Suite. The XRD patterns were normalized to the maximum peak intensity to facilitate comparison between samples. The intensity values were divided by the highest intensity recorded in each diffractogram, resulting in normalized intensities expressed on a relative scale.

The antibacterial properties of the cement composites were evaluated using two methods, modified based on previously reported procedures [4, 5].

The first, referred to as the contact method, involved placing specimens (5 × 5 × 2 mm) directly on the surface of sterile tryptic soy agar (TSA). After 12 h of exposure at room temperature, the samples were aseptically removed, and the agar plates were incubated at 30°C for 24 h. Microbial growth was subsequently assessed visually.

In the second method, approximately 500 mg of material was introduced into sterile conical flasks containing 50% tryptic soy broth (TSB). The samples were incubated for 24 h at 30°C with continuous agitation (110 rpm). After incubation, the optical density at 600 nm (OD_{600}) was measured, and the values were converted to microbial cell concentration using the *E. coli Cell Culture Concentration from OD_{600} calculator*. All experiments were conducted in triplicate.

2.5. Environmental impact evaluation

The environmental impact of the designed material solutions was evaluated in terms of the embodied carbon footprint at the product stage (A1–A3), expressed as the equivalent mass of emitted carbon dioxide per cubic meter of mortar (eq kg CO_2/m^3). The assessment was conducted in accordance with PN-EN 15804:2012+A2:2019 – *Sustainability of construction works – Environmental product declarations – Core rules for the product category of construction products* [9]. For the purposes of this study, the analysis was limited to modules A1–A3 (raw material supply, transport, and manufacturing). This approach enables a consistent and reliable comparison of material compositions at the production stage, where the dominant environmental impacts occur.

Carbon footprint calculations were performed using OneClick LCA software (One Click LCA©, Version 0.30.0, Database version 7.6, Helsinki, Finland) [10]. Specific carbon footprint values for individual materials are presented in Table 1. The carbon footprint of the primary materials – namely, cement and aggregates – was determined based on Environmental Product Declarations (EPDs) provided by their respective manufacturers. In contrast, the carbon footprint of the designed admixture was estimated using literature data concerning the environmental impacts associated with DES and ZnO.

Table 1
Environmental impacts of the materials used

Material	Environmental impact (eq kg CO_2/kg)	Source
CEM II/B-V	0.473	[11]
CEM II/A-LL	0.473	
CEM V/A	0.430	
Water	0.0003	[10]
Sand	0.000779	
DES	1.82	[12]
ZnO	1.25	[13]

It should be noted that the scope of the environmental assessment reflects the early, laboratory-stage development of the material; therefore, the cradle-to-gate approach (A1–A3) and the embodied carbon footprint were selected as the most reliable and comparable indicators. Extending the analysis beyond this scope would introduce significant uncertainty due to the lack of durability data and defined use-phase scenarios.

3. RESULTS AND DISCUSSION

3.1. Consistency of cementitious mortars

The consistency of the samples was evaluated using the flow table test, and the results are summarized in Fig. 1. The addi-

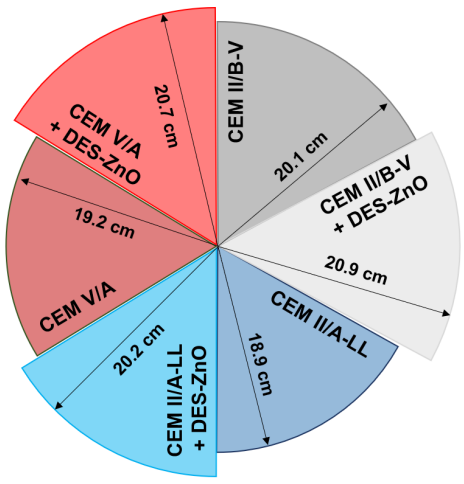


Fig. 1. Flow (cm) of cementitious mortars with and without DES-ZnO admixture

tion of DES-ZnO led to an increase in flow values across all composites, indicating a slight but significant improvement in workability.

The most pronounced difference was observed for the CEM V/A-based composite, where the inclusion of DES-ZnO increased the flow from 19.2 to 20.7 cm ($\Delta = 1.5$ cm). This measurement exhibited some experimental uncertainty, but the effect is clearly noticeable. For the CEM II/A-LL-based composite, the flow increased by 1.3 cm (from 18.9 to 20.2 cm), also demonstrating a substantial influence of the admixture. The smallest, yet still measurable, increase occurred for the CEM II/B-V-based composite, with a rise of 0.8 cm (from 20.1 to 20.9 cm).

The variable response of the composites to the DES-ZnO addition may be attributed to differences in the mineralogical composition and the content of supplementary constituents in the cements, which can modulate the water demand and interactions with the additive particles. These results indicate that DES-ZnO incorporation enhances the workability of cementitious mortars, with the magnitude of the effect being dependent on the type of base cement.

3.2. Heat of hydration

Figure 2 presents the cumulative heat evolution of hydration for the analyzed cement systems over 72 hours. Regardless of the type of cement, all samples exhibit the typical behavior of Portland cement hydration, characterized by a rapid increase in heat release during the initial hydration stage, followed by a gradual decrease in the reaction rate at later stages of maturation. This behavior is commonly observed in calorimetric studies of cements and reflects the sequential stages of hydration reactions occurring in the cement–water system [14].

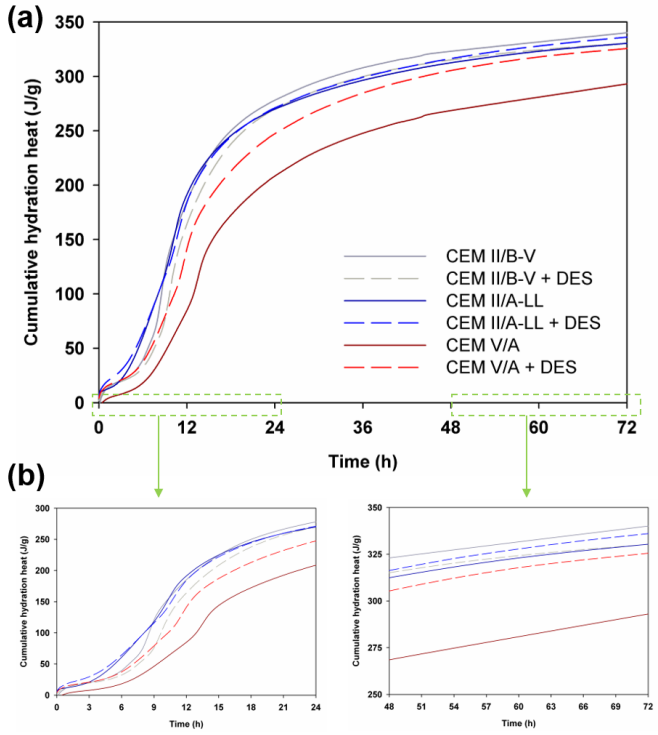


Fig. 2. Cumulative heat of hydration of various cements as a function of time. Panel (a) – full course up to 72 h; panels (b) – magnification of the early (0–24 h, left) and late (48–72 h, right) hydration stages

The highest cumulative heat values over the entire analyzed period are observed for CEM II/A-LL cement, primarily due to its relatively high Portland clinker content. A higher proportion of clinker phases, especially alite (C_3S), promotes more intensive early hydration reactions, leading to faster formation of hydration products, mainly C–S–H gel and portlandite [14, 15]. In contrast, CEM V/A cement exhibits significantly lower cumulative heat values, which is attributed to the substantial content of mineral additives in its composition. The presence of components such as fly ash or blast-furnace slag reduces the fraction of reactive clinker in the system, thereby decreasing the intensity of early hydration reactions. This phenomenon is commonly referred to as the "clinker dilution effect" and has been widely documented in studies on multi-component cements [16].

A closer examination of the 0–24 h period (see Fig. 2b) indicates that the most pronounced differences between the tested cements occur during the period of most intensive hydration. For CEM II/A-LL, the cumulative heat curve rises more rapidly between approximately 8 and 16 hours, indicating a higher rate of hydration of the clinker silicate phases. During this period, intensive formation of hydration products, particularly C–S–H gel, takes place, which directly corresponds to increased heat release [15]. Conversely, for CEM V/A, the cumulative heat rises more slowly, reflecting the lower reactivity of the system containing a larger fraction of mineral additives. In such systems, part of the hydration reactions occurs at later stages, when the mineral additives begin to react with the hydration products of the clinker, as has been extensively described for pozzolanic and slag-containing cements [14, 16].

The addition of DES induces minor yet noticeable changes in the hydration behavior of all analyzed cements. For the CEM II systems, a slight reduction in cumulative heat is observed compared to the corresponding reference samples, suggesting that the presence of DES may partially affect the dissolution rate of clinker phases or the initial stage of hydration product formation. Similar effects have been reported for various organic additives and chemical admixtures, which can interact with cement particle surfaces or ions in the pore solution, thereby influencing hydration reactions [17]. In contrast, the CEM V/A system containing DES-ZnO exhibited slightly higher cumulative heat values during the later stage of the analyzed period (48–72 h). This behavior may be associated with delayed hydration and pozzolanic or latent hydraulic reactions characteristic of multi-component low-clinker cements containing supplementary cementitious materials. The observed effect suggests that the influence of DES-ZnO on hydration kinetics is composition-dependent and may become more pronounced in systems with higher mineral additive content.

Importantly, despite these differences, the overall shape of the hydration curves remains similar for all analyzed systems, indicating that the fundamental hydration mechanism is preserved, while the reaction kinetics are only moderately modified.

Analysis of the later hydration period (48–72 h), presented in the inset of Fig. 2b, shows a marked reduction in the rate of heat evolution. This is since a massive portion of the most reac-

tive clinker phases has already hydrated, and further reactions proceed more slowly because of the progressive accumulation of hydration products on the cement particle surfaces [15]. Despite the reduced reaction rate, the relative ranking of the tested cements is maintained – CEM II/A-LL continues to exhibit the highest cumulative heat, whereas CEM V/A shows the lowest.

The obtained results indicate that both cement composition and the presence of DES influence the hydration kinetics of the analyzed systems. Although the effect of DES on the overall heat evolution was moderate, the mechanical results indicate that even minor changes in hydration behavior may influence the development and organization of the cement matrix.

3.3. Mechanical properties

The average flexural and compressive strengths of the investigated cement composites at curing ages of 3, 7, 28, and 56 days are presented in Fig. 3. A clear, time-dependent increase in both flexural and compressive strength was observed for all cement types, consistent with the typical hydration behavior of Portland and blended cements, where progressive formation of C–S–H gel and other hydration products contribute to the gradual development of mechanical strength [18].

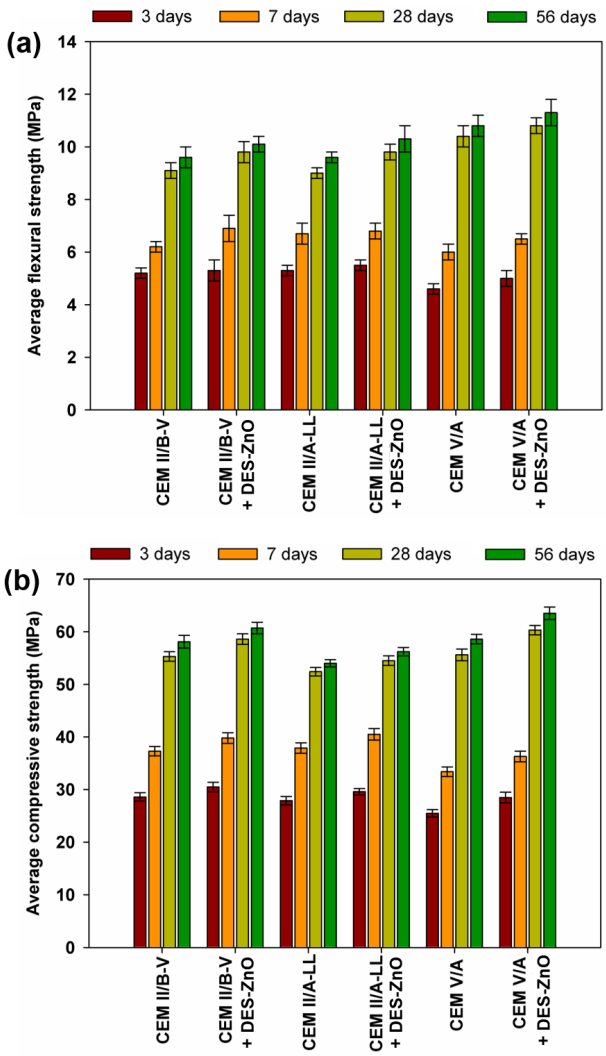


Fig. 3. Mechanical strength results after 3, 7, 28, and 56 days of maturing for all tested composites (a) average flexural strength and (b) average compressive strength, respectively

For flexural strength (see Fig. 3a), the initial values at 3 days ranged from approximately 4.5 to 5.5 MPa. Cement composites containing DES-ZnO exhibited higher early-age flexural strength compared to the reference systems, suggesting that the additive affects the early formation and organization of the cement matrix. This beneficial effect became more pronounced after 7 days, with DES-modified cement composites consistently outperforming their unmodified counterparts. At 28 and 56 days, all cements showed substantial strength development, with the highest flexural strength observed for CEM V/A + DES-ZnO (~ 11–12 MPa), suggesting that the addition of DES-ZnO positively affects the long-term mechanical performance of low-clinker cement systems.

Compressive strength results (see Fig. 3b) followed a similar trend. DES-containing cements achieved 25–30 MPa after 3 days and increased steadily to 55–65 MPa at 56 days, consistently surpassing the corresponding reference systems. CEM II/B-V + DES-ZnO and CEM V/A + DES-ZnO exhibited the highest compressive strengths across all curing periods, highlighting the positive effect of DES-ZnO on the mechanical performance of blended cements. In contrast, the reference cements, particularly CEM V/A, showed slower strength development, which may be associated with the higher content of supplementary cementitious materials and their characteristic hydration behavior [19].

The improvement in mechanical performance suggests that DES-ZnO influences the development of the cement matrix in low-clinker systems. However, the observed strength enhancement cannot be explained solely by differences in hydration heat evolution, indicating that additional microstructural factors may also contribute to the final mechanical performance.

Overall, the results indicate that both curing time and cement composition are critical determinants of flexural and compressive strength. The incorporation of DES-ZnO improved both early-age and long-term strength, particularly in cements with reduced clinker content. These findings highlight the importance of interactions between chemical admixtures and binder composition in the development of advanced low-carbon cement materials.

3.4. SEM analysis

The SEM micrographs presented in Fig. 4 illustrate the microstructural morphology of the investigated cement mortar composites after 28 days of curing. Selected characteristic regions, including hydration-product-rich areas, partially unreacted particles, visible pores, and microcracks, were marked directly in the images to improve readability and facilitate comparison between the analyzed systems.

The reference cement composites (Fig. 4a–c) exhibit a relatively heterogeneous microstructure with locally visible voids, microcracks, and irregularly distributed hydration products. In several regions, loosely packed morphologies and partially unreacted particles can also be observed, particularly in the blended cement systems. In contrast, the DES-ZnO-modified compos-

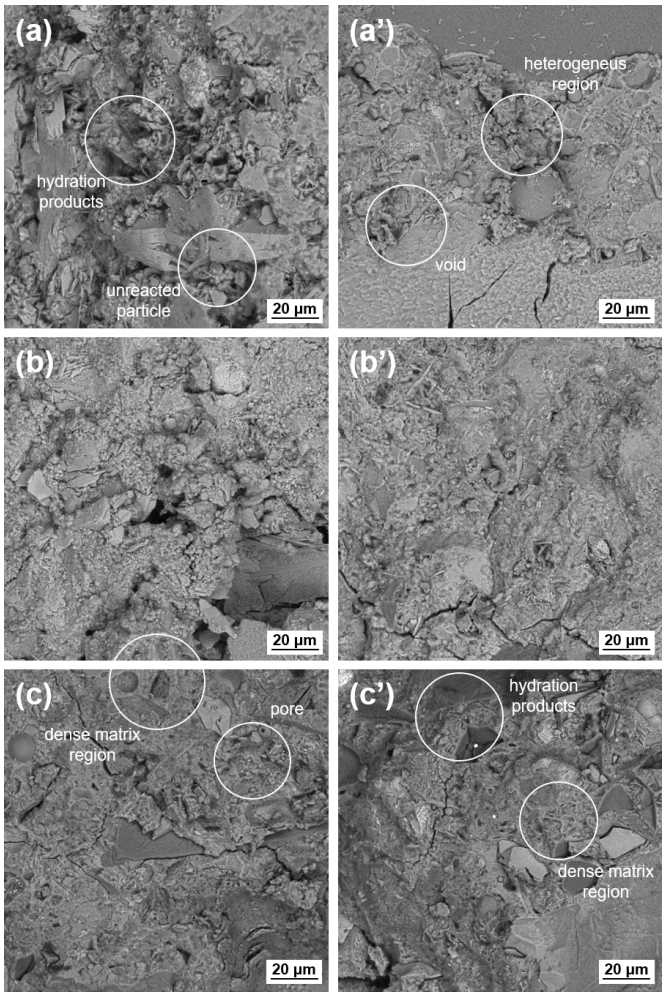


Fig. 4. SEM images of all analyzed cement composites: (a) CEM II/B-V, (a′) CEM II/B-V + DES-ZnO, (b) CEM II/A-LL, (b′) CEM II/A-LL + DES-ZnO, (c) CEM V/A, and (c′) CEM V/A + DES-ZnO

ites (Fig. 4a′–c′) generally show a more continuous and compact matrix with a lower occurrence of visible defects and a more homogeneous distribution of hydration products. These differences are particularly noticeable in the CEM II/A-LL and CEM V/A systems (Fig. 4b′ and 4c′), where the microstructure appears more uniform compared to the corresponding reference samples.

The SEM observations are qualitatively consistent with the XRD analysis (Fig. 5), hydration heat evolution (Fig. 2), and mechanical test results (Fig. 3). The calorimetric curves indicate that the addition of DES-ZnO affects the hydration process, although the magnitude of this effect depends on the cement composition. Similarly, the DES-modified mortars exhibited higher compressive and flexural strength values, especially at later curing ages.

The combined SEM, XRD, calorimetric, and mechanical results suggest that DES-ZnO influences the microstructural development of low-clinker cement systems. The observed increase in matrix continuity and reduction of visible defects may therefore contribute to the improved mechanical performance of the modified composites.

3.5. XRD analysis

The X-ray diffraction patterns obtained for the base cements: CEM II/B-V (Fig. 5a), CEM II/A-LL (Fig. 5c), CEM V/A (Fig. 5e), and the corresponding cements modified with 0.25 wt.% of a deep eutectic solvent containing ZnO (see Figs. 5b, 5d, and 5f) exhibit a similar set of crystalline phases typical for Portland–fly ash blended cements. The dominant reflections correspond to clinker phases such as alite and quartz originating from fly ash. In addition, minor reflections assigned to portlandite, mullite, and gypsum were also detected. When comparing the base and modified cement samples, there is no noticeable difference in the types of crystalline phases identified. In the modified samples, no distinct separate reflections corresponding to ZnO. However, in the case of the CEM II/A-LL modified sample (Fig. 5f), it is possible to identify an additional reflection at 68.1°, which can also correspond to zincite. Similarly, a not clear, partially overlapped peak at 36.6°, additionally visible in the diffractogram of DES-ZnO modified CEM V/A (Fig. 5d), can also be evidence for the presence of ZnO. In the diffractograms for all modified cement composites, weak peaks originating from ZnO can be overlapped by stronger reflections related to other cement components, suggesting that ZnO occurs in low amounts and/or in a poorly crystalline form.

A characteristic feature of the diffractograms obtained for the DES-ZnO-modified cements is a significantly lower intensity of main diffraction peaks than for base cement samples. In this respect, in order to make a better comparison between samples, the intensities in the diffraction patterns were normalized to the maximum peak intensity. In the case of modified cements, a slightly increased diffuse background in the range of approximately 10–25° was observed. This broad diffuse scattering, commonly referred to as the amorphous halo, can be associated with the presence of poor crystalline or amorphous phases. It suggests a relative increase in the amorphous phase content compared to the base cement. The reason for these observations can be the screening effect of the amorphous layer formed on cement particles as a consequence of modification by DES-ZnO.

3.6. Antibacterial properties

The results of microbiological assessment of the investigated cement composites, including qualitative contact method observations and quantitative optical density (OD_{600}) measurements, are summarized in Table 2. The data obtained indicate a clear influence of cement composition and the incorporation of DES-ZnO on microbial viability.

The reference cement samples exhibited varying degrees of microbial growth, as evidenced by both the qualitative contact method and OD_{600} values. In particular, CEM V/A showed the highest microbial activity, with an optical density of 0.134 corresponding to $1.07 \cdot 10^8$ cells/mL, which may be attributed to its higher content of supplementary cementitious materials and more favorable conditions for microbial proliferation.

In contrast, all cement composites modified with DES-ZnO demonstrated a consistent reduction in microbial growth. This effect was observed qualitatively, where reduced or no visible microbial presence ("+ – –" or "– – –") was recorded, as well

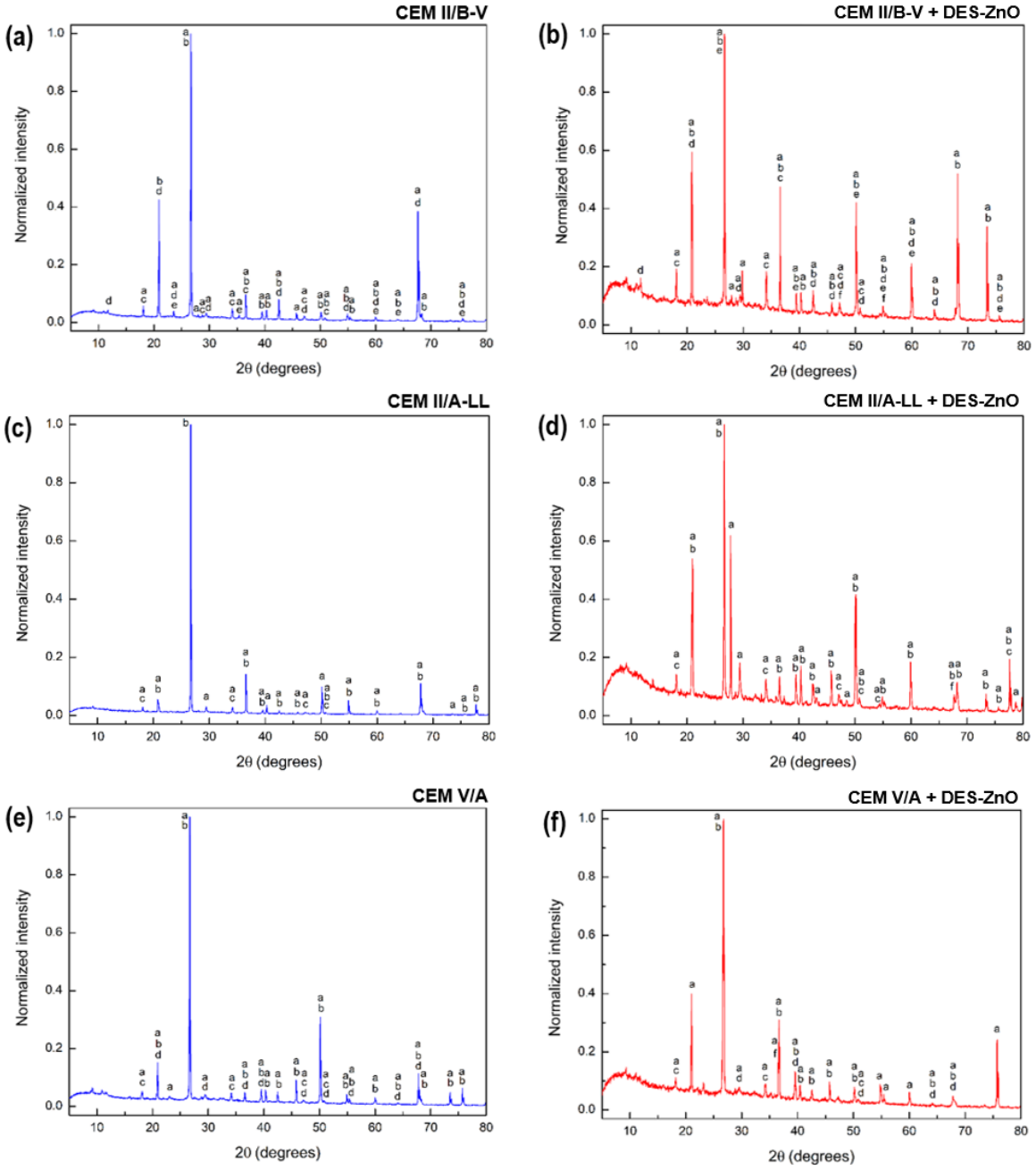


Fig. 5. XRD patterns of base cements: CEM II/B-V, CEM V/A, CEM II/A-LL, and modified with 0.25% DES-ZnO. Peak labels corresponding to identified phases: a – alite, b – quartz, c – portlandite, d – gypsum, e – mullite, f – zincite. The intensities in the diffractograms were normalized to the maximum peak intensity

as quantitatively, with lower OD_{600} values and decreased cell counts. Notably, CEM V/A + DES-ZnO exhibited complete inhibition in the contact method ("– – –") and one of the lowest microbial cell counts ($6.88 \cdot 10^7$ cells/mL), indicating a strong antimicrobial effect.

The reduction in microbial activity can be attributed to the synergistic action of DES and ZnO. Zinc oxide is widely recognized for its antimicrobial properties, associated with the generation of reactive oxygen species and disruption of microbial cell membranes [20], while deep eutectic solvents may enhance the dispersion and stability of active components within the cement matrix. This combined effect likely limits microbial colonization and proliferation within the material.

Microbial colonization of cement-based materials is increasingly recognized as a key factor affecting the long-term durability and service life of construction materials. The formation of biofilms on cement surfaces may promote biodeterioration processes, including localized acidification, moisture retention, and progressive surface degradation. These phenomena are particularly relevant in humid environments and infrastructures ex-

Table 2
Enhanced antibacterial performance of cement composites incorporating DES-ZnO

Sample type	Contact method, after 24 h incubation	Optical density measurement method (OD_{600})	Microbial cell count, cells/mL
CEM II/B-V	+ + +	0.112	$8.96 \cdot 10^7$
CEM II/B-V + DES-ZnO	+ – –	0.087	$6.96 \cdot 10^7$
CEM II/A-LL	+ + –	0.102	$8.16 \cdot 10^7$
CEM II/A-LL+ DES-ZnO	+ – –	0.091	$7.28 \cdot 10^7$
CEM V/A	+ – –	0.134	$1.07 \cdot 10^8$
CEM V/A + DES-ZnO	– – –	0.086	$6.88 \cdot 10^7$

posed to biological contamination, where microbial activity may accelerate the deterioration of cementitious matrices.

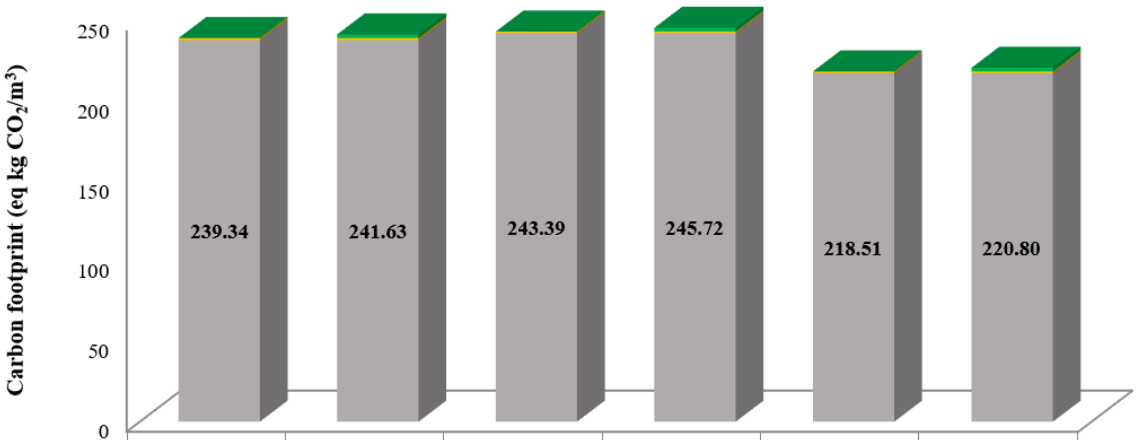
Therefore, the antimicrobial performance observed for the DES-ZnO-modified composites represents not only a biological effect but also a potentially beneficial contribution to material durability. Reduced microbial growth may limit the development of biofilms and decrease the risk of biologically induced degradation processes occurring during long-term service of cement-based materials

Overall, the results demonstrate that the incorporation of DES-ZnO effectively suppresses microbial growth in cement composites, improving their resistance to biological degradation. This finding highlights the potential of DES-ZnO as a multifunctional additive for the development of advanced cement-based materials with enhanced durability and antimicrobial performance.

Similar antimicrobial effects have previously been reported for other additives used in cementitious and construction materials, including silver nanoparticles (AgNPs), TiO_2, Cu-based compounds, and quaternary ammonium compounds. Among these systems, AgNPs are often considered highly effective antimicrobial agents; however, their higher cost and potential environmental concerns may limit large-scale applications. TiO_2-based materials exhibit photocatalytic antimicrobial activity, although their efficiency is frequently dependent on UV irradiation conditions. In comparison, ZnO-based systems are characterized by relatively good chemical stability, broad-spectrum antimicrobial activity, lower cost, and compatibility with cement matrices, which makes them attractive multifunctional additives for cement-based composites [21, 22].

3.7. Environmental impact

All mixtures were recalculated per unit volume (kg/m^3), as shown in Fig. 6. The incorporation of DES-ZnO slightly increases the embodied carbon footprint of all mortars by approximately 2–3 eq kg CO_2/m^3. Reference mixtures range from 218



	CEM II/B-V	CEM II/B-V + DES-ZnO	CEM II/A-LL	CEM II/A-LL + DES-ZnO	CEM V/A	CEM V/A + DES-ZnO
DES-ZnO	0.000	2.290	0.000	2.329	0.000	2.299
Sand	1.176	1.176	1.196	1.196	1.181	1.181
Water	0.076	0.076	0.077	0.077	0.076	0.076
Cement	238.085	238.085	242.115	242.115	217.249	217.249

Fig. 6. Environmental impact of cement mortars with DES-ZnO admixture (values of individual components are presented in the table, while the total carbon footprint is shown in the chart

to 245 eq kg CO_2/m^3, with the lowest values observed for CEM V/A and the highest for CEM II/A-LL. Despite the increase associated with DES-ZnO, the relative ranking of cement types remains unchanged, confirming that cement composition is the dominant factor controlling the carbon footprint at the product stage. Blended cements (e.g., CEM V/A) consistently exhibit the lowest emissions.

The additional environmental burden of DES-ZnO is limited due to its low dosage, which is consistent with previous findings [23]. Importantly, when considered together with the observed improvements in mechanical performance, the use of DES-ZnO may indicate potential for enhanced durability and extended service life; however, this aspect was not directly evaluated within the scope of the present study. Future research will focus on comprehensive durability assessments to verify whether the improved material performance can translate into extended service life and, consequently, a reduction of life-cycle environmental impacts. As a result, while a slight increase in embodied carbon at the production stage was observed, its possible offset from a full life-cycle perspective remains to be demonstrated.

4. CONCLUSIONS

This study demonstrates that the incorporation of DES-ZnO provides a consistent and multifunctional modification strategy for cementitious mortars, particularly effective in low-clinker systems. The results obtained allow the following key conclusions to be drawn:

1. DES-ZnO acts as a workability-enhancing additive, with the magnitude of the effect dependent on cement composition, showing the strongest impact in blended, low-clinker systems.
2. The presence of DES-ZnO leads to a moderate modification of hydration behavior, with the effect depending on cement composition. For the investigated systems, the overall hydration mechanism remained preserved, while slight differences in cumulative heat evolution were observed.
3. A systematic improvement in mechanical performance is observed across all curing stages, with the most pronounced gains in low-clinker cements, confirming the beneficial effect of DES-ZnO on strength development in sustainable binder systems.
4. SEM observations indicated that DES-modified systems exhibited a more homogeneous and continuous cement matrix with a lower occurrence of visible defects compared to the corresponding reference samples. These microstructural observations were qualitatively consistent with the mechanical and calorimetric results.
5. DES-ZnO introduces a clear antimicrobial functionality, significantly limiting microbial growth and, in some cases, enabling complete inhibition, which extends the functional performance of cement-based materials beyond purely structural applications.
6. From an environmental perspective, DES-ZnO causes only a marginal increase in embodied carbon, while cement composition remains the dominant factor affecting the environmental footprint of the analyzed systems.

Overall, the results identify DES-ZnO as a multifunctional modifier capable of improving the performance of low-clinker cementitious materials through combined effects on workability, mechanical properties, microstructural organization, and antimicrobial resistance. These findings demonstrate the potential applicability of DES-based admixtures in the development of advanced low-carbon cement systems.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

DATA AVAILABILITY

Data will be made available on request.

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